



## Species-specific accumulation of polybrominated diphenyl ether flame retardants in birds of prey from the Chesapeake Bay region, USA

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Birds of prey breeding in the Chesapeake Bay (USA) exhibited species-specific PBDE accumulation patterns.

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### ABSTRACT

Compared to organochlorines, little is known about polybrominated diphenyl ether (PBDE) contamination of birds of prey breeding in the Chesapeake Bay, the largest estuary in the U.S. This study examined and compared PBDE contamination in eggs of osprey, double-crested cormorant, brown pelican and peregrine falcon from this area. Several legacy persistent organic pollutants such as PCBs and DDE were also investigated. The level of urbanization of the landscape appeared to influence the level of PBDE exposure. PBDE congener distribution patterns varied between piscivorous and terrestrial-feeding birds. This suggests individual congeners may be subject to differences in bioaccumulation, biomagnification or metabolism in the aquatic and terrestrial food webs. Biomagnification of PBDEs was studied in the Bay aquatic food chains for the first time. A biomagnification factor of 25.1 was estimated for ΣPBDEs for the fish – osprey egg food chain. Hazard quotients, applied as a preliminary evaluation, indicated that PBDEs may pose a moderate hazard to ospreys and peregrine falcons through impairment of reproductive performance.

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### 1. Introduction

As the largest estuary in the United States, the Chesapeake Bay provides a critical habitat for a vast number of resident and migratory bird species. The Bay supports one of the largest osprey (*Pandion haliaetus*) breeding populations in the world (Watts and Paxton, 2007). A survey performed in the mid-1990s estimated the osprey breeding population consisted of about 3500 pairs (Watts and Paxton, 2007), compared to an estimated 1450 pairs in 1973 (Henny et al., 1974). This region is also home to a number of peregrine falcon (*Falco peregrinus*) pairs, thanks to a successful long-term recovery effort. Several piscivorous species, such as double-crested cormorant (*Phalacrocorax auritus*) and brown pelican (*Pelecanus occidentalis*), did not nest in the Bay historically, but recent range expansions have occurred (e.g., Smith Island, MD). Several avian species in the Bay have suffered dramatic population declines in the post-World War II era, largely due to reproduction suppression induced by environmental contaminants (Rattner and McGowan, 2007). Widely applied organochlorine pesticides, specifically DDT and its breakdown products, were probable

causative agents of eggshell thinning deemed responsible for reproductive failure in some avian species (Anderson and Hickey, 1972). Numerous studies have indicated that major organochlorine contaminants such as *p,p'*-DDE and polychlorinated biphenyls (PCBs) have declined in bird eggs and tissues, although these chemicals may still exert sublethal and reproductive effects in some locations (Rattner and McGowan, 2007). However, compared to organochlorines, little is known about brominated flame retardants contamination in the Chesapeake Bay avifauna.

Brominated flame retardants are of concern because they are present in bulk in textiles, thermoplastics, polyurethane foams and electrical products. The most studied are polybrominated diphenyl ether (PBDE) flame retardant additives, marketed in the form of three major commercial formulations: Penta-, Octa- and Deca-BDE. Studies show that some PBDE congeners have become widely distributed in abiotic media, wildlife, and humans, reaching even remote areas (Hale et al., 2003; Hites, 2004; Law et al., 2006; de Wit et al., 2006). Although the production of Penta- and Octa-BDEs was phased out in North America in 2004, recent studies have yet to identify an associated diminution of contamination in wildlife here. Toxicological studies of PBDEs in birds are scarce. Available data suggest that an exposure to environmentally relevant PBDEs can induce changes in thyroid, vitamin A, glutathione homeostasis, and oxidative stress in American kestrel (*Falco sparverius*) chicks, as

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well as reproductive courtship behaviors in adult kestrels (Ferne et al., 2005; 2008). A Penta-BDE formulation, DE-71, has also been observed to reduce eggshell thickness (Ferne et al., 2009), and decrease pipping and hatching success in kestrels and cause sublethal effects (i.e., ethoxyresorufin-O-dealkylase induction) in hatching chickens (McKernan et al., 2009). The observations merit concern as the threshold levels observed in these laboratory exposure studies approached concentrations detected in some North American wild birds. Examination of osprey eggs collected from Oregon and Washington States (USA) discovered that concentrations in the vicinity of 1000 ng/g wet wt may reduce osprey reproductive performance (Henny et al., 2009a). To date only two studies have reported PBDE burdens in Chesapeake Bay avifauna (Rattner et al., 2004; Potter et al., 2009). Data are lacking from some important tributaries (i.e., York River and Rappahannock River) and virtually nothing is known about recently colonized double-crested cormorants and brown pelicans. Therefore, this study was undertaken to examine PBDE contamination in selected bird species, mostly from the lower Bay. Special attention was paid to species-specific contamination patterns.

## 2. Materials and methods

### 2.1. Samples

A total of 38 peregrine falcon, 13 osprey, 12 double-crested cormorant and 10 brown pelican eggs were examined (Fig. 1). All eggs were nonviable and collected after the end of their normal incubation periods. It is noted that this collection strategy may be biased, leading to higher concentrations reported if any of the contaminants was having an adverse effect on hatchability. Egg lengths, widths, and total egg weights were measured. Egg contents were frozen until analyzed.

### 2.2. Analysis

Analytical methods were similar to those described in Chen et al. (2008), with minor modifications. Freeze-dried egg contents and sodium sulfate blanks were subjected to enhanced solvent extraction (Dionex ASE 200, Sunnyvale, CA). Before extraction, the surrogate standard PCB-204 (Ultra Scientific, North Kingstown, RI) was added to samples to estimate recoveries. Lipid contents were determined by evaporation of a fraction of each extract to a constant weight. The remainder of each extract was then purified by size exclusion chromatography (Envirosep-ABC, 350 × 21.1 mm column; Phenomenex, Torrance, CA), and further purified on 2-g, silica gel solid-phase extraction columns (International Sorbent Technology, UK). The first fraction was eluted from the silica column with 3.5 mL of hexane and was discarded. Second and third fractions were obtained by elution with 6.5 mL of 60:40

hexane/dichloromethane and 8 mL of dichloromethane, respectively. The latter two fractions contained halogenated compounds of interest and were combined for instrumental analysis. Decachlorodiphenyl ether (Ultra Scientific, North Kingstown, RI) was added to purified extracts as the internal standard.

PBDE congeners were analyzed on an Agilent 6890N gas chromatograph (GC) (Agilent Tech., Palo Alto, CA), coupled to a JEOL mass spectrometer (JMS-GC Mate II, JEOL, Peabody, MA). A 30-m DB-5HT column (0.25 mm i.d., 0.1 μm film thickness, J&W Scientific, Folsom, CA) was used to separate the PBDE congeners of interest (BDE-15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 201, 202, 203, 206, 207, 208, 209). A pressure pulse split/splitless injector was used, with an injector temperature of 300 °C and pressure of  $3.4 \times 10^5$  Pa. Detection was in the electron-capture negative ionization (ECNI) mode, monitoring mass to charge ratios ( $m/z$ ) of 79 and 81 for PBDEs and 37 and 35 for chlorinated standards. The initial column temperature was held at 90 °C for 4 min; increased to 150 at 30 °C/min; to 300 at 10 °C/min (held for 15 min); and finally to 350 at 30 °C/min (held for 15 min).

Chlorinated pesticides were examined on a Varian 3400 GC (Varian, Walnut Creek, CA), coupled with a Varian Saturn 4-D MS, in the electron ionization (EI) mode. As BDE-154 and polybrominated biphenyl (PBB)-153 were indistinguishable under ECNI mode, they were determined by EI. The GC was equipped with a 60-m DB-5 column (0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA). Injections were made in splitless mode, with an injector temperature of 320 °C. The initial column temperature was held at 75 °C for 1 min; then increased to 350 at 4 °C/min and held for 1 min. PCB congeners of interest were separated on a Varian CP-3800 GC (Varian, Walnut Creek, CA) equipped with a 60-m DB-5 column (0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA), coupled with a Varian Saturn 2000 MS (Varian, Walnut Creek, CA). Detection was in the EI mode. Injections were made in splitless mode, with an injector temperature of 320 °C. The initial column temperature was held at 90 °C for 1 min, and then programmed to 320 °C at 4 °C/min, and held for 10 min.

### 2.3. Biomagnification factor

Biomagnification factor (BMF) was calculated based on a simple model that apportions the contamination contribution from multiple prey species (Elliott et al., 2005). This gives a more accurate estimation than calculating BMFs simply from individual prey – predator food chains. The model has the form:

$$Y = \text{BMF}[F_1(X_1) + F_2(X_2) + \dots + F_n(X_n)] \quad (1)$$

where  $Y$  = median PBDE concentration (lipid based) in predatory species,  $F_1$  = percent biomass of item one in diet,  $X_1$  = median PBDE concentration (lipid based) in item one,  $F_n$  = percent biomass of the  $n$ th item in diet,  $X_n$  = median PBDE concentration (lipid based) in the  $n$ th item in diet.

### 2.4. Hazard quotient

Hazard quotients (HQs) were determined to provide a preliminary quantitative evaluation of PBDE hazards to birds of prey. HQs are calculated by dividing the measured concentration (MEC) of contaminants in target species with the critical

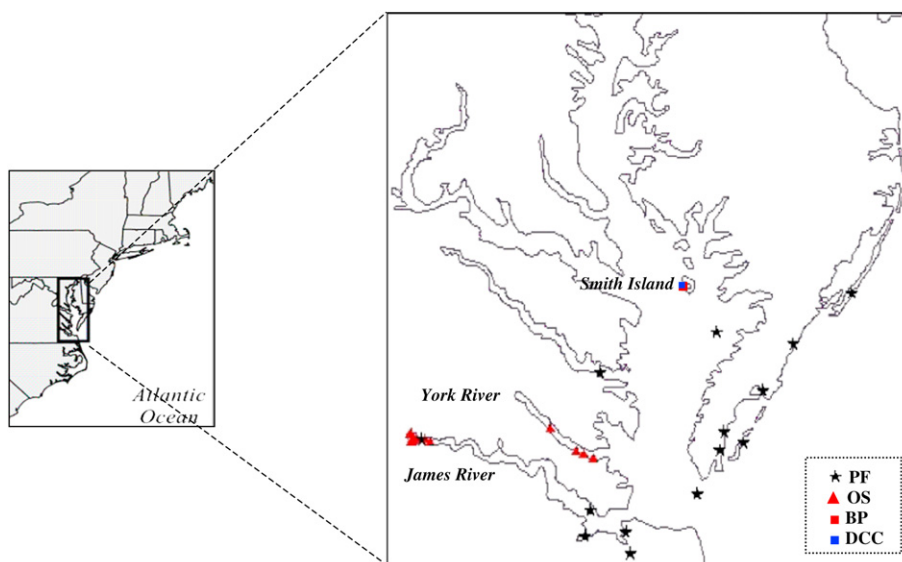


Fig. 1. Distribution of peregrine falcon (PF), osprey (OS), brown pelican (BP) and double-crested cormorant (DCC) nests sampled in the Chesapeake Bay region.

effect concentration below which no adverse effect is expected (PNEC or predicted no effect concentration) (Lam et al., 2005). In this study, the MECs were replaced by median contaminant concentrations in each species, and the PNECs were derived from previously published toxicological studies. Uncertainties need to be considered when estimating PNECs from reference data, including: use of a lowest-observed-effect-level (LOEL) instead of a no-observed-effect-level (NOEL); use of subchronic, rather than chronic or lifetime exposure; and cross species extrapolation of effects concentrations (Newman and Unger, 2003). For conservative purposes, an uncertainty factor of 10 was assigned to encompass multiple potential variations, although strictly speaking each uncertainty should be assigned a separate uncertainty factor. For interpretation, an HQ < 0.1 indicates no hazard, 0.1–1 a low hazard, 1–10 a moderate hazard, and >10 a high hazard (Lemly, 1996).

### 2.5. QA/QC

Spiking tests were performed to evaluate the recoveries of major PBDE congeners, as previously described (Chen et al., 2008). Briefly, chicken eggs free of PBDEs were spiked with 0.5 µg each of BDE-28, -47, -99, -100, -153, -154, -183 and -209 standards. Five experimental groups, each consisting of five spiked samples, were processed. The mean (±standard error) recoveries of individual congeners ranged from 74.9 (±1.3) % for BDE-154 to 89.5 (±2.2) % for BDE-209. In addition, surrogate standard PCB-204 exhibited good recoveries, 84.2 (±11.0) %, among all blanks and authentic samples.

### 2.6. Statistical analysis

For measurements below limits of detections (a signal of five times the noise level), a regression plotting method was applied to assign values for statistical analysis (Newman, 1995). Because the stage and condition of added eggs varied, an adjustment of moisture and lipid losses was applied to better interpret residue levels (Stickel et al., 1973). The final concentrations were expressed as ng/g wet wt, unless otherwise noted. The residue levels were corrected based on PCB-204 recoveries. To avoid pseudoreplication, a clutch mean was calculated if more than one egg was analyzed from a single clutch in the same year. This clutch mean was then included as a single data point for statistical analyses. Non-normally distributed data were logarithmically transformed to approximate a normal distribution before being subjected to analysis of variance (ANOVA) and Scheffe's post hoc analysis (SPSS 13.0). The level of significance was set at  $\alpha = 0.05$ .

## 3. Results and discussions

### 3.1. Concentration data and interspecies comparisons

Median  $\sum$ PBDE concentrations were 290 ng/g wet wt in ospreys, 182 in peregrine falcons, 28 in brown pelicans and 12 in double-crested cormorants. These levels were generally one to two magnitudes lower than  $\sum$ PCBs in the same species (Fig. 2). In ospreys,  $\sum$ PBDE and  $p,p'$ -DDE concentrations were similar.

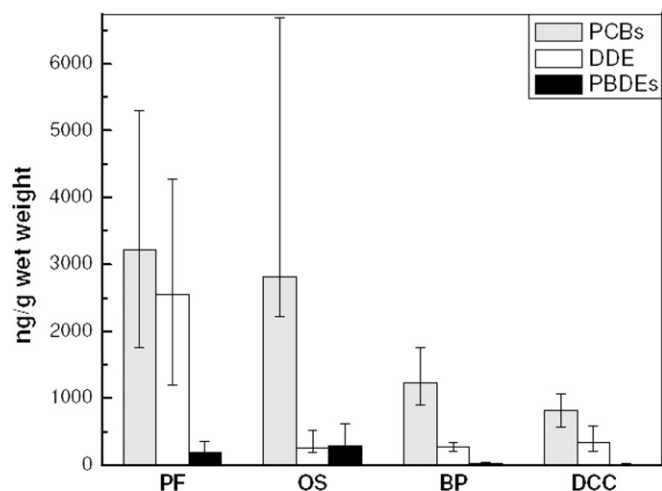


Fig. 2. Median  $\sum$ PBDE,  $\sum$ PCB and  $p,p'$ -DDE concentrations (ng/g wet wt) in eggs of peregrine falcon (PF), osprey (OS), brown pelican (BP) and double-crested cormorant (DCC). Error bars represent 75 and 25 percentiles.

Comparable results have been reported in ospreys from the northern Bay (Rattner et al., 2004). The other fish-eating species, pelicans and cormorants, contained similar DDE concentrations as ospreys, but significantly lower  $\sum$ PBDE levels ( $p < 0.0001$ ). Though factors such as migration and food choices may contribute to interspecies variances, local exposure levels in their breeding habitats may play a role here because they feed essentially to acquire resources for egg production. Smith Island, where cormorant and pelican eggs were collected, is an offshore island in the Chesapeake Bay with a human population density of about 81.7/sq mile (US Decennial Census, 2000). In contrast, osprey eggs were collected from more populated areas, e.g., Hopewell, VA, located adjacent to the James River, with a population density of 2182/sq mile (US Decennial Census, 2000). As PBDEs are present in products common in homes and workplaces, populated areas may contain proportionately more such products and hence be richer in bioavailable PBDEs. Also large tributaries such as the James River normally host several sewage treatment plants, which may serve as potential contaminant sources to the watershed (Hale et al., 2006). Studies on northeastern and mid-Atlantic U.S. peregrine falcons also reported an association between contamination levels in eggs and human population densities (Chen et al., 2008; Potter et al., 2009). This supposition is further supported by results for our osprey eggs. Those collected from the James River contained significantly higher (432 vs. 64 ng/g wet wt) levels than those from Gloucester County along the York River. The latter area has a lower human population density (160.6/sq mile; US Decennial Census, 2000). It should be noted that other factors, such as female ages and migration patterns, may also affect the contamination burdens in eggs (Elliott et al., 2007). However, data concerning such differences are limited.

Peregrine falcon eggs contained  $\sum$ PCB and  $\sum$ PBDE concentrations similar to those of the ospreys. However, DDE burdens were significantly higher in the former. Peregrines in the mid-Atlantic region are mostly non-migratory (Clark et al., 2008). They feed primarily on other birds, and in coastal areas, migratory shorebirds may constitute a large percentage of the diet. For example, Steidl et al. (1997) estimated that two-thirds of the peregrine diet in the New Jersey area consisted of such birds. Contaminated migratory birds may contribute substantially to DDE burdens in these peregrines. However, urban peregrines may feed to a greater extent on resident birds, such as pigeons and starlings (Chen et al., 2008). Therefore, eggs collected near densely human-populated areas (i.e., Hopewell, VA, as indicated by solid circles in Fig. 3) may exhibit relatively lower DDE, but higher PBDE concentrations. After excluding these outliers, DDE exhibited a significant correlation with  $\sum$ PBDEs in concentration, similar as those observed for other species (Fig. 3).

### 3.2. PBDE biomagnification from fish to osprey eggs

While some PBDE biomagnification studies have been conducted in aquatic systems, no such reports are available from the Chesapeake Bay region to date. An evaluation of PBDE magnification in the falcon food chain was not feasible in this study, as no contamination data were available for important dietary items. Fish – osprey food chains in the James River were considered here, as contaminant data in major prey items were available. Compositions of osprey diets were described by Glass and Watts (2009). Seven fish species were included in the BMF estimation, which cumulatively represented 91% of dietary items (Table 1). Fish contamination data were obtained from the Virginia Department of Environmental Quality (DEQ) fish monitoring project (Hale unpublished data). For calculation purposes, the median concentration of those seven major species was assigned to the

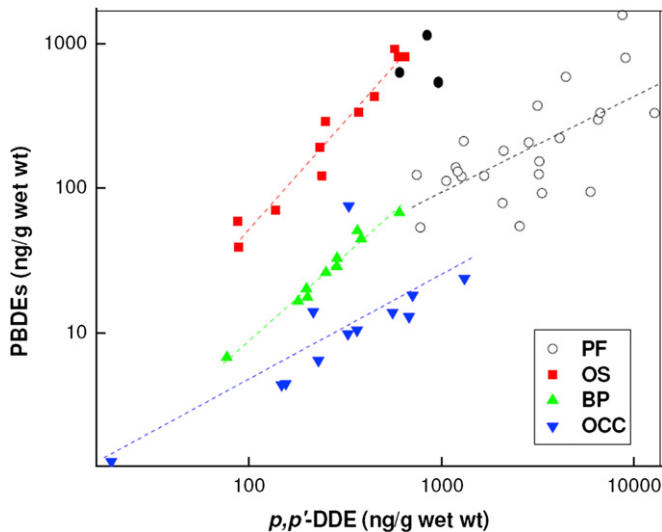


Fig. 3. Correlations between  $p,p'$ -DDE and  $\Sigma$ PBDE concentrations in eggs of osprey ( $r = 0.954$ ,  $p < 0.0001$ ), brown pelican ( $r = 0.978$ ,  $p < 0.0001$ ), double-crested cormorant ( $r = 0.595$ ,  $p < 0.005$ ), and peregrine falcon ( $r = 0.654$ ,  $p < 0.0001$ ; after excluding three outliers indicated by solid circles).

remaining 9% of diet. The BMF for  $\Sigma$ PBDEs in the fish – osprey egg food chain was estimated to be 25.1, similar to  $\Sigma$ PCB (BMF = 23.9) and DDE (BMF = 18) values determined (Table 1). This indicated that PBDEs had similar biomagnification potential as PCBs and DDE in the studied aquatic system. Examination of fish and osprey eggs from Oregon (USA) exhibited a BMF of 12–13 for PCBs and 103–112 for DDE (Henny et al., 2009b). A study from coastal Florida reported a similar PBDE BMFs in the fish – marine mammal (shark/dolphin) chains (ranging 31–85), but relatively higher BMFs for  $\Sigma$ PCBs (16–502) (Johnson-Restrepo et al., 2005). Another study reported  $\Sigma$ PBDE BMFs ranging from 11 to 53 in the North Sea fish – marine mammal food chains (Boon et al., 2002). Biomagnification studies in terrestrial systems are rare. A Belgium study on passerine – sparrowhawk food chains reported BMFs of 17 for  $\Sigma$ PBDEs and 22 for  $\Sigma$ PCBs. Though the biomagnification potential of PBDEs varied among different food chains, a BMF of  $>5$  was observed in most cases, indicating substantial magnification. However, exceptions occurred in several recent trophic biomagnification studies, where PBDEs exhibited very limited biomagnification potentials with increasing trophic levels (Elliott et al., 2009; Kelly et al., 2008).

### 3.3. PBDE congener distribution patterns

Fish-eating birds and peregrines exhibited distinctly different PBDE congener distribution patterns (Fig. 4). BDE-47 was the dominant congener in fish-eating birds, followed by BDE-99, -100, -153, -154, -49, -183, -28/33, -197, -202 and -138. In contrast, peregrine eggs were dominated by BDE-153, followed by -99, -100, -154, -47, -183, -209, -197, -207, -196, -201, -203, -208, -202, -138 and -206. Several highly brominated congeners, such as BDE-196, -201, -203, -206, -207, -208 and -209, were only observed in peregrine eggs. Differing congener patterns suggest varying exposure, bioaccumulation, biomagnification or biotransformation of congeners between species. Food web magnification models proposed by Kelly et al. (2007) may be appropriate in illustrating the different patterns here. In the aquatic piscivorous food web, biomagnification capacity of organic contaminants is primarily controlled by  $K_{ow}$  (octanol–water partition coefficient), assuming no metabolic transformation. The chemicals with a  $\log K_{ow}$  between  $\sim 5.9$  and  $\sim 7.2$  are subject to the greatest biomagnification (Kelly et al., 2007). The biomagnification potential declines significantly for chemicals with  $\log K_{ow}$  above 7.2 or less than 5.9. No biomagnification is suggested for chemicals with a  $\log K_{ow}$  higher than 8 or less than 4.5. The  $\log K_{ow}$  values for BDE-47 and BDE-153 are 6.0–6.8 and 7.6–7.9, respectively (Palm et al., 2002; Tittlemier et al., 2002). Therefore, in the aquatic piscivorous system, BDE-47 may be subject to greater biomagnification than BDE-153, resulting in a dominance of the former congener in fish and fish-eating birds. In terrestrial food web models, biomagnification is believed to be controlled by both  $K_{ow}$  and  $K_{oa}$  (octanol–air partition coefficient), assuming no metabolic transformation. Chemicals with a  $\log K_{ow}$  of  $\sim 4$  to  $\sim 8$  and  $\log K_{oa} > 8.2$  are subject to greatest biomagnification. Both BDE-47 and -153 fall into this category. However, BDE-47 has been reported to be vulnerable to biotransformation in some terrestrial-feeding birds of prey (e.g., American kestrel) (Fernie et al., 2006). Other studies suggested that the PBDE congeners most resistant to biotransformation are those with halogen substitution patterns similar to the most bioaccumulative PCBs (e.g., PCB-153) (Sørmo et al., 2006). Voorspoels et al. (2007) reported an increase in BMFs for both passerine – sparrowhawk and rodent – buzzard food chains from BDE-28 to BDE-153/-154, i.e., with increasing bromination. Therefore, a greater relative abundance of BDE-153 than BDE-47 in terrestrial birds of prey may be due to a combination of its significant biomagnification and low biotransformation potential. However, the actual contamination scenarios may be more complicated than simply inferred from these food web models. For

Table 1  
Biomagnification factors (BMFs) of contaminants from fishes<sup>a</sup> to James River osprey eggs.

Species	Scientific name	Percentage in osprey diet (%) <sup>b</sup>	$\Sigma$ PBDEs <sup>c</sup> (ng/g lipid wt)	$\Sigma$ PCBs <sup>c</sup> (ng/g lipid wt)	$p,p'$ -DDE <sup>c</sup> (ng/g lipid wt)
Channel & blue catfish	<i>Ictalurus punctatus</i> and <i>Ictalurus furcatus</i>	51.7	446	4806	473
Gizzard shad	<i>Dorosoma cepedianum</i>	28	258	4390	444
Atlantic croaker	<i>Micropogonias undulatus</i>	6.6	68	1040	167
White Perch	<i>Morone americana</i>	2	158	3270	437
Stripped bass	<i>Morone saxatilis</i>	1.3	1320	19,610	1810
Hickory shad	<i>Alosa mediocris</i>	0.8	1150	20,140	1700
Largemouth bass	<i>Micropterus salmoides</i>	0.3	514	3800	375
Other		9.3	446	4390	444
Osprey egg	<i>Pandion haliaetus</i>		9530	112,050	8400
BMF			25.1	23.9	18.0

<sup>a</sup> Fish contaminant data were from the Virginia Department of Environmental Quality fish monitoring project (Hale unpublished data).

<sup>b</sup> Diet composition data were from Glass and Watts (2009).

<sup>c</sup> Median concentrations.

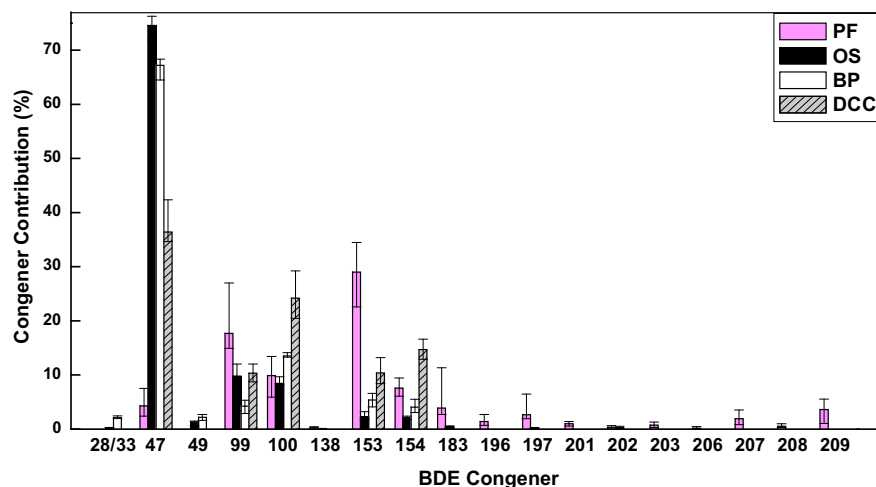


Fig. 4. Median PBDE congener distributions in eggs of peregrine falcon (PF), osprey (OS), brown pelican (BP) and double-crested cormorant (DCC). Error bars represent 75 and 25 percentiles.

example, aquatic birds from an electrical waste-recycling site in China exhibited substantial accumulation of BDE-153 and BDE-209 (Luo et al., 2009). This was possibly due to the ingestion of contaminated soil, seeds or insects.

#### 3.4. Deca (BDE-209) and its potential degradation

BDE-209 merits particular attention. It is the predominant congener in Deca-BDE, the product historically used in greatest amounts worldwide and the only PBDE formulation still manufactured. In the present study, BDE-209 was detected in all peregrine eggs, but not in any of the aquatic species. Heavy molecular weight (959 Da), large molecular size, and high Log  $K_{ow}$  ( $\sim 9.9$ ) may limit its bioconcentration potential in aquatic organisms. Its high  $K_{ow}$  also may result in a lack of biomagnification capacity in aquatic piscivorous food webs (Kelly et al., 2007). However, elevated BDE-209 levels may be seen in fish near point source emission. For example, substantial BDE-209 concentrations were observed in omnivorous fishes from a stream receiving wastewater effluents, in turn influenced by a plastic manufacturer. This suggested a contribution from contaminated sediment-associated dietary items (La Guardia et al., 2007). Some terrestrial animals, particularly apex predators, have also been reported to exhibit higher BDE-209/ $\Sigma$ PBDE ratios than aquatic organisms (Lindberg et al., 2004; Christensen et al., 2005). Soil initially received much of BDE-209 released (Palm et al., 2002), hence its incidental or purposeful ingestion may influence burdens in some organisms.

In our study, peregrine eggs contained a median BDE-209 concentration of 6.9 ng/g wet weight or 101 ng/g lipid weight. This value is lower than that reported in a northeastern U.S. peregrine population (26 ng/g wet wt or 480 ng/g lipid wt) (Chen et al., 2008). A portion of the northeastern peregrine eggs was from metropolitan areas (e.g., Boston and Springfield, MA). A significant correlation between BDE-209 concentrations in peregrine eggs and town human populations, as observed in the northeastern study, suggested that birds living in more urbanized areas were subject to elevated Deca-BDE exposure. In general, the U.S. peregrine eggs exhibited elevated BDE-209 concentrations compared to those from Sweden (82 ng/g lipid wt) and Greenland (11 ng/g lipid wt), and to Belgium buzzards (24 ng/g lipid wt) and sparrowhawks (17 ng/g lipid wt) (Lindberg et al., 2004; Vorkamp et al., 2005; Voorspoels et al., 2006). This may be a result of intense Deca-BDE usage in North America.

Additional concerns about Deca-BDE include its potential degradation to less halogenated, more bioavailable/bioaccumulative congeners. Previously, BDE-209 was reported to be partially debrominated when present on sediment, soil and sand in the presence of artificial and natural sunlight (Söderström et al., 2004). In vivo and in vitro Deca-BDE exposure studies, using rainbow trout and common carp, reported the presence of penta- to nona-congeners hypothesized to be debromination products (Stapleton et al., 2006). In our study, several nona- and octa-BDEs were detected in peregrine eggs, including BDE-196, -197, -201, -202, -203, -206, -207 and -208. Together they contributed approximately 10% of  $\Sigma$ PBDEs. These congeners all exhibited significant correlations in concentration with BDE-209 ( $p < 0.01$ ), whereas tetra-, penta- and hexa-congeners did not. Among them, BDE-207 exhibited the most significant correlation with BDE-209 ( $r = 0.933$ ,  $p < 0.0001$ ). The median BDE-207/BDE-209 concentration ratio was 1:1.5 in peregrine eggs, much higher than those in commercial Deca-BDE formulations (e.g., 1:400 in Saytex 102E, Albemarle Corp., Louisiana) (La Guardia et al., 2006). This suggests that a considerable fraction of this congener may originate from the degradation of BDE-209. This agrees well with a Deca-BDE exposure study performed with European starlings (*Sturnus vulgaris*), where BDE-207 was observed to be a dominant debromination product (Van den Steen et al., 2006). Aquatic bird eggs in our study did not contain detectable BDE-209. Nona- and octa-BDEs were below quantitation, with the exception of BDE-197 and -202, which were at very modest concentrations (i.e.,  $\sim 0.5\%$  of  $\Sigma$ PBDEs). This is similar to a congener pattern observed in the previously mentioned common carp exposure study, where no octa-, nona- and deca-BDE congeners were observed, except for BDE-202 (Stapleton et al., 2006). These results suggest a species-specific bioaccumulation and/or biotransformation of the highly brominated congeners, particularly BDE-209.

#### 3.5. Evaluation of PBDE hazards to birds

Hazard quotients (HQs) were used to quantitatively evaluate potential PBDE risks to Chesapeake Bay ospreys and peregrine falcons. DDE hazard was also evaluated, as it has traditionally been considered to be the most deleterious agent to bird populations. The PNECs of DDE in ospreys and peregrines were calculated by dividing the reported levels associated with 20% eggshell thinning in respective species by an uncertainty factor of 10. PBDE

**Table 2**  
Hazard quotients (HQs) of PBDEs and *p,p'*-DDE for osprey and peregrine falcon eggs.

		Osprey	Peregrine falcon
PBDEs	LOEL ( $\mu\text{g/g}$ wet wt)	1.0 <sup>a</sup>	1.8 <sup>b</sup>
	PNEC ( $\text{ng/g}$ wet wt)	100	180
	MEC ( $\text{ng/g}$ wet wt)	290	182
	<b>HQ</b>	2.9	1.0
<i>p,p'</i> -DDE	LOEL ( $\mu\text{g/g}$ wet wt) <sup>c</sup>	8.7 <sup>d</sup>	15.0 <sup>e</sup>
	PNEC ( $\text{ng/g}$ wet wt)	870	1500
	MEC ( $\text{ng/g}$ wet wt)	250	2550
	<b>HQ</b>	0.3	1.7

<sup>a</sup> Threshold level above which osprey reproductive performance may be reduced (Henny et al., 2009a).

<sup>b</sup> LOEL associated with pipping and hatching success in American kestrel (McKernan et al., 2009).

<sup>c</sup> LOEL associated with 20% eggshell thinning.

<sup>d</sup> Data from Wiemeyer et al. (1988).

<sup>e</sup> Data from Peakall, 1976.

toxicological data in birds of prey are scarce. McKernan et al. (2009) recently reported a LOEL for PBDEs, associated with impaired pipping and hatching success in American kestrels, of 1800 ng/g wet wt. A PNEC of PBDEs was estimated for peregrine falcon by dividing this LOEL by an uncertainty factor of 10. Similarly, a PNEC of PBDEs was estimated for ospreys by applying a threshold level of 1000 ng/g ww above which osprey reproductive performance may be reduced (Henny et al., 2009a). As described in Table 2, HQs of DDE were 0.3 for osprey and 1.7 for peregrine, which indicated that DDE may still pose a moderate hazard to the later species via reduced eggshell thickness. Eggshell thinning is one of the most important factors responsible for impaired reproduction in birds of prey (Anderson and Hickey, 1972). Our study observed mean shell thinning of 14% in ospreys and 11.4% in peregrine falcons, in contrast with pre-DDT era figures. HQs of PBDEs were 2.9 and 1.0 for ospreys and peregrines, respectively (Table 2). This indicated that PBDEs may pose a moderate hazard to both species through impairment of reproductive performance. It was also suggested that PBDEs may pose a greater hazard in ospreys than in peregrines. This is in contrast with DDE, where the HQ for the latter species is greater.

Several uncertainties limit the application of PBDE HQs for risk evaluation. For example, no toxicity threshold data are available for peregrine falcons and PNEC estimates must be extrapolated from kestrels. In addition, for birds only a limited number of the toxicity endpoints have been evaluated to date. Toxicity of different congeners differs. Because PBDE profiles in fish-eating and terrestrial-feeding birds differ, hazard evaluations based on specific (e.g., BDE-47 and -153) or different suites of congeners are necessary. However, such toxicological data are even scarcer. Further, interactions between PBDEs and other contaminants or stressors may result in toxic effects that differ from those predicted using individual chemical data. Despite the limitations, these concerns merit further attention as continuing releases from existing PBDE-treated products and other reservoirs may exacerbate the level of hazard to Chesapeake Bay birds of prey.

#### 4. Conclusion

Diet and habitat may influence contamination patterns in various Chesapeake Bay bird species. Birds nesting in more densely human-populated areas are likely to be subject to greater PBDE exposure. PBDEs exhibited substantial biomagnification in the James River fish – osprey food chain, with a calculated BMF of 25.1. As the first PBDE biomagnification report for Chesapeake Bay birds, the BFM determined here may be useful for predicting the exposure

of ospreys breeding in other tributaries. Different PBDE congener distribution patterns were observed between piscivorous birds and peregrines. BDE-47 dominated congener patterns in the former birds. More brominated congeners such as BDE-153 were predominant in peregrines. BDE-209, the major congener in Deca-BDE formulations, only was detected in peregrines. These observations suggest differences in bioaccumulation, biomagnification or metabolism between individual BDE congeners in different food webs, likely influenced by habitat or feeding strategies. While existing PBDE levels in the environment may present only a moderate risk to the studied populations, some populations from the northern section of the Bay may encounter greater exposure. For example, ospreys from the Anacostia and middle Potomac Rivers were reported to contain PBDE levels ranging from 560 to 725 ng/g wet wt (Rattner et al., 2004). As PBDEs are still being released from both existing flame retardant-treated products and other sources, additional monitoring will be necessary to evaluate potential adverse effects on the birds of prey.

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#### Appendix. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envpol.2009.10.042.

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