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Flame retardants and organochlorine pollutants in bald eagle plasma from the Great Lakes region

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ABSTRACT

We report measurements of polybrominated diphenyl ethers and of emerging flame retardants in the plasma of nestling bald eagles sampled from early May to late June of 2005. Concentrations of total PBDEs ranged from 0.35 ng g^{-1} ww to 29.3 ng g^{-1} ww (average = 5.7 ± 1.9 ng g^{-1} ww). The most abundant congeners were BDE-47, BDE-99, and BDE-100. The fully brominated congener, BDE-209, was detected in approximately one third of the samples at an average concentration of 1.2 ± 0.72 ng g^{-1} ww. Several emerging flame retardants, such as pentabromoethylbenzene (PBEB), hexabromocyclododecanes (HBCDs), and Dechlorane Plus (DP), were detected in these samples. Polychlorinated biphenyls (PCBs) and organochlorine pesticides were also detected at levels close to those previously published. A statistically significant relationship was found between total PBDE concentrations and total PCB and *p,p′*-DDE concentrations, suggesting that these compounds share a common source, which is most likely the eagle's food.

1. Introduction

It came as a shock to the American public when bald eagles, one of the most significant symbols of the United States, were found to be contaminated with persistent organic pollutants (POPs). As a result, bald eagle populations were threatened, and they were listed as an endangered species in the late 1970s in most of the United States and in Canada. Luckily, thanks to legislative efforts to control and reduce persistent pollutants, to protect and restore habitat, and to eliminate harassment of the eagles and their eggs, bald eagle populations have started to recover. Nevertheless, in some regions, including the Great Lakes, this recovery has not been as successful as hoped, and these populations are still experiencing poor reproductive success and poor juvenile and adult survival rates (Elliott and Harris, 2001/2002).

Bald eagles are indigenous to the Great Lakes, and they are top predators of the Great Lakes food web. They feed on fishes, waterfowl, and small mammals, depending on season, location, availability, competition, and other variables. Their position in the food web makes bald eagles susceptible to accumulating high concentrations of environmental contaminants. In fact, bald eagles are excellent biosentinels of Great Lakes water quality, particularly for bioaccumulative halogenated compounds, which are delivered to the Great Lakes largely through atmospheric deposition (Bowerman et al., 2002).

Historically, monitoring programs using eagles and other raptors as sentinels have focused on the bird's eggs as the media for assessing contaminant levels and trends. Despite some obvious advantages, such as ease of collection and proximity between the target chemical and the developing embryo, egg sampling also has some drawbacks. These include the destructive nature of the sampling technique and a high level of nest disturbance that significantly increases the frequency of nest abandonment (Strause et al., 2007). Conversely, using plasma as the sampling medium allows collecting blood without destroying the individual, collecting samples from the same nest over time, and collecting samples from nestlings. This last aspect is especially relevant when trying to use birds as sentinels for a specific area, since nestlings are sedentary and their accumulation of toxic pollutants results mainly from parentally transferred food.

Brominated flame retardants (BFRs) are a broad category of chemicals that include polybrominated biphenyls (PBBs), hexabromocyclododecanes (HBCDs), and polybrominated diphenyl ethers (PBDEs). Flame retardants are added to numerous commercial products to reduce their flammability, and their usage has increased rapidly since the 1980s, probably as a result of more stringent fire safety regulations. As a result of this heavy usage, PBDEs are ubiquitous in the environment, having been detected in air, sediments, biota, and people (Hites, 2004).

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Bowing to environmentalist's pressure, in 2004, two commercial PBDEs mixtures were voluntarily withdrawn from the United States' market (Penta-BDE and Octa-BDE). The other widely used commercial mixture, Deca-BDE, was until recently largely unregulated in the United States and Canada, but it too is being withdrawn from the market, in this case, by the end of 2013 (Hess, 2010). In addition, flame retardant producers have been replacing banned or retired products with unregulated compounds. For example, 1,2-*bis*(2,4,6-tribromophenoxy)ethane (TBE) was reintroduced as a substitute for Octa-BDE; similarly, decabromodiphenylethane (DBDPE) was marketed as an alternative to BDE-209. The persistence of the older brominated flame retardants, together with the market shift towards unregulated compounds, requires a continuous monitoring effort to keep track of their levels in the environment.

The exposure of predatory birds to contaminants such as 2,2-*bis*(4-chlorophenyl)-1,1-dichloroethene (DDE), chlorinated pesticides, and polychlorinated biphenyls (PCBs), caused eggshell thinning, reproductive and developmental challenges, and eventually mortality (Elliott and Harris, 2001/2002). PBDEs and several other halogenated flame retardants are equally persistent and bioaccumulative, and although their toxicity is not completely understood, exposure of rodents to PBDEs has been associated with altered neural development, abnormal endocrine and liver functions, and reproductive failures (Birnbaum and Staskal, 2004). It has been recently reported that decreased plasma thyroxine (T4) and vitamin A levels were observed in American kestrels after a dose of a PBDE mixture *in ovo* and post-hatch (Fernie et al., 2006).

The potential toxicological effects of PBDEs, as well as their ubiquity in the environment, suggests that the concentrations of these compounds should be measured regularly in bald eagles, a species that has already proven to be particularly susceptible to the effects of persistent organic pollutants. This need is supported by a recent study from Dykstra et al. (2005), who showed that the reproductive rate of Lake Superior bald eagles did not increase through the 1990s, despite a general decrease of both DDE and PCB concentrations in biota. This finding may indicate that ecological factors were hindering the bird's productivity, but more importantly, this finding may indicate that other contaminants (i.e. flame retardants) have emerged as possible threats.

In this paper, we report concentrations of PBDEs and emerging brominated and chlorinated flame retardants in the plasma of nestling bald eagles from the Great Lakes region, together with some PCB and pesticide concentrations for context.

2. Materials and methods

2.1. Sample collection

In this preliminary survey, 15 samples were collected within the Great Lakes watershed in 2005. The sampling locations are given in Fig. 1; the samples were spatially distributed to cover as much area as possible. Since the samples were collected as part of the Michigan Bald Eagle Biosentinel Program, only nests located within the state of Michigan were sampled. Specifically, three samples were collected near the southern shore of Lake Superior; six samples were collected in Lake's Michigan watershed, covering mostly the eastern shore; and six samples were collected on the Michigan side of Lake Huron.

Details of the sampling procedures can be found elsewhere, and only a brief description is given here (Wierda, 2009). Nestling eagles were captured, restrained, processed, and returned to the nest individually. Blood was collected from the brachial vein, and morphological measurements of culmen, hallux claw, and bill depth were collected using a caliper. The length of the eighth primary feather and the spread of the footpad were measured with a ruler. From these data, the sex and the estimated age of the nestling were determined (Wierda, 2009). Nestlings were also weighed.

2.2. Materials

Standards for the most common legacy pesticides (25 different compounds including DDTs, endosulfans, chlordanes, HCHs, methoxychlor, and endrin) and PCBs (congeners 8, 18, 28, 44, 52, 66, 77, 101, 105, 110, 118, 128, 138, 153, 156, 170, 180, 187, 195, 206 and 209) were purchased at AccuStandard and Ultra Scientific (Wierda, 2009).

A PBDE standard mixture (BFR-PAR) was purchased from Wellington Laboratories (Guelph, ON). This solution contained the following PBDE congeners: 1, 3, 7, 10, 15, 17, 28, 30, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 139, 140, 153, 154, 156, 169, 171, 181, 183, 184, 191, 196, 197, 201, and 203 to 209. Other compounds included in this standard mixture were: hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), 2,2′,4,4′,5,5′-hexabromobiphenyl (BB-153), 1,2-*bis*(2,4,6-tribromophenoxy)ethane (TBE), and decabromodiphenylethane (DBDPE). Hexabromocyclododecane (α-HBCD) from AccuStandard, Dechlorane Plus (DP) from OxyChem, BDE-118 from AccuStandard (New Haven, CT), and $^{13}C_{12}$-BDE-209 from Wellington Laboratories were added individually to the calibration standard.

2.3. Analytical procedures

The protocol for extraction, cleanup, and analysis of the pesticides and PCBs is described elsewhere and only a limited description will be provided here (Bowerman et al., 1995). Approximately 1 mL of plasma was weighed, denaturated with 0.5 mL of methanol, extracted with 5 mL of dichloromethane three times, and purified using alumina and silica solid phase extraction. The extracts were then analyzed by dual column gas chromatography with electron capture detection. The internal standard method was used for quantitation with 1-bromo-2-nitrobenzene and PCB-198 as the internal standards.

For the brominated flame retardants, 2.5–5 mL of plasma were weighed, spiked with surrogate standards (BDE-77, BDE-166, and $^{13}C_{12}$-BDE-209), denaturated with 2 mL of HCl and 6 mL of 2-propanol, and extracted with (1:1) hexane/methyl *t*-butyl ether. Lipids were removed using sulfuric acid. The extracts were cleaned on an alumina column capped with anhydrous sodium sulfate using hexane and (4:6) hexane/dichloromethane as eluents. Two procedural blanks were included in every batch of six samples.

The samples were analyzed for the flame retardants on an Agilent 6890 series gas chromatograph coupled to an Agilent 5973 mass spectrometer. The 2 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. An Rtx-1614, 15-m long × 250 μm i.d., 0.10-μm phase thickness, fused silica capillary GC column (Restek Corporation, Bellefonte, CA) was used for determination of all the congeners. The GC oven temperature program was as follows: isothermal at 100 °C for 2 min, 25 °C min^{-1} to 250 °C, 3 °C min^{-1} to 270 °C, 25 °C min^{-1} to 325 °C, and held at 325 °C for 11 min. The GC to MS transfer line was held at 280 °C. The mass spectrometer was operated in the electron capture negative ionization mode with selected ion monitoring. Details on the monitoring ions are reported elsewhere (Venier and Hites, 2008). The internal standard method was used for quantitation with BDE-118 as the internal standard.