Congener Patterns of Higher Brominated PBDEs in Biotic and Abiotic Matrices: What do they Reveal?

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Abstract

The high levels of BDE-209 and total PBDEs present in peregrine falcon eggs provide an opportunity to measure and examine the metabolic fate of the higher-brominated PBDEs (hepta-, octa-, nona-BDEs), and to compare patterns of these congeners with those found in PBDE commercial mixtures as well as environmental matrices (sludge, sediment, dusts). We found differences between peregrine eggs and commercial mixtures: BDE-184 (hepta-BDE) and BDE-202 (octa-BDE) were present in peregrine eggs but not in commercial mixtures. We found higher percentages of BDEs-207 and -208 (nona-BDEs) in the eggs. BDE-207 is the major nona-BDE in peregrine eggs and other biota, while BDE-206 is the major nona-BDE in environmental matrices. These clear differences between eggs/biota and commercial mixtures in patterns of higher-brominated BDEs offer compelling evidence for the biological debromination of BDE-209.

Introduction

The use of "Deca" as a flame retardant in plastic products has led to its appearance worldwide in sediments, sludge, dusts (indoor and outdoor), air, and water, as well as in biota. The instability of the decabromodipheny ether molecule (BDE-209) when exposed to UV light, heat, or reductive geochemical conditions, as well as the appearance of possible products of biological debromination in biota, suggest that an enormous reservoir of BDE-209 exists in sediments, dusts, and discarded flame-retarded plastics that may be transformed over the long-term into the more bioavailable lower-brominated congeners. It is not clear from measurements made to date in marine/aquatic species how prevalent the higher-brominated congeners are in the aquatic food web. These congeners appear to be present, if at all, at low levels. Our finding of high levels of BDE-209 and the higher-brominated congeners in peregrine falcon eggs[1] offers the opportunity to assess the biotransformation of BDE-209 in two ways: 1) examine levels and homolog ratios of the higher-brominated PBDEs (hepta-, octa-, nona-BDEs) in biota; and 2) compare and contrast congener patterns in peregrine eggs with patterns found in PBDE commercial mixtures and in environmental matrices (sludge, sediment, dusts). Other recent studies have also reported the presence of higher-brominated PBDEs in terrestrial biota[2,3,4,5,6].

Materials and Methods

Peregrine falcon eggs were collected in 1986-2007 as part of the Peregrine Recovery Program in California. Some were collected as addled eggs in wild nests when nestlings were banded. Other eggs were brought in for captive incubation after two weeks of nest incubation, and those that did not hatch were frozen and archived. Eggs were received frozen and were stored at -20^{o}C until analysis. Samples were prepared in 4 steps: lyophilzation, accelerated solvent extraction (ASE200), fat determination, clean-up on acid-, base-, and neutral-silica gel, and gel permeation chromatography. An aliquot representing 0.1-0.3g of fat was spiked with eight $^{13}C_{12}$-PBDEs and fifteen $^{13}C_{12}$-PCBs from Wellington Labs. Inc., Guelph, ON, Canada or Cambridge Isotope Labs. Inc., Andover, MA, USA. The final extract volume was 10 µL after addition of the recovery standards ($^{13}C_{12}$ BDE-77, -154, -207,.and $^{13}C_{12}$ PCB-47, -178). Levels of PBDEs were measured using isotope dilution/HRGC-HRMS (ThermoFinngan MAT95, Bremen, Germany) equipped with DB-5MS (15 m × 0.25 mm i.d., 0.1 um film thickness, J & W Scientific, Folsom, CA) and operated in electron impact ionization-selective ion monitoring mode with 8,000 resolution. Molecular ions were monitored to identify tri- to penta-BDEs, and M-2Br ions identified hexa-, and deca-BDEs.

Results and Discussion

Figures 1-3 compare homolog ratios for hepta-, octa-, and nona-BDEs in peregrine falcon eggs and commercial PBDE mixtures[7]. We found BDE-184 (hepta-BDE) and BDE-202 (octa-BDE) to be present in peregrine eggs. These are not reported in commercial mixtures[7] (Figures 1-2). We also found that BDEs-207 and -208 (nona-BDEs) were present at higher percentages in the eggs than are reported for the mixtures[1,7] (Figure 3). In addition, we found BDE-207 to be the major nona-BDE in peregrine eggs (also reported for other biota[2,3,4,5,6]). This is in contrast to environmental matrices, where BDE-206 is reported as the major nona-BDE [8](Figure 4).

These results are consistent with metabolic debromination of BDE-209 in the peregrine falcon. For the hepta-BDEs, the large proportion (~20%) of BDE-184 of Σhepta-BDEs in eggs and its absence from commercial mixtures (Figure 1) suggests biotransformation of BDE-209 by three successive meta-debrominations. For the octa-BDEs, the presence of BDE-202 in the eggs and its absence from commercial mixtures (Figure 2) suggests biotransformation of BDE-209 by successive para- and meta-debrominations.

For the nona-BDEs, the higher proportion of BDE-208 in eggs vs. commercial mixtures could result from either 1) debromination of BDE-209, or 2) preferential uptake compared to the other nona-BDEs (BDE-206, -207) from the "Deca" or "Octa" commercial mixtures (Figure 3). Preferential uptake of BDE-208 is considered unlikely because the K_{OWs} for three nona-BDEs are similar [2,12,13]. A more reasonable explanation of the higher proportion of BDE-208 in the eggs is the para-debromination of BDE-209. The proportion of BDE-207 in eggs also differs from the proportions found in the mixtures (Figure 3), and the same argument can be made, using meta-debromination.

Figure 4 shows homolog ratios for the nona-BDEs, and the striking contrast in nona-BDE congener patterns between "abiotic" vs "biotic" matrices. Whereas BDE-206 (ortho-debromination) predominates in the "abiotic" matrices (sludge, sediment, dusts), BDE-207 (meta-debromination) predominates in terrestrial biota. BDE-209 is known to be present at significant levels in the "abiotic" and "biotic" matrices shown in Figure 4. The prevalence of BDE-206 in "abiotic" systems suggests that ortho-debromination of BDE-209 is the favored pathway for abiotic debromination. The prevalence of BDE-207 in biota suggests that meta-debromination of BDE-209 is the favored pathway for biological transformation. Future work will examine levels of unidentified hexa-, hepta-, and octa-BDE homologs which may help to further clarify the biotransformation of BDE-209.

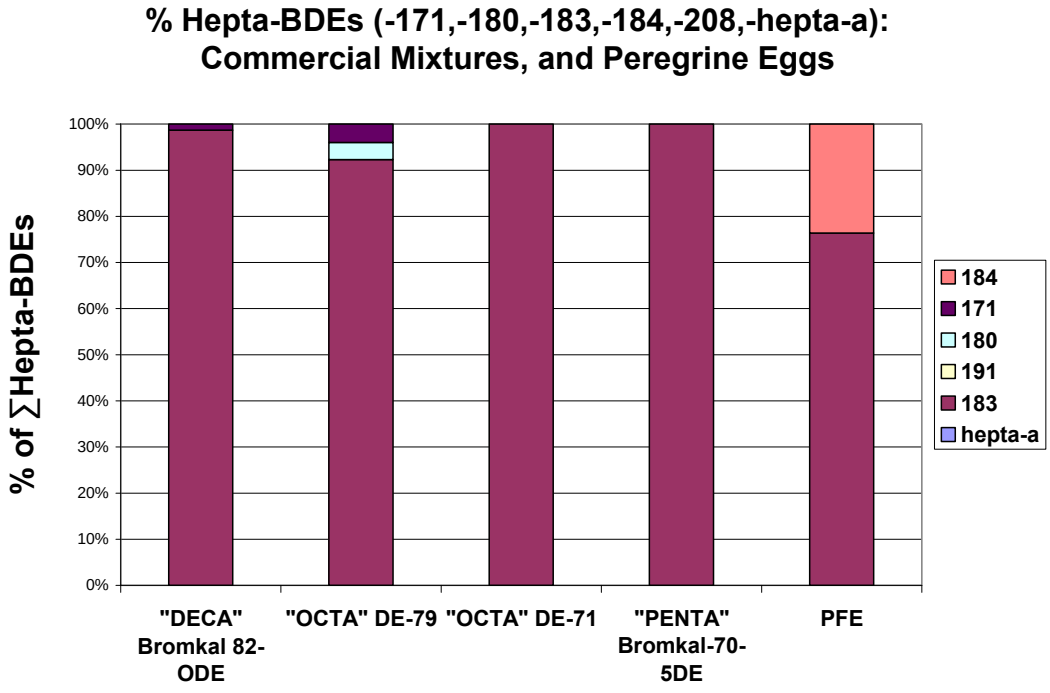

Figure 1: Homolog ratios for hepta-BDEs in peregrine falcon eggs and commercial PBDE mixtures (1,7).

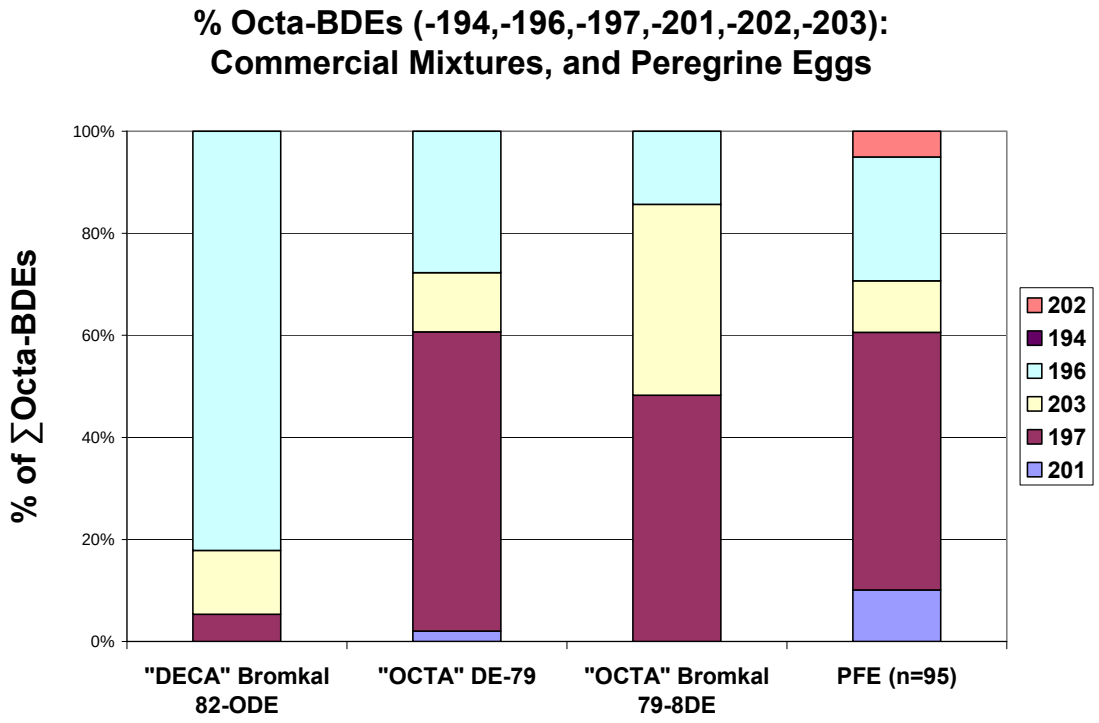

Figure 2: Homolog ratios for octa-BDEs in peregrine falcon eggs and commercial PBDE mixtures (1, 7).

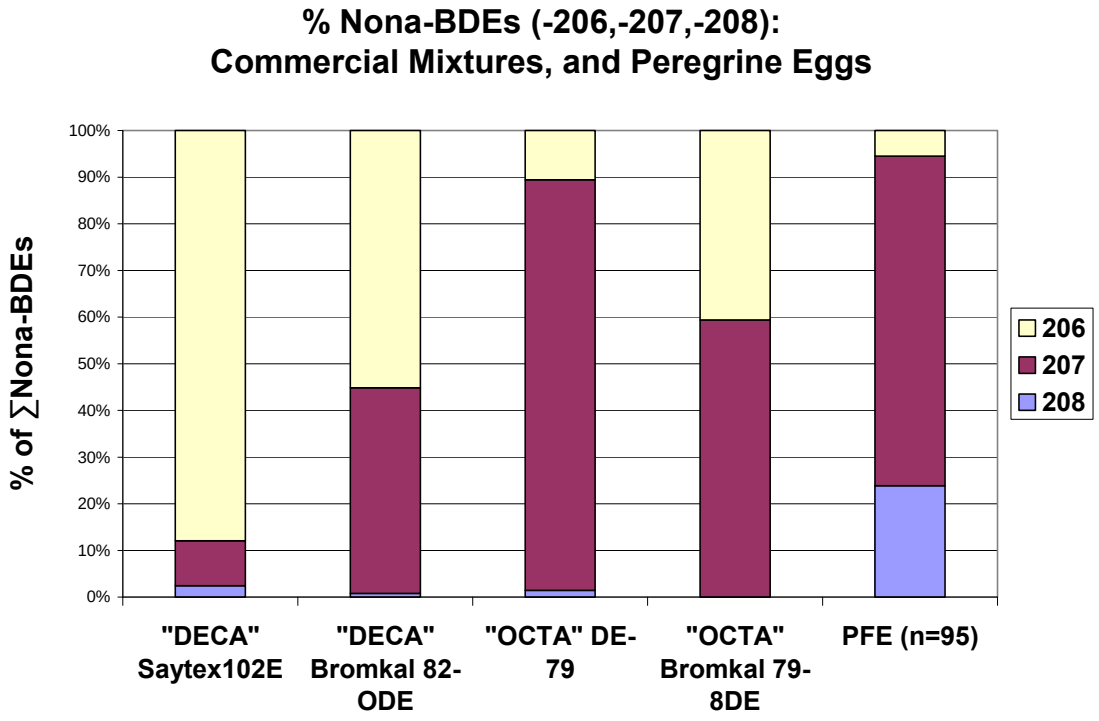

Figure 3: Homolog ratios for nona-BDEs in peregrine falcon eggs and commercial PBDE mixtures (1,7).

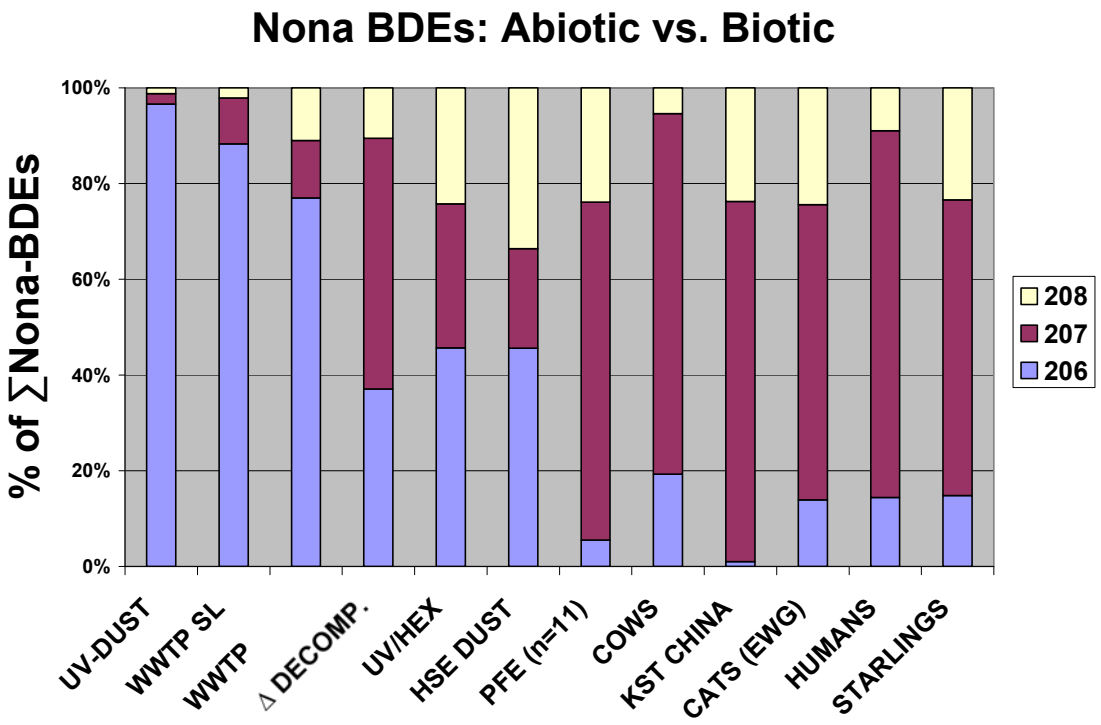

Figure 4. Plot of homolog ratios for the 3 nona-BDEs in various abiotic and biotic matrices (vertical bar 1-is from reference (11); 2 and 3(8); 4 (unpublished from ECL); 5(10); 6(9); 7 (1); 8 (2); 9 (3); 10 (4); 11 (5); 12 (6).

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