Detection of polybrominated diphenyl ethers in tilapia (*Oreochromis mossambicus*) from O'ahu, Hawai'i

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Polybrominated diphenyl ethers (PBDEs) have been detected for the first time at a range from 231.58 to 685.61 ng g^{-1} lipid weight in the muscles of tilapia (*Oreochromis mossambicus*) collected from O'ahu, an island of the geographically isolated Hawaiian archipelago.

The Hawaiian Islands are located in the middle of the Pacific Ocean and are geographically isolated. Rapid urban development during the second half of the twentieth century has resulted in environmental pollution within the islands, especially on O'ahu. Heavy metals and organic contaminants, including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), have been found on O'ahu.[1,2]

Polybrominated diphenyl ethers (PBDEs) are synthetic organic compounds used extensively as additive flame-retardants in a wide variety of commercial and household products. With the vast use of PBDEs over the past few decades, they have become ubiquitous contaminants in the environment. Once in the environment, PBDEs, like other persistent organic pollutants (POPs) such as PCDD/Fs and PCBs, can be absorbed into organisms and accumulate in upper trophic-level species throughout the food chain, including marine mammals, some birds and fish, and humans.[3]

Although some organic pollutants have been found in Hawai'i, such as PAHs and PCBs, to our knowledge, PBDEs have not been reported in Hawai'i to date, especially in the local aquatic environment. In this study, we collected fish samples from the Manoa stream and Ala Wai Canal, a small artificial waterway located on the southern coast of the island of O'ahu, Hawai'i, that spans a large portion of the city of Honolulu and the economically important resorts in Waikiki. PBDEs were analyzed in the fish muscle samples and the contaminative status of the PBDEs was then revealed.

Tilapia (*Oreochromis mossambicus*) with approximately 200 g body weight were collected from one site (site 1) of the Manoa stream (which flows into the Ala Wai Canal) and two sites (site 2 and 3) of the Ala Wai Canal in Honolulu, O'ahu (Fig. 1). Seventeen (site 2) or eighteen fish (sites 1 and 3) were sampled from the selected sites. The fish muscles were isolated, homogenized and lyophilized for chemical analysis. The average lipid contents were determined as 3.62% (1.88–9.86%) for site 1, 3.24% (1.80–6.19%) for site 2 and 2.77% (1.50–6.27%) for site 3.

Eight PBDE congeners (BDE28, 47, 99, 100, 153, 154, 183 and 209) were analyzed in the present study. Most of the PBDE congeners were detected in the fish samples (the recoveries of labeled compounds were 58 to 106%), however, BDE183 and BDE209 were found to be below their LODs in all of the samples and therefore excluded from the calculation of the total PBDE concentrations. The average of the total PBDEs in the fish samples were 567.32 ± 53.8, 231.58 ± 17.51, and 685.61 ± 78.82 ng g^{-1} lipid weight for sampling sites 1, 2, and 3, respectively. Comparative analysis (one-way ANOVA) revealed that the concentration of total PBDEs in site 2 was significantly lower than those detected in the other two sites ($p < 0.01$). This variation may reflect the difference in water exchange in site 2, with more agricultural and urban runoff occurring in the other two sites.

PBDEs have been reported in many fish species around the world. The PBDE concentrations in fish are highly variable depending on the type of fish and the location from which they were collected. In general, the concentrations of PBDEs in fish in Europe are significantly lower than in fish from North America and Asia. The average PBDE concentrations were 120 and 1050 ng g^{-1} lipid weight for the European and the North American fish,[4] respectively. PBDEs have also been detected at 18–1100 and 34.1–444.5 ng g^{-1} lipid weight in the muscles of fish from the Yangtze River[5] and Pearl River estuary[6] in China, respectively. The observed PBDE concentrations in the present study were found to lie between the concentrations found

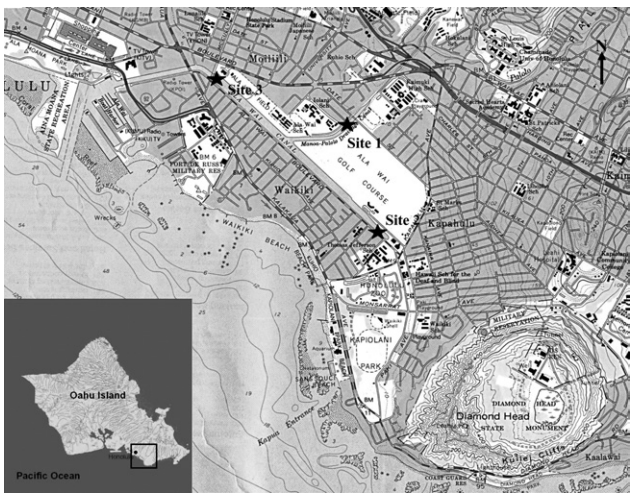

Fig. 1 Map of sampling sites. The sampling sites are indicated by "★". One sampling site (site 1) was located in the Manoa stream. The two other sampling sites (site 2 and 3) were located in the Ala Wai Canal. The stream water flows into the ocean through one of the ends (Site 3) of the Ala Wai Canal.

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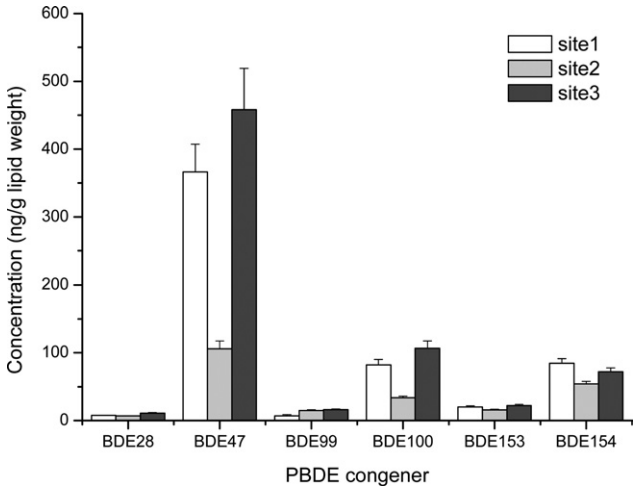

Fig. 2 Congener pattern of PBDEs detected in fish samples from 3 sampling sites. The results indicate that BDE47 is the major congener.

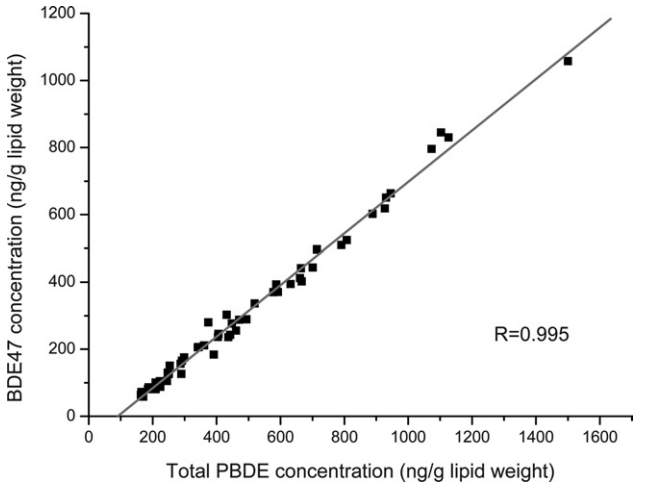

Fig. 3 Linear regression of the concentrations between BDE47 and total PBDEs ($R = 0.995$).

in fish from Europe and North America/China, and are closer to the average level of North America/China. The Hawaiian Islands are far from the continents and few industries have been developed in the islands. However, relatively high levels of PBDEs are still found in the islands. These results indicate that the contamination by PBDEs is a growing environmental problem.

Among the congeners detected in the fish samples, BDE47 was found to be the most abundant congener (Fig. 2). This congener contributed, on average, to 63.29 ± 1.39%, 44.60 ± 1.49% and 64.38 ± 1.50% of the total PBDEs in sites 1, 2 and 3, respectively. The other two major congeners were determined to be BDE100 and BDE154. These three congeners, together, constituted more than 90% of the total PBDEs in both sites 1 and 3, and more than 80% of the total PBDEs in site 2. BDE47 has been found to be the major residual congener in organisms. It was reported that this congener predominated about 50% or more of the total PBDEs in fish species from North America, the European Union[4] and China.[5,6] This abundance of BDE47 and BDE100 might be suggestive of exposure to commercial penta-BDE mixtures that were used almost entirely in North America.[7] However, for North American fish, the ratio of BDE47 to BDE99 is approximately 2 : 1, which is significantly lower than the ratio in European and Chinese fish (about 5 : 1 or more).[3,5,6] In the present study, the indexes were approximately 52 : 1 for site 1, 7 : 1 for site 2 and 28 : 1 for site 3, due to the relatively low concentrations of BDE99, and quite different from those reported. However, the parameter is similar to those found in the fish from China Pearl River estuary in China, in which BDE99 was also detected at very low concentrations.[6] These results may suggest a species-specific difference in PBDE bioaccumulation or a complex exposure to PBDEs in the Hawaiian aquatic environment.

A linear relationship was observed between the concentrations of BDE47 and the total PBDEs ($R = 0.995$, Fig. 3). This result revealed that the concentrations of BDE47 could potentially indicate the total PBDE levels in the fish from Hawaiian waters.

In the present study, BDE183 and BDE209 were not detected in the fish samples. Similarly in previous studies, PBDEs with 7–10 bromines have hardly been reported in wild fish, while tetra- and penta-BDEs were highly bioaccumulated in these organisms. It is likely that preferential accumulation, greater exposure to and bioavailability of the tetra- and penta-BDEs are responsible for their prevalence in fish.[8] Burreau *et al.*[9] also reported that highly brominated congeners of PBDEs had only little or no biomagnification in fish from the Baltic Sea, likely due to their large molecular size or high molecular weight.

In our other study, PCBs were detected in the fish from the same sampling sites. Their concentrations varied from 51.9 to 89.4 ng g^{-1} lipid weight (unpublished data) and are several times less than those of PBDEs. Several studies on PBDEs have shown that the levels of these contaminants have increased exponentially over the past three decades, in both humans and wildlife.[4,10] On the contrary, PCBs have been reported to be declining in many areas of the world due to the ban on PCB production and use.[11,12] Although PCB concentrations are often found to be higher than that of PBDEs in fish, the reverse results have also been reported.[13] The contamination of PCBs on O'ahu may mainly originate from PCB leakage from transformers stored by the U.S. Navy (http://starbulletin.com/2003/11/30/news/story9.html). In recent years, some efforts have been taken to clean up PCB-contaminated soil. Thus, PCBs are expected to decrease with time on O'ahu. However, little attention has been paid for the detection and monitoring of contamination by PBDEs. The results obtained from the present study clearly indicate that there is a heavier contamination by PBDEs than by PCBs in the island. Therefore, it is urgently necessary to monitor and assess PBDEs within the Hawaiian Islands.

Approximately 2 g of muscle from each fish was sampled. After spiking with ^{13}C-labeled surrogates, the sample was then Soxhlet-extracted with dichloromethane : *n*-hexane (1 : 1, v/v) for 24 h, and the lipid content was determined. The extract was passed through a multilayered column packed with 5 g inactive Al_2O_3 (3%, w/w), 4 g activated silica, 10 g acidified silica (44%, w/w) and 2 g activated silica from the bottom to the top. The column was then eluted with 200 mL dichloromethane : *n*-hexane (5 : 95, v/v). Recovered extract dried *via* evaporation under gentle nitrogen flow. After ^{13}C-labeled injection standards were added, extract volume was adjusted to 10 μL with nonane, and ready for instrumental analysis.

PBDE congeners, except for BDE209, were determined on an Agilent 6890 N-5975B GC-MS system equipped with a DB-5 ms column (J&W Scientific, Folsom, CA, USA). One microlitre of sample was injected by an auto-sampler in splitless mode. The carrier gas was

helium delivered at 2 mL min^{-1}. The temperatures of the injection and ion resource were 250 °C and 230 °C, respectively. The oven temperature was programmed as follows: initial temperature 60 °C for 2 min, heated to 200 °C at 10 °C min^{-1} and held for 2 min, to 300 °C at 20 °C min^{-1} and held for 10 min. BDE209 was determined on the same instrument using a DB-5 ms column (J&W Scientific, Folsom, CA, USA). The carrier gas was helium at 1 mL min^{-1}. The oven temperature was programmed as follows: initial temperature 150 °C for 1 min, heated to 300 °C at 30 °C min^{-1} and held for 10 min. The other conditions were the same as those of the other PBDE congeners. PBDE congeners were quantified by an isotope dilution method based on selected ion monitoring (SIM).

Present detection of PBDEs in tilapia from Hawaiian waters suggests that it is urgently necessary to monitor and assess PBDEs within the Hawaiian Islands despite its geographical position far from the continents.

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