“TERRESTRIAL” VS “AQUATIC” FOOD WEBS: HIGH BDE-209, -183, and -153 LEVELS IN PEREGRINE FALCON EGGS FROM CALIFORNIA

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Abstract

In a study of PCB, PBDE, and DDT/DDE levels in 105 peregrine falcon eggs from California, twenty eggs from fourteen falcons have been analyzed for PBDEs. In contrast to the congener patterns seen in California aquatic biota (fish, harbor seals, and terns), in which lower brominated PBDEs (BDE-47, -99, and -100) predominated, the major congener in the peregrine eggs were the higher brominated PBDEs (BDE-153, -183, and -209), and these levels were higher in eggs in nests from urban vs rural areas (highest: ∑PBDEs 55 ppm; BDE-153 11.5 ppm; BDE-183 4.5 ppm; BDE-209 3.4 ppm). Some eggs show intermediate congener patterns, suggesting the birds feed on prey from both the “aquatic” and “terrestrial” food webs.

Introduction

In our biomonitoring program to examine levels of chemicals of concern in wildlife and residents in California, we have measured levels of polybrominated diphenyl ethers (PBDEs) in biota from the San Francisco Bay region (harbor seals[1-2], fish[3], terns[4-8]), in fish from Coastal California[9-10], and in adipose[1-2], serum[11-14], and breast milk[15-18] samples from Californians. PBDE levels are among the highest in the world, with the lower brominated tetra-, penta-, and hexa-PBDEs (BDE-47, -99, -100, -153, and -154) the major congeners. The.higher brominated hepta-deca congeners (e.g. BDE-183) are only minor components, and little or no BDE-209 is found in these samples. The penta- and octa-commercial mixtures which contain these lower brominated congeners are no longer in use in the US. There are currently no restrictions on the use of decaBDE, the PBDE technical product in highest production volume. Recent studies report significant levels of BDE-209 in red foxes[19], harbor seals[20], interior grizzly bears[21], and birds of prey in Sweden[22] and Bejing, China[23]. We examined PBDE levels in eggs from peregrine falcons, an endangered raptor, and report here results from 20 of the 105 California eggs obtained for the study.

Materials and Methods

Peregrine falcon eggs were collected 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°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 seven $^{13}C_{12}$-BDEs. The final extract volume was 10 µL after addition of the recovery standards ($^{13}C_{12}$ BDE-77, $^{13}C_{12}$ BDE-154, and $^{13}C_{12}$ BDE-207). The target analytes were identified and measured using a Finnigan Mat-95 high-resolution GC/MS equipped with a splitless injector and a 15-meter DB 5 ms column operating in electron impact ionization-selective ion monitoring mode with 9,000 resolution. Molecular ions were monitored to identify tri- to hexa-BDEs, and M-2Br ions identified hepta-, and deca-BDEs.

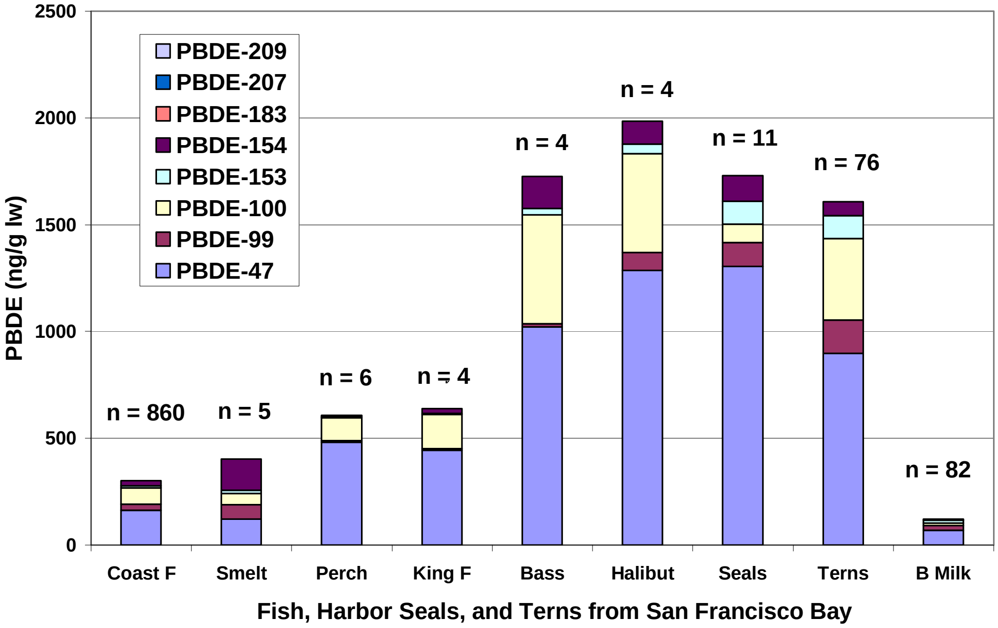
Results and Discussion

Figure 1 illustrates the “aquatic food web” PBDE congener pattern seen in California marine/aquatic biota (fish, harbor seals, Forster’s terns from San Francisco Bay), where the major congeners are the lower brominated PBDEs (BDE-47, -99, -100). Breast milk and adipose samples from Californians show a similar pattern. Figure 2 contrasts this “aquatic food web” pattern (tern eggs) with the “terrestrial food web” PBDE congener pattern seen in eggs from California peregrine falcons (CA-1-13), where the higher brominated congeners (BDE-153, -183, and -209) predominate. Figure 2 also shows PBDE levels in California peregrines are 10-15 fold higher than those in Swedish peregrines. BDE-209 is absent from aquatic biota, but BDE-209 levels in California peregrine eggs are high, higher than in eggs from Sweden (Figure 3) but not as high as levels reported for raptor eggs from China[22]. Maximum values among the California peregrines were: ∑PBDEs 55 ppm; BDE-153 11.5 ppm; BDE-183 4.5

ppm; BDE-209 3.4 ppm. The peregrine egg with 55 ppm ∑PBDEs is not shown in Figure 2.

Peregrines feed mainly on birds-on-the-wing, and prey remains near nests in California urban environments indicate pigeons, doves, swallows, and starlings as significant prey. The urban peregrines have the “terrestrial food web” pattern. Three birds, with feeding ranges that bridge aquatic and urban environments, have an intermediate pattern, with both the higher and lower brominated congeners well represented (CA-12, -13, Figure 2, and CA-14 not shown). This suggests these peregrines prey not only on birds in the urban food web, but on those in the aquatic food web.

Figure 1. PBDEs in "Aquatic Food Web": California SFB Fish (2003), Harbor Seals (1989-98), Forster's Terns (2000-03), and Coastal Fish (2001)



The unusual levels of BDE-153, -183, and -209 in the “terrestrial food web” peregrines deserve further attention. Analysis of remaining samples will examine factors related to the sources, pathways, and patterns of PBDE exposures (e.g. metabolic pathways, changes of congener levels over time, urban vs rural patterns, coastal and interior patterns, prey assessment for different regions), and to possible relationships between these exposures and adverse reproductive outcomes.

Acknowledgements

We thank the many ornithologists and bird enthusiasts who have supported the collection and preservation of peregrine falcon eggs. Their efforts have enabled the US peregrine populations to survive DDT-induced egg-shell thinning and reproductive failure in the mid-1950s-60s, and to restore the California breeding pair population from a low of 2 known to >200 over the past thirty years.

Figure 2. PBDEs in "Terrestrial Food Web": Peregrine Falcon Eggs from Sweden (n=35; 1999) and California (n=14; 1997-2005)

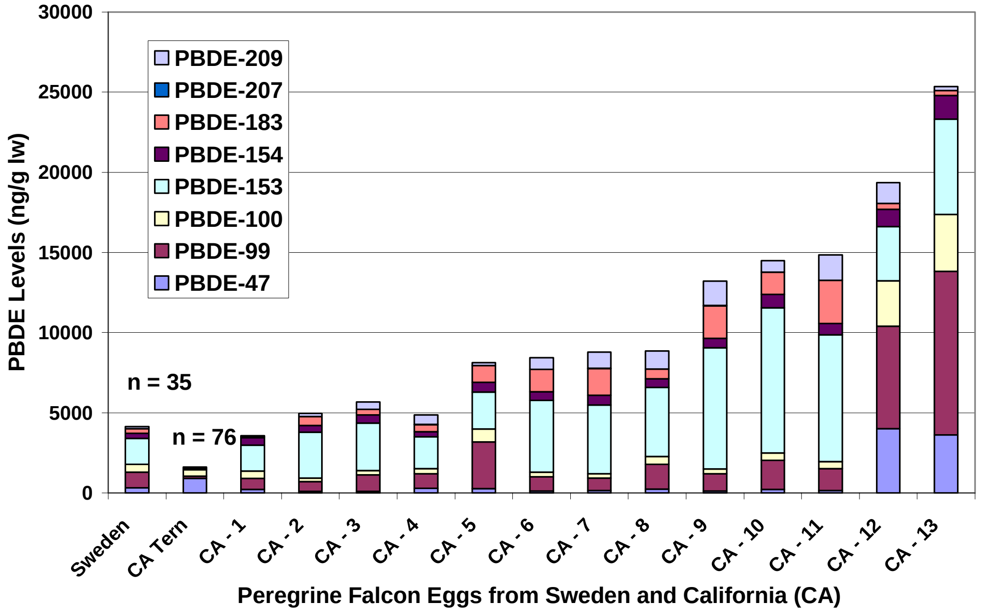
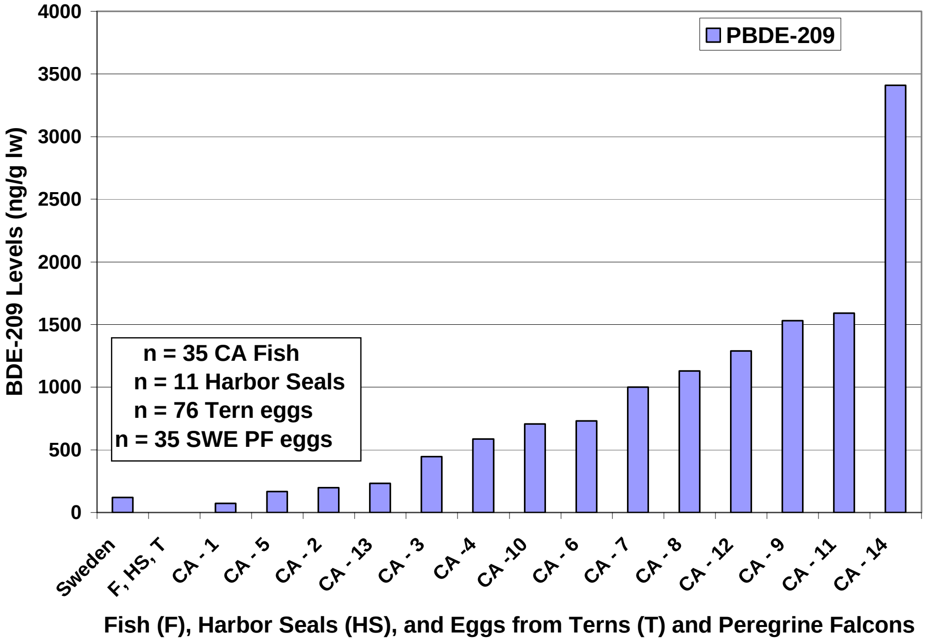


Figure 3. BDE-209 in "Aquatic" vs Terrestrial" Food Webs: California Fish, Harbor Seals, Terns, and Peregrine Falcons



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