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Polybrominated diphenyl ether flame retardants in birds of prey from the U.S. and China

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Polybrominated Diphenyl Ether Flame Retardants in Birds of Prey from the U.S. and China

A Dissertation

Presented to

The Faculty of the School of Marine Science
The College of William and Mary in Virginia

In Partial Fulfillment

of the Requirements for the Degree of

Doctor of Philosophy

by

Da Chen

2009
APPROVAL SHEET

This dissertation is submitted in partial fulfillment of

the requirements for the degree of

Doctor of Philosophy

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ABSTRACT

Polybrominated diphenyl ether (PBDE) flame retardants are widely used as non-reactive additives in textiles, polyurethane foams, plastics, furnishings, and electronic products. As a result of substantial, long-term usages, PBDEs have contaminated humans, wildlife, air, water, soil, and sediment, even in remote areas. Although the North American and Asian (particularly Chinese) markets have consumed the majority of global PBDE production, knowledge about PBDE contamination is limited in these two regions. Therefore, this research aimed to investigate PBDE contamination in some Chinese and North American areas by examining the birds of prey that have been considered as sensitive monitoring species for organochlorine contamination. Particular interests were in the bioaccumulation of BDE-209, a predominant congener in Deca-BDE and the only PBDE formulation still in use worldwide. It is widely believed to have limited bioavailability. The study was primarily performed in three regions: Beijing in North China, New England and the Chesapeake Bay regions in the U.S. To our best knowledge this study is the first to examine PBDE contamination in terrestrial raptors from both North America and Asia. The results revealed (1) dissimilar PBDE congener distribution patterns between aquatic and terrestrial birds of prey, suggesting that individual congeners may be subject to differences in bioaccumulation, biomagnification or metabolism in the aquatic and terrestrial environments; (2) substantial biomagnification of PBDEs (BMF = 41.4) in the Chesapeake Bay fish – osprey egg chain; (3) an influence by diet preference and living habitat on the contamination burdens and congener profiles in the birds; (4) substantial PBDE contamination in the Chinese
birds of prey, indicating elevated exposure due to extensive application of PBDEs in the city; (5) record-high BDE-209 concentrations in Chinese kestrels and U.S. peregrine falcon eggs, indicating the substantial accumulation of this congener in the terrestrial birds of prey; (6) significantly higher BDE-209 concentrations in the urban peregrine falcon eggs, indicating a greater abundance of Deca-BDE in the urban environment; (7) a rapid increase in BDE-209 concentrations in the northeastern U.S. peregrine eggs, which may have resulted from the continuing use of Deca-BDE; and (8) a potential breakdown of BDE-209 to less brominated and more bioavailable congeners. A review of studies in birds of prey worldwide clearly indicated a greater abundance of BDE-209 in the North American and Chinese birds compared to European species. This follows well the global market demand pattern of Deca-BDE, in which North America and Asia have historically consumed 44% and 41% of the world’s total production, respectively. The above findings of high BDE-209 concentrations, short doubling time, and potential biodegradation in the terrestrial birds of prey, indicate the need to limit unnecessary Deca-BDE release to the environment.
Polybrominated Diphenyl Ether Flame Retardants in Birds of Prey
from the U.S. and China
General Introduction

1. Polybrominated diphenyl ether (PBDE) flame retardants

Flame retardants are used to protect the public from accidental fires by reducing the flammability of combustible materials such as synthetic polymers (WHO, 1997). Brominated flame retardants (BFRs) are a very important group, and include polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD). BFRs have numerous applications due to their exceptional effectiveness at fire prevention. In addition to reducing the likelihood that an item will ignite, BFRs can slow down the spread of flames and postpone the occurrence of flashover point, hence providing the occupants more time to escape. PBDE flame retardants are widely used as non-reactive additives in textiles, polyurethane foams, thermoplastics and electronic products. Figure 1 shows the general chemical structure of PBDEs. The family of PBDEs consists of 209 theoretical congeners, differing in the number and position of bromine atoms on the two phenyl rings. The same nomenclature is applied to PBDEs as PCBs.

![PBDEs](image)

**Figure 1.** The general structure of PBDEs.

There are three major commercial PBDE mixtures. Penta-BDE consists of 50-62% pentabromodiphenyl ethers and 24-38% tetrabromodiphenyl ethers. Octa-BDE contains
62% hexabromodiphenyl ethers and 34% octabromodiphenyl ethers. Deca-BDE is composed of 97-98% decabromodiphenyl ether (WHO, 1994). Table 1 lists the estimated world market demand for PBDE flame retardants in 2001. The North American market consumed over half of the world’s PBDE production, in general, and 98% of Penta-BDE, in particular (Hale et al., 2003). Asia had limited Penta-BDE demand, but consumed similar amounts of Octa- and Deca-BDE as North America. The pattern of demand is a function of the suite of products produced and the regulatory framework.

Table 1. Estimated world market demand (metric tons) for PBDEs in 2001 (BSEF, 2003)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>North America</th>
<th>Europe</th>
<th>Asia</th>
<th>Rest of World</th>
<th>Total</th>
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<tbody>
<tr>
<td>Penta-BDE</td>
<td>7,100</td>
<td>150</td>
<td>150</td>
<td>100</td>
<td>7,500</td>
</tr>
<tr>
<td>Octa-BDE</td>
<td>1,500</td>
<td>610</td>
<td>1,500</td>
<td>180</td>
<td>3,790</td>
</tr>
<tr>
<td>Deca-BDE</td>
<td>24,500</td>
<td>7,600</td>
<td>23,000</td>
<td>1,050</td>
<td>56,100</td>
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2. Exposure of humans and wildlife

As non-reactive additives, PBDEs can enter the environment through spills, leaching and volatilization during production; volatilization and leaching coincident with use; losses from use and disposal in particulate form; and leaching during recycling processes (Darnerud et al., 2001; Hale et al., 2003; Watanabe and Sakai, 2003). PBDEs are hydrophobic and lipophilic in general. The less brominated BDEs (e.g., BDE-47) are more volatile, water soluble, and bioavailable, whereas the more brominated congeners (e.g., BDE-209) are less mobile and tend to accumulate near emission sources, such as wastewater treatment and plastics manufacturing plants (Watanabe and Sakai, 2003). As a result of substantial, long-term usages, PBDEs have contaminated humans, wildlife, air, water, soil, and sediment, even in remote areas (de Wit, 2002; Hale et al., 2003; Hites, 2004; Law et al., 2006). Several PBDE congeners (i.e., BDE-47, -99, -100, -153 and -
have become ubiquitous environmental contaminants, detectable in most environmental components worldwide. Humans may be exposed to PBDEs via direct contact with PBDE-treated household products, inhalation of dust and airborne particulates, and food intake. Human exposure in indoor environment is believed to be of major importance as we spend most of our time therein. Studies suggested that indoor air contains significantly higher PBDE concentrations than outdoor air (Butt et al., 2004). A significant positive correlation was observed between PBDE concentrations in human breast milk and indoor dust (Wu et al., 2007). Higher PBDE concentrations were observed in California resident serum and dust samples than other regions of North America (Zota et al., 2008). This was inferred to be a consequence of the state’s stricter furniture flammability standards. Persons of lower economic status exhibited elevated serum PBDE concentrations in the California study. This may relate to Penta-BDE releases from foams in older, lower quality furnitures, more likely present in lower income homes. A recent hand wipe study suggested that dust particles and subsequent hand-to-mouth contact may be an important exposure route (Stapleton et al., 2008a). Occupational exposure may elevate body burdens in workers in PBDE-involved manufacturing and recycling factories. For example, foam recyclers and carpet installers exhibited one order of magnitude higher PBDE levels than the general U.S. population (Stapleton et al., 2008b). Occupational exposures have also resulted in unusual PBDE congener profiles in the exposed workers. For example, Swedish computer disassembly plant workers exhibited serum PBDEs dominated by BDE-183, followed by BDE-153, BDE-47 and BDE-209 (Sjödin et al., 1999). In contrast, BDE-47 is often the predominant congener in the general population.
In the wild, top predators are subject to heightened PBDE exposure. This may be associated with substantial biomagnification potentials of PBDEs. For example, biomagnification factors (BMFs) for PBDEs ranged from 31 – 85 and 11 – 53 in the fish – marine mammal food chains from coast Florida and North Sea, respectively (Johnson-Restrepo et al., 2005; Boon et al., 2002). Though the biomagification potential of PBDEs varied among food chains, a BMF of > 5 was observed in most cases, indicating substantial biomagnification capacities. In many cases, birds exhibited elevated PBDE concentrations relative to marine/terrestrial mammals and other wildlife from the same regions. For example, seabird eggs contained PBDE concentrations three times higher than harbor seal blubbers from the San Francisco Bay (She et al., 2002; 2003). Guillemot eggs from the Baltic Sea contained PBDE concentrations 2 – 3 times higher than grey seals and ringed seals from the same region (Sellstrom et al., 2003; Haglund et al., 1997). In British Columbia (Canada), great blue heron (Ardea herodias) eggs exhibited PBDE burdens four times higher than porpoises (Elliott et al., 2005; Ikonomou et al., 2002).

Birds of prey feed high in food webs. They can accumulate contaminants through bioaccumulation and biomagnification, making them particularly sensitive to environmental contamination. Resident birds are useful indicators of local contamination, whereas migratory birds can reflect the situation on broader scale. Examination of addled eggs is considered a non-destructive way to investigate contamination in birds, particularly for threatened species. During the breeding season energy reserves are mobilized and females ingest large quantities of food in order to lay eggs. The assimilated protein, fat and associated contaminants are transferred into the eggs.
Therefore, the examination of eggs may be useful in characterizing contamination in both
the mother and offspring.

3. Toxicity

Critical effects and doses vary between different PBDE formulations. The critical
effects of Penta-BDEs reported in mammals include disruptions in neurobehavioural
development (from 0.6 – 0.8 mg/kg body weight) and thyroid hormone homeostasis
(from 6 – 10 mg/kg body weight) (Darnerud, 2003). Penta-BDEs can cause neurotoxicity
in mice via thyroid hormone disruption and actions on signal transmission in brain
(Darnerud 2003). Octa-BDEs can cause fetal toxicity and teratogenicity in rats and
rabbits. The effects are normally seen at early developmental stages. The effects appear at
2 mg/kg body weight in rabbits and higher doses in rats (Darnerud, 2003). Deca-BDEs
can cause morphological effects in the thyroid, liver and kidney of adult animals (from 80
mg/kg body weight) (Darnerud, 2003). Adenomas and carcinomas were observed in
carcinogenicity study in rats and mice, but at very high doses (≥ 1200 mg/kg body
weight/day) (Darnerud, 2003).

Toxicological studies on PBDEs in birds are scarce. Available data suggest that an
exposure to a technical Penta-BDE, DE-71, can induce changes in thyroid, vitamin A,
glutathione homeostasis, oxidative stress, and immunomodulatory changes in American
kestrel (Falco sparverius) chicks at a dose of 15.6 ng/g bird/day (Fernie et al., 2005a; b).
Exposure of adult kestrels can induce changes in reproductive courtship behaviors
(Fernie et al., 2008). Additionally, the exposure to DE-71 has been reported to decrease
pipping and hatching success in kestrels and cause sublethal effects (i.e., ethoxyresorufin-
O-dealkylase induction) in hatching chickens (McKernan et al., 2008). A lowest-effect-
observed-level (LOEL) of PBDEs was reported to be 1800 ng/g wet weight (McKernan et al., 2008). Exposure can also alter kestrel eggshell thickness and affect reproductive success (Fernie et al., 2009). This merits scrutiny as the effect levels observed in exposure studies approached concentrations detected in some North American wild birds.

4. Regulations and consequencies

The European Union has banned the manufacturing and usage of Penta- and Octa-BDE since Aug 2004. The EU Restriction of Hazardous Substances (RoHS) Directive banned the use of Penta- and Octa-BDE in new electrical and electronic equipments since July 2006 and Deca-BDE since July 2008. However, a EU risk assessment released in 2008 concluded that there is a need for further information and/or testing to evaluate Deca-BDE’s risks to human health and environment (Official Journal of Environmental Union, 2008). Several European countries had already voluntarily ceased production and use of Penta-BDE in the 1980s. As a consequence, some investigators have reported concentrations of Penta-BDE constituents to be on the decline there. For example, concentrations in guillemot (Uria algea) eggs from the Baltic Sea increased from the 1970s to the 1980s, with a rapid decrease thereafter (Sellström et al., 2003). Concentrations in Swedish human breast milk increased exponentially up to the late 1990s, and then declined after 1998 (Meironyte et al., 1999). PBDE levels in Swedish pike (Esox lucius) increased from the 1960s to the mid-1980s and then slowly decreased (Kierkegaard et al., 2004).

Compared to elsewhere in the world, Penta-BDE was used extensively in North America. Before manufacturing of Penta- and Octa-BDEs ceased in late 2004, the North American market consumed 98% of the world’s Penta-BDE demand (Hale et al., 2003).
In the United States, legislation to phase out the use of Penta- and Octa-BDE at the individual state level has been adopted in California, Hawaii, Illinois, Maine, Maryland, Michigan, New York, Oregon and Rhode Island. However, no actions have been taken at the federal level. Additionally, only two states (Washington and Maine) restrict the use of Deca-BDE formulations. Canada has no documented manufacturing of the Penta- and Octa-BDEs. Regulations released on July 9th, 2008 ban the manufacturing of all PBDEs and the import and use of tetra- through hexa-BDEs. These do not ban hepta- through deca-BDE and thus allow the continued use of the commercial Deca-BDE mixture (ecojustice.ca et al., 2009). To date no evidences of declining trends in PBDE concentrations have been observed in the North American environment. In fact, concentrations have been reported to have increased exponentially from 1981 – 2000 in male ringed seals *Phoca hispida* from Canadian Arctic, with doubling times of 4.7 years for penta-, 4.3 for hexa- and 8.6 for tetra- congeners (Ikonomou et al., 2002). PBDE levels in beluga whales *Delphinapterus leucas* from the St. Lawrence Estuary (Canada) increased throughout the period of 1988-1999 (Lebeuf et al., 2004). The Great Lakes herring gull eggs and various aquatic bird species from British Columbia (Canada) also exhibited exponential increases in PBDE concentrations throughout the 1980s – 2000s (Elliott et al., 2005; Norstrom et al., 2002). Because PBDE formulations were normally used at percent levels in polymer products and many of these finished goods have long service lives, releases from in-service and discarded products may continue for decades.

PBDEs are subject to less regulation in Asia. For example, there is no national regulation on PBDE usage in Japan. However, the industries there have voluntarily replaced PBDEs with other flame retardants (Watanabe and Sakai, 2003). PBDE levels in
Japanese sea bass and gray mullet from Osaka Bay exhibited an increasing trend from 1986 to 1989, and then a drastic decrease after 1990 (Ohta et al., 2001). PBDE concentrations in human milk samples increased significantly from 1973 to 1988, but leveled off after 1993 (Hori et al., 2002). The concentration decreases in humans and wildlife were inferred to be a consequence of the cessation of manufacturing of tetra-BDE formulations after 1990 (Watanabe and Sakai, 2003). China is another important consumer of BFRs, due to its role as one of the world’s largest manufacturers and consumers of textiles, plastics and electronic products. However, relative to the U.S. and Europe that recently phased out the production of Penta and Octa mixtures, China currently lacks any specific regulations on PBDE production or usage. Hence PBDE burdens in the Chinese environment may be increasing, in step with the rapid economic development. For example, Ramu et al. (2006) reported that PBDE concentrations in finless porpoises (Neophocaena phocaenoides) from China rapidly increased from 1990 to 2000. In some regions on the east coast of China, PBDE contamination may be exacerbated by illegal recycling of obsolete electronic products or “E-wastes” transported from western countries (Puckett et al., 2002). Studies have reported substantial contamination in the wildlife from those recycling sites (Luo et al., 2009a; b).

While the production of Penta- and Octa-BDEs has been banned or has voluntarily ceased in some regions, Deca-BDE remains in use worldwide. Deca-BDE has long been the dominant PBDE product in use and in 2001, represented over 80% of the world’s total PBDE market demand (BSEF, 2003). Its major constituent, BDE-209, has been observed to be particularly abundant in abiotic matrices, i.e., sewage sludge, dust and soil. However, it has been less frequently detected in the wildlife and humans than the
major tetra- and Penta-BDE congeners. The reported concentrations in biota have generally been low. Therefore, it was inferred that this congener may have very limited bioavailability. However, recent studies indicated that some top predators, particularly terrestrial birds of prey, may be subject to elevated BDE-209 exposure (Lindberg et al., 2004). Some in vitro and in vivo exposure studies suggested biodegradation of BDE-209 to less brominated and hence more bioaccumulable congeners (Stapleton et al., 2006). Therefore, more studies are required to better evaluate the risks of Deca-BDE exposure that humans and wildlife are subject to.

5. Research purposes

In contrast with the intensive use of PBDEs in the U.S. and China, relatively few studies have been performed to examine resultant contamination of wildlife in general and birds of prey in particular. Especially lacking are data from the Chinese environment. Though a few studies have been performed to examine PBDE burdens in Chinese sediments, air, aquatic biota, and humans, no data are available on birds of prey. Therefore, the primary purposes of this study were to examine and compare the PBDE contamination scenarios in birds of prey from the U.S. and China.

Regions of investigation were in the northeastern and Mid-Atlantic (Chesapeake Bay) regions of the U.S. and northern China. A number of peregrine falcon (*Falco peregrinus*) eggs were obtained from the northeastern U.S., historically home to a large breeding population. Examination of terrestrial-feeding birds, particularly peregrine falcon, may be very suitable for evaluating Deca-BDE exposure (Lindberg et al., 2004). Peregrine egg samples were collected during the period 1996 – 2006. This provided an opportunity to examine temporal trends in PBDE contamination. Eggs were collected
from urban and rural nests, which allowed exploration of differential exposure as a function of local human development.

Additional samples were available from the Chesapeake Bay region. The Chesapeake Bay is the largest estuary in the U.S. and home to a number of bird species. While several studies of organochlorine contamination in birds have been performed in this region, little is known about PBDE contamination in the avifauna. Species available for study were peregrine falcon, osprey (*Pandion haliaetus*), brown pelican (*Pelecanus occidentalis*) and double-crested cormorant (*Phalacrocorax auritus*). This study aimed to increase our knowledge about the influences of diet and living habitat on PBDE accumulation in several avian species feeding in aquatic and terrestrial food webs. PBDE biomagnification was also examined in the James River fish – osprey food chain. To date only one study has examined the PBDE biomagnification in the avian food webs (Voorspoels et al., 2007).

Avian samples were also available from Beijing, a large city in North China. A collaboration was initiated with the Beijing Raptor Rescue Center (BRRC), which maintained an archive of dead birds from various terrestrial species. Chinese raptors were chosen due to: 1) the elevated PBDE burdens, especially of the more brominated congeners, reported in such species by European researchers; and 2) the significant potential for PBDE exposure in China by virtue of that country’s burgeoning textile/plastics/electronics industries and the exportation of PBDE-containing electronic wastes to China by other nations. The results of these efforts will supplement the current knowledge about PBDE contamination on an international scale.
References


Fernie, K.J.; Shutt, J.L.; Letcher, R.J.; Ritchie, J.I.; Sullivan, K.; Bird, D.M. Changes in reproductive courtship behaviors of adult American kestrels (Falco sparverius) exposed to environmentally relevant levels of the polybrominated diphenyl ether mixture, DE-71. Toxicol. Sci. 2008, 102, 171-178.


McKernan, M.A.; Rattner, B.A.; Hale, R.C.; Ottinger, M.A. Toxicity of polybrominated diphenyl ethers (DE-71) in chicken (Gallus gallus), mallard (Anas platyrhynchos), and American kestrel (Falco sparverius) embryos and hatchlings. Environ. Toxicol. Chem. 2009, 28, 1007-1017.


Chapter I

Polybrominated Diphenyl Ether in Birds of Prey from Northern China
Polybrominated Diphenyl Ether in Birds of Prey from Northern China

Abstract: Birds of prey from Northern China (Beijing area) were examined for polybrominated diphenyl ethers (PBDEs). A total of 47 specimens from eight different species were analyzed. Muscle and liver were analyzed separately for each bird. Kidneys were pooled by species. Common kestrels exhibited the highest PBDE levels (median muscle and liver concentrations of 9,900 and 7,900 ng/g lw, respectively), with maxima in an individual bird of 31,700 in muscle and 40,900 ng/g lw in liver. Congener profiles differed between some species, but were generally dominated by the more brominated congeners (e.g., BDE-153, -209, -183, -207). BDE-209 was especially elevated compared to other published reports. Interspecies differences in congener concentrations and profiles may be due to diet, behavior, or biotransformation capacities. BDE-209 was detected in 79.4% of the samples. Common kestrels contained the highest BDE-209 levels (median/maxima of 1400/6220 in muscle and 1030/12,200 ng/g lw in liver). BDE-209 was the dominant congener in tissues from some buzzards, scops owls and long-eared owls. It was the second most abundant congener in common kestrels. The remarkable levels and dominance of BDE-209 may relate to significant production, usage or disposal of Deca-containing products in China. These observations reinforce the growing view that organisms using terrestrial food chains may have greater exposure to BDE-209.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardant additives widely used in textiles, thermoplastics, polyurethane foams and electronic products. The three major
commercial PBDE mixtures are Penta-, Octa-, and Deca- (WHO, 1994). Some PBDE congeners have become widely distributed in abiotic media, wildlife and people, reaching even remote areas (de Wit, 2002; Hale et al., 2006; Hites, 2004; Law et al., 2006). Toxicological studies are limited but suggest that the different congeners possess varying potencies (Darnerud, 2003). In some cases observed toxicity may be a function of differential uptake or bioavailability. PBDE levels in the environment have generally been increasing since the 1970s. However, some European studies have reported a recent decrease of the less brominated congeners, perhaps as a function of the voluntary cessation of Penta- consumption there (Law et al., 2008). The European Union banned both Penta- and Octa- in 2004. The majority of documented global Penta use has been in North America. While the major manufacturer there discontinued production in December 2004, recent studies have yet to identify a diminution in wildlife PBDE concentrations (Hale et al., 2003). Continued usage of Deca- has been controversial on both continents, with some concerned about potential health, bioaccumulation and persistence issues and others underlining the current lack of scientific documentation of such concerns in real-world scenarios.

In contrast to Europe and North America, few reports have described PBDE burdens in Asia. Particularly lacking are data from China, despite its position as one of the world’s largest manufacturers and consumers of textiles, plastics and electronic products. PBDE formulations in the 2001 Asian demand consisted primarily of Deca- (93.3%), with lesser amounts of Octa- (6.1%) and Penta- (<1%) (BSEF, 2003). It is hence likely that Deca- is the predominant formulation in the Chinese market, although survey data are not available. Another issue contributing to PBDE contamination is the transport of
obsolete electronic products or "E-wastes" from western countries to China for recycling (Puckett et al., 2002). It has been estimated that 50 – 70% of U.S. E-wastes generated were exported to China (Puckett et al., 2002). In Guangdong Province, China, for instance, approximately 145 million electronic devices were "recycled" in 2002, containing up to $2.61 \times 10^8$ kg of PBDEs (Martin et al., 2004). Once there, primitive methods are generally used in an attempt to recover valuable metals from the electronics. Large amounts of plastic and electronic parts are either burned or subsequently dumped (Puckett et al., 2002). While a few studies have been performed on Chinese PBDE burdens in sediments (Chen et al., 2006a; Mai et al., 2005), air (Chen et al., 2006b; Jaward et al., 2005), aquatic biota (Liu et al., 2005; Ramu et al., 2005) and humans (Bi et al., 2006), no data are available on terrestrial wildlife. Limited European reports have indicated that terrestrial wildlife may contain elevated proportions of Deca- (predominantly BDE-209) (Law et al., 2006). In most cases concentrations have been modest and the detection frequencies low. An exception has involved predatory birds. For example, a study of Swedish falcons detected BDE-209 in 18 of 21 eggs analyzed at concentrations of up to 430 ng/g lipid weight (Lindberg et al., 2004). Other raptor species from Europe (i.e., sparrowhawk, kestrel, buzzard and owl) have also been reported to contain BDE-209 in tissues or eggs (de Boer et al., 2004; Voorpoels et al., 2006). Based on the above considerations we obtained and analyzed PBDE burdens in a number of raptor species from Northern China.

2. Materials and Methods

2.1. Samples
Birds were obtained from the collection at the Beijing Raptor Rescue Center (BRRC, China) between March 2004 and January 2006. Species examined were the common kestrel (*Falco tinnunculus*, N=6); Eurasian (*Accipiter nisus*, N=11) and Japanese sparrowhawk (*Accipiter gularis*, N=6); scops (*Otus sunia*, N=6), long-eared (*Asio otus*, N=6) and little owl (*Athene noctua*, N=6); common (*Buteo buteo*, N=3) and upland buzzard (*Buteo hemilasius*, N=3). These species are all listed in China as National Key Protected Wild Animals. Accordingly, only birds that were received dead, died during attempted rehabilitation or were euthanized at the Center due to serious injuries were available for sampling. Specimens were maintained intact at -20 °C until dissected, minimizing potential introduction of contaminants, and were in good condition (showing no signs of decay). See Appendix 1 for more detailed information (diet and migratory habits) on each species.

2.2. Analysis

Pectoral muscle and liver from each bird were excised, weighed and transferred to residue-grade solvent rinsed glass jars. These were frozen until initiation of chemical analysis. Due to their small size kidneys were pooled by species. Tissues and sodium sulfate blanks were freeze-dried and then subjected to enhanced solvent extraction (Dionex ASE 300, Sunnyvale, CA), employing two 5-minute extraction cycles with dichloromethane (DCM) at 100 °C and 1500 psi, followed by a 60% vessel flush (a solvent flush equivalent to 60% of cell volume is passed through the cell). Before extraction, samples and blanks were spiked with surrogates (PCB-204 and $^{13}$C$_{12}$-PCB-141) for evaluation of recovery. Lipids were determined by evaporation of a fraction of each extract to a constant weight. The remainder of each extract was purified by gel
permeation chromatography, with a 50 cm × 2.5 cm i.d. glass column packed with 40 g SX-3 “Bio-Beads” (Bio-Rad Laboratories, Hercules, CA) and eluted with DCM/hexane (1/1 in volume) for lipid removal. The fraction eluting from 90 to 280 mL, containing PBDEs and other organohalogen compounds, was collected and concentrated. This fraction was further purified on 2-g silica gel solid-phase extraction columns (Isolute®, International Sorbent Technology, UK). The first fraction eluted from the silica column with 3.5 mL hexane was discarded. The second fraction, which contained PBDEs and other halogenated compounds, was obtained by elution with 6.5 mL of 60:40 hexane:DCM. Following solvent exchange to hexane, the second fraction was concentrated and spiked with internal standards (13C12-PCB-208 and unlabelled PCB-82).

Samples were analyzed on a Shimadzu Model 2010 gas chromatograph, coupled with a Model QP2010 mass spectrometer (Shimadzu, Japan) using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A DB-XLB capillary column (J&W Scientific, Folsom, CA; 30 m × 0.25 mm i.d., 0.25 μm film) was used to separate the PBDE congeners examined (1, 2, 3, 10, 7, 11, 8, 12, 13, 15, 30, 32, 17, 25, 33, 28, 35, 37, 75, 49, 47, 66, 77, 100, 119, 99, 116, 118, 155, 85, 126, 154, 153, 138, 166, 183, 181, 190). Methane was used as a chemical ionization moderating gas at an ion source pressure of 2.4 × 10⁻³ Pa. Carrier gas was helium, and 1 μL injections were made in the splitless mode. Initial column temperature was held at 110 °C for 1 min, and then programmed to 180 °C at 8 °C/min (held for 1 min), to 240 °C at 2 °C/min (held for 5 min), to 280 °C at 2 °C/min (held for 25 min) and to 290 °C at 5 °C/min (held for 13 min). A CP-Sil 13 CB (12.5 m × 0.25 mm i.d., 0.25 μm film) capillary column was used to separate BDE-197, -203, -196, -208, -207, -206 and -209. The oven temperature was
programmed from 110 to 300 °C at a rate of 8 °C/min (held for 20 min). Ion fragments m/z 79 and 81 ([Br]) were monitored for all congeners except for BDE-209 for which m/z 79, 81, 486.7 and 488.7 were recorded. Fragments m/z 372, 374 and 376 were monitored for surrogate $^{13}$C$_{12}$-PCB-141 and 474, 476 and 478 for the internal standard $^{13}$C$_{12}$-PCB-208. Quantification was performed using calibration curves made from standard solutions at five to nine concentration levels. The limit of quantification (LOQ), defined as a signal of five times the noise level (S/N = 3 for BDE-209), ranged from 0.06 to 52.6 ng/g lipid weight for mono- to nona- congeners and 1.20-10$^5$ for BDE-209, depending on the sample size.

2.3. QA/QC

Proper handling was employed from sample collection to chemical analysis to minimize the potential sample contamination, cross contamination and PBDE degradation. Instrumental QC included regular injection of solvent blanks and standard solutions. The method QC was ensured through analysis of procedural blanks, blind triplicate samples, triplicate spiked blanks (PBDE standards spiked into sodium sulfate) and triplicate spiked matrices (PBDE standards spiked into pre-extracted samples). In total 17 procedural blanks were analyzed sequentially with the samples. Only trace levels of BDE-47, -66 and -99 were detected in blanks and the mean values were subtracted from samples. BDE-209 was only detected in two blanks, but at nonquantifiable (S/N < 3) levels. Surrogate standard recoveries of $^{13}$C$_{12}$-PCB-141 ranged from 80.7% to 110% (RSD < 8%), after omission of a single outlier (59.7%). The percent relative standard deviations (%RSDs) for detected congeners were all ≤6% in blind triplicate samples except for BDE-209, which had RSD of 8.9%. The mean recoveries of ten individual
congeners (28, 47, 66, 100, 99, 85, 154, 153, 138 and 183) spiked into pre-extracted matrices ranged from 70.2 to 108% (RSDs < 8%). The mean recovery of BDE-209 was 82.0 ± 7.9% (RSD <10%) in triplicate spiked blanks.

2.4. Statistical analysis

Among all screened PBDE congeners, only those with at least 65% of all measurements above the pertinent LOQ were used in statistical analyses (i.e., BDE-28, -49, -47, -100, -119, -99, -118, 154, -153, -138, -183, -181, -203, -196, -208, -207 and -209). “∑PBDEs” is defined here as the sum of these 17 congeners. For results less than the LOQs, a regression probability plotting method was applied to assign values for statistical analysis (Newman 1995). All levels were recovery corrected and are presented on a lipid weight (lw) basis. All concentration data were logarithmically transformed to approximate a normal distribution before inter-species statistical evaluations with ANOVA and Scheffe’s post-hoc test (SPSS 13.0, SPSS Inc.). Data were further evaluated with principal components analysis (PCA), programmed with R Language (www.r-project.org). The level of significance was set at α = 0.05 throughout this study. For each species, no significant relationship was observed between PBDE levels and any of the biological variables (i.e., body mass, age, sex). Thus, these variables were not used to correct or further subclassify data.

3. Results and Discussion

3.1. Concentration data and interspecies comparisons

Among the species examined, ∑PBDE levels were highest in common kestrel (median: 9900 ng/g lw in muscle; 7900 in liver; and 5340 in pooled kidneys) (Figure 2).
To date few reports have evaluated PBDE levels in avian kidneys. Maxima were detected in muscle (31,700 ng/g lw) and liver (40,900 ng/g lw) of a kestrel. These concentrations rival the highest reported in wildlife to date. Large differences in PBDE levels among individual kestrels (ranging 279 – 31,700 in muscle and 126 – 40,900 ng/g lw in liver) suggest varying exposure or depuration. Previous avian studies on other organohalogen compounds have indicated that factors such as the individual’s dietary habits, body condition, age and sex may be important (Wienburg et al., 2004). Eurasian sparrowhawks contained median $\Sigma$PBDEs of 4300 ng/g lw in muscle and 4000 ng/g lw in liver. Their pooled kidneys had $\Sigma$PBDEs of 4020 ng/g lw. While these levels were statistically similar to the Chinese kestrel burdens, another study reported significantly higher levels in Belgium sparrowhawks than kestrels (Jaspers et al., 2006). The authors of that study suggested that the interspecies contaminant differences might be due to varying dietary habits. Sparrowhawks feed primarily on small birds. Kestrel diet consists mainly of insects and small animals, normally with a modest contribution from small birds (Snow and Perrins, 1998). Additional factors (e.g. migratory habits) may have contributed to the different results in the two studies. Kestrels examined in the present study are believed to remain mainly in Beijing area all year round, establishing nests and foraging in urban fringes or urban centers. Eurasian sparrowhawks are mainly migrants. They stay in Beijing in the spring and autumn, but over-winter in southeastern China and spend summer in the areas well north of China (e.g., Siberia). Therefore kestrels may have greater exposure to Chinese urban PBDE sources. In contrast, Eurasian sparrowhawks in the present study contained statistically higher $\Sigma$DDT levels (median: 158.7 mg/kg lw in liver) relative to kestrels (median: 8.6 mg/kg lw in liver). This was primarily contributed
Figure 2. Median $\sum$PBDE levels (ng/g lipid weight) in various tissues of eight bird species from the northern China. Error bars represent 75% and 25% percentiles. Species abbreviations: CK=common kestrel (N=6); SH=Eurasian sparrowhawk (N=11); JSH=Japanese sparrowhawk (N=6); LO=little owl (N=6); SO=scops owl (N=6); LEO=long-eared owl (N=6); UB=upland buzzard (N=3); CB=common buzzard (N=3).

by their migration to southeastern China where heightened DDT exposure has occurred (Chen et al., 2009). A similar species, the Japanese sparrowhawk (Accipiter gularis), had $\sum$PBDE burdens statistically similar to Accipiter nisus, perhaps related to comparable dietary and migratory habits. Buzzards and some of the Chinese owls examined contained statistically lower PBDE burdens than sparrowhawks. Upland buzzards exhibited median $\sum$PBDEs of 440 ng/g lw in muscle and 170 ng/g lw in liver. Common buzzards contained PBDEs within the same magnitude (median: 125 ng/g lw in muscle and 100 ng/g lw in liver), as did scops owls (median: 200 ng/g lw in muscle and 250 ng/g lw in liver). Owls and buzzards have similar dietary habits, feeding mainly on small
mammals such as mice, field voles, rats and insects (Snow and Perrins, 1998; Mackinnon et al., 2000). Avian prey constitute a small percentage of their diet and this might contribute to the 1 – 2 orders of magnitude lower body burdens versus those in Eurasian sparrowhawks. Among the three owl species, little owls (Athene noctua) contained significantly higher \( \sum \)PBDEs (median: 1890 ng/g lw in muscle and 2350 ng/g lw in liver) than scops and long-eared owls. Little owls are year-round residents in the Beijing area, whereas the other two species migrate (Mackinnon et al., 2000). Hence longer exposure to Chinese urban PBDE sources might contribute to the higher levels in little owls. A previous study has reported a decrease in air PBDE concentrations along a Canadian urban-rural transect (Harner et al., 2006). Though they are both residents in Beijing, little owls contained lower levels than common kestrels. Little owls prefer to build their nests in forests located in parks or suburban areas. Kestrels are more active in the urban center areas, building their nests on man-made structures. More intimate contact with human activities may increase the kestrels’ exposure to urban PBDE sources. Differences in diet, biotransformation or uptake capacities may also contribute to the inter-species differences. Small sample size, individual exposure history, as well as varying age, sex or body condition, may further confound comparisons. Inclusion of different PBDE congeners in the totals presented in other published bird studies may also contribute. The Chinese kestrels had median muscle and liver PBDE levels much higher than reported for avian species from other countries (i.e., 10-1000x those in Belgian birds and in peregrine falcon eggs from Greenland (Jaspers et al., 2006; Voorspoels et al., 2006a; Vorkamp et al., 2005), 10-100x those in cormorants and herons from UK and in Norwegian eggs from various species (D’Silva et al., 2004; Herzke et al., 2005; Law et al., 2002), 10x those in
Swedish peregrine falcon and guillemot eggs and in Japanese cormorant eggs (Lindberg et al., 2004; Sellstrom et al., 2003; Watanabe et al., 2004), and 1-10x those in eggs of various aquatic species from North America (Norstrom et al., 2002; Rattner et al., 2004; She et al., 2003)). However, some of the studies referenced had maxima in individual birds on the same magnitude as those reported in our study.

3.2. Congener profiles and PCA

Distinct congener profiles were observed among the different species examined (Figure 3). Profiles were generally dominated by the more brominated congeners. This differs dramatically from what has been observed in fish and piscivorous birds where BDE-47 usually dominates (Law et al., 2008). Profiles in muscle and liver of Eurasian sparrowhawks were dominated by BDE-153, followed by -99, with lesser contributions from -47, -183, -154, -209 and -207. Similar profiles were found in little owls. These distributions are similar to those reported in other raptor studies (Lindberg et al., 2004; Voorspoels et al., 2006a) except that slightly elevated BDE-209 contributions were present in our samples. In muscle and liver of Japanese sparrowhawks collected in China, BDE-99, -153 and -47 were the major congeners (at roughly equivalent concentrations). These were followed by BDE-209, -207 and -183. Because the two buzzard species had statistically similar ∑PBDE levels and congener profiles and sample size was limited (n = 3 each), they are discussed together here. Buzzards exhibited roughly similar contributions of BDE-209, -183 and -153 in muscle. These congeners were dominant in this tissue, followed by -207 and -47. In liver and kidney, BDE-209 was the major congener, followed by -153, -183, -207 and -47. Long-eared owls had similar profiles to buzzards as follows: 153 > 209 > 183 ~ 47 ~ 99 > 207 ~ 208 in muscle; 209 > 153 ~ 207.
Figure 3. PBDE congener profiles in common kestrel (A), Eurasian (B) and Japanese sparrowhawk (C), little (D), scops (E), and long-eared owl (F), and upper (G) and common buzzard (H). BDE-28 and -49 were excluded from these profiles due to their modest contributions. Error bars represent 75% and 25% percentiles.
Contributions by congeners with six or more bromines ranged from 71.8% to 98.6% in buzzards and 58.3% to 91.5% in long-eared owls. Voorspoels et al. (2006a) reported that in Belgian owls and buzzards BDE-47, -99 and -153 were the most abundant congeners, each contributing between 15% and 35% to the ∑PBDEs. Our findings may indicate a greater prevalence of deca- through octa-BDEs in China. Congeners in Chinese scops owls prevailed in the following order: muscle 209 > 153 > 99 > 47 > 207 > 208 > 183; liver 209 > 207 > 153 > 208 > 99 > 183 > 47; kidney 209 > 153 > 99 > 183 > 47 > 208 > 207. BDE-153 was the dominant congener in the three tissues examined in the kestrels, followed by -209 > -207 > -203 > -208 > -183 > -196 in muscle and liver; and by -203 > -207 > -209 > -208 > -196 > -183 in kidney. The sum of the individual contributions of BDE-207, -208, -203 and -196 in kestrels was as much as 57.6% of ∑PBDEs, whereas the BDE-47 percentages were as low as 0.01%. Biotransformation in kestrels may be responsible for the modest BDE-47 percentages. This view is supported by a recent lab study wherein kestrel nestlings were fed a Penta-BDE mixture (predominantly BDE-47) daily (Fernie et al., 2006). After 36 days, kestrels contained greater amounts of BDE-100 and -99 than BDE-47 (Fernie et al., 2006). In contrast to the Chinese kestrels, elevated BDE-47 contributions were reported in Belgium kestrels, representing approximately 9% of liver and 5% of muscle PBDE burdens (Jaspers et al., 2006). However, this comparison may be confounded by the fact that different numbers of congeners were summed in these studies (17 vs. 8), as well as the small sample sizes available (N = 6 and 3, respectively).
PCA provides an informative visual display, facilitating inter-species comparisons. The biplot of PCA displays four clusters (Figure 4). Cluster I (Eurasian sparrowhawk) and II (Japanese sparrowhawk and little owl) appeared to be enriched in BDE-99, -47 and other less brominated congeners relative to the other clusters. Preferential excretion or metabolism of higher brominated congeners may be suggested for these species. Alternatively, it may be a function of exposure. Cluster IV (kestrel) tended to be enriched in BDE-209 and some nona- and octa- congeners, relative to the other clusters. The score point of kestrel kidney was located outside of the kestrel cluster (muscle and liver samples), indicating a significant difference in congener levels and profiles between these tissues. Species included in Cluster III (buzzard, scops and long-eared owl) were similar in terms of levels and profiles, as reflected by their overlapping positions in the biplot. Cluster I, III and IV separated well from each other, indicative of significantly different profiles.

3.3. BDE-209

Deca- has historically been the dominant PBDE product in terms of market demand and remains widely used worldwide. While production and usage of the Penta- and Octa-mixtures have been discontinued in several countries, the European Commission exempted Deca- in 2005 from inclusion in the Restrictions on Hazardous Substances Used in Electrical and Electronics Applications Directive. Examination of available published data indicated modest toxicity in most studies and limited bioaccumulation potential. BDE-209 has been less frequently reported in wildlife than constituents of Penta-BDE. However, some studies have indicated that BDE-209 can be degraded, principally photochemically or via biotransformation mechanisms, to less brominated
Figure 4. Biplot from the Principle Component Analysis (Comp.1: 83.82% variance; Comp. 2: 12.58% variance). Species identification: CK=common kestrel; SH=Eurasian sparrowhawk; JSH=Japanese sparrowhawk; LO=little owl; SO=scops owl; LEO=long-eared owl; BU=buzzard (upland and common buzzard). Tissue identification: _M= muscle; _L=liver; _K=kidney.

congeners that are more bioavailable and toxic (Law et al., 2006). Interestingly, BDE-209 has been detected with greater frequency in terrestrial versus aquatic wildlife, albeit generally at low concentrations. In terrestrial mammals such as grizzly bears and red foxes, BDE-209 has been the dominant congener in some specimens, with levels up to 41.7 and 760 ng/g lw, respectively (Christensen et al., 2005; Voorpoels et al., 2006b). BDE-209 has been reported more frequently in avian species. For example, it was
detectable in 6 out of 44 livers from Belgian buzzards, sparrowhawks and owls (up to 190 ng/g lw) and 19 out of 25 serum samples (up to 58 ng/g lw) (Voorspoels et al., 2006a). de Boer et al. (2004) reported BDE-209 levels up to 412 ng/g lw in eggs of kestrels, sparrowhawks and peregrine falcons from the UK and Sweden. Other falcon egg studies found BDE-209 levels ranging from 3.8 to 250 ng/g lw in a South Greenland population and < 20 to 430 in Swedish birds (Lindberg et al., 2004; Vorkamp et al., 2005).

Compared to previous reports, the Chinese raptors contained remarkably higher burdens of the more brominated congeners, including BDE-209. BDE-209 could be quantified in 79.4% of all tissues examined. Especially high levels were found in common kestrels (median: 1400 ng/g lw in muscle and 1030 ng/g lw in liver). One specimen contained 6220 ng/g lw in muscle and 12,200 in liver, which are among the highest BDE-209 levels reported in wildlife to date. It has been reported that BDE-209 levels in urban air samples from China were higher than those in North American and European studies (Chen et al., 2006b). The pooled kidneys of kestrels had a lower percentage of BDE-209 (as well as elevated contributions from -153) relative to other tissues. Similar results were also found in Japanese sparrowhawks. Buzzards and long-eared owls generally contained the lowest levels (11 – 133 and <1.2 – 528 ng/g lw, respectively) among the raptors examined here. Nonetheless, in specimens of these species where BDE-209 was detectable it was a dominant congener. BDE-209 was detected in all buzzards with contributions up to 71.0% of the $\Sigma$PBDEs. It was also dominant in 3 of 6 liver tissues of long-eared owls with contributions up to 72.0%, and in 3 of 6 muscle tissues of scops owls with contributions as high as 84.0%. These results reinforce the growing view that significant bioaccumulation of BDE-209 can occur in
some terrestrial food chains, especially when abundant Deca- sources are present. Interestingly, species with the highest PBDE burdens generally had lower BDE-209 relative contributions (i.e., < 29.9% in kestrels and < 26.9% in Eurasian sparrowhawks) than less contaminated birds (i.e., buzzards and some owls) (Figure 5). Statistically, higher relative BDE-209 contributions in liver were found in buzzards ($p = 0.039$) and long-eared owls ($p = 0.043$) relative to Eurasian sparrowhawks, respectively. Among the three owl species, little owls had much higher $\sum$PBDEs but statistically lower BDE-209 contributions. This pattern may relate to differences in uptake, distribution or metabolism of individual PBDE congeners between the different species.

### 3.4. Potential PBDE sources

The levels and congener profiles observed in the present study may relate to the significant production, usage and disposal of Deca-containing products in China. While little Penta- has reputedly been used in Asia (150 metric tons (MT) in 2001) relative to the past major consumer, North America (7100 MT), similar demands for Deca- were reported (23,000 and 24,500 MT, respectively) (BSEF, 2003). Data from the 2001 US EPA’s Toxics Reduction Inventory (TRI) on estimated industrial emissions in the U.S. suggested that the textile industry released the most Deca- to the surface water, air and publicly-owned wastewater treatment works (POTWs), followed by the chemical industry, electronics and plastics industries (Hale et al., 2006). No comparable data are available for China. However, all these industries are substantial in China. Considerable production is eventually exported to North American and European markets where fire retardancy regulations have been historically strict.
Figure 5. Relative contributions of BDE-209 to ΣPBDEs in various raptors. Error bars represent 75% and 25% percentiles. Species identification: CK=common kestrel; SH=Eurasian sparrowhawk; JSH=Japanese sparrowhawk; LO=little owl; SO=scops owl; LEO=long-eared owl; BU=buzzard (upland and common buzzard).

The raptors sampled in this study were mostly from relatively urbanized areas. Due to expanding human development and the mobility of these birds, the likelihood of their encountering contaminants is high and increasing. For example, some raptors roost on man-made structures (e.g. chimneys or towers) and incorporate synthetic materials such as plastics in their nests. Hence the potential of exposure from urban-related PBDE sources is accentuated. Uptake may be direct via exposure to products or degradates or via the food chain by consuming prey that come in contact with these materials. To illustrate, crickets have been observed to consume Penta-laden polyurethane furniture foam and pass PBDEs to frogs that in turn preyed upon them (Hale et al., 2002). Similar exposure scenarios likely occur for other insects, small mammals and birds that constitute
the raptor diet. Clearly, a better understanding of the potential sources of PBDEs to the Chinese environment in general and to birds of prey in particular is required.

References


Wienburg, C.L.; Shore, R.F. Factors influencing liver PCB concentrations in sparrowhawks (Accipiter nisus), kestrels (Falco tinnunculus) and herons (Ardea cinerea) in Britain. Environ. Pollut. 2004, 132, 41-50.

Chapter II

Polybrominated Diphenyl Ethers in Peregrine Falcon (*Falco peregrinus*)
Eggs from the Northeastern U.S.
Polybrominated Diphenyl Ethers in Peregrine Falcon (*Falco peregrinus*)
Eggs from the Northeastern U.S.

**Abstract:** A total of 114 peregrine falcon eggs from nests in Connecticut, Massachusetts, Maine, New Hampshire, Rhode Island, and Vermont were analyzed for polybrominated diphenyl ethers (PBDEs). Eggs were collected from 1996 to 2006, excluding 1997 and 1998. Total PBDE concentrations ranged from 74.5 to 6610 ng/g wet weight, with a median of 440. These levels were generally higher than those observed in European peregrine eggs, but comparable to those in North American seabird eggs. Congener patterns differed from such seabirds and were dominated by BDE-153, followed by BDE-99, -183, -209, -197, -207, -154, -100 and -196; with lesser contributions from BDE-47, -208, -203, -201, -206, -202, -138 and -119. Urban and rural falcon eggs contained similar total PBDE concentrations, but different congener profiles. Urban eggs exhibited higher BDE-209 concentrations and greater percentages of other highly brominated congeners. BDE-209 was detectable in all eggs, with concentrations ranging from 1.4 to 420 ng/g wet weight. Five octa- and three nona- brominated congeners were also frequently detected, some likely derived from the biodegradation of BDE-209. Temporal analyses indicated no significant changes in concentrations of total PBDEs, or most individual congeners, during the study period. An exception was BDE-209. It exhibited a significant increase, with a doubling time of 5 years. Current PBDE burdens may be insufficient to cause noticeable adverse effects at the population level, as the number of territorial pairs increased in the past decade. However, the high BDE-209 concentrations, short doubling time, and likely biodegradation observed in peregrine eggs from the northeastern U.S. may support the need for additional Deca-BDE regulations.
1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used extensively as flame retardant additives in textiles, thermoplastics, polyurethane foams, and electronic products. There are three major PBDE commercial mixtures: Penta-, Octa- and Deca-BDEs. The North American market consumes over half of the world’s PBDE production in general and 98% of Penta-BDE in particular (Hale et al., 2003). Consequently, PBDE concentrations reported in North America are comparable to or exceed those observed elsewhere in the world (Hale et al., 2003). For example, PBDE concentrations in U.S. sewage sludges were at least 10-fold higher than European levels. Recent North American temporal trend studies generally show increasing environmental and human concentrations. No manufacturing of the Penta- and Octa-BDE formulations occurred in Canada and production ceased in the U.S. at the end of 2004. To ensure flame retardancy, these formulations were used at percent levels in polymer products. Many of these finished goods have long service lives. Thus, releases from in-service and discarded products may continue for decades. In contrast, a decrease in the levels of some of the less brominated congeners has been reported in Europe, perhaps due to the voluntary cessation of Penta-BDE production in some countries beginning in the 1980s (Law et al., 2006).

Deca-BDE (predominantly BDE-209) remains the major PBDE mixture in production worldwide. Its continued use, however, is under increasing scrutiny. In 2005, the European Commission exempted Deca-BDE from inclusion in the Restrictions on Hazardous Substances Used in Electrical and Electronics Applications Directive. Recent studies, however, revealed significant bioaccumulation of BDE-209 in European and
Chinese terrestrial raptors (Lindberg et al., 2004; Chen et al., 2007), suggesting that apex terrestrial predators may experience heightened exposure. These findings, as well as increasing evidence of degradation of BDE-209 into less brominated and more bioavailable and toxic congeners, have convinced several U.S. states (e.g., Maine and Washington) to ban the manufacture, sale and use of Deca in some products (e.g., mattresses and furniture). Nonetheless, adequate data remain lacking on PBDEs in general and the higher brominated congeners in particular, in North American terrestrial wildlife.

Lindberg et al (2004) recently reported substantial accumulation of some highly brominated congeners (i.e., BDE-153, -183, and -209) in Swedish peregrine falcon (Falco peregrinus) eggs. Very limited data have been published on North American eggs (Hooper et al., 2007). In 1999, the peregrine was removed from the U.S. list of threatened and endangered species (US Fish and Wildlife Service, 1999). Its near extinction in the early 1970s was largely attributed to impaired reproduction due to high body burdens of chlorinated insecticides (Anderson and Hickey, 1972). Peregrine falcons are top predators and biomagnify persistent organic pollutants (POPs). While rare, peregrines have a worldwide distribution. This study was undertaken to examine PBDEs in peregrine eggs collected from six northeastern U.S. states.

2. Materials and Methods

2.1. Samples

A total of 114 eggs were collected from nests in Connecticut (N = 4), Massachusetts (N = 26), Maine (N = 1), New Hampshire (N = 58), Rhode Island (N = 8), and Vermont
from 1996 to 2006, excluding 1997 and 1998 (Table 2; Figure 6). Biological information on northeastern peregrines (genus, diet and migration) (Corser et al., 1999) are listed in the Appendix II. All eggs were nonviable and collected after the end of incubation periods. Egg lengths, widths, and total egg weights were measured. Egg contents were transferred to solvent-rinsed glass jars and frozen until chemical analysis.

2.2. Analysis

All organic solvents used were of pesticide residue analysis grade (Honeywell Burdick & Jackson, Morristown, NJ). Egg contents and sodium sulfate blanks were freeze-dried for 48 hours. Following the addition of the surrogate standard (PCB-204: Ultra Scientific, North Kingstown, RI), samples (typically 1.7 g) were subjected to enhanced solvent extraction (Dionex ASE 200, Sunnyvale, CA), employing two 5-min extraction cycles with dichloromethane (DCM) at 100°C and 1000 psi. Lipids were determined by evaporation of a fraction of each extract to a constant weight. The remainder of each extract was purified by size exclusion chromatography (Envirosep-ABC, 350 × 21.1 mm column; Phenomenex, Torrance, CA), which separates the large molecular weight biogenic compounds from the halogenated compounds of interest. The resulting fraction of interest was further purified on 2-g silica gel solid-phase extraction columns (Isolute, International Sorbent Technology, UK). The first fraction was eluted from the silica column with 3.5 mL of hexane and was discarded. The second fraction, which contained PBDEs and other halogenated compounds, was obtained by elution with 6.5 mL of 60:40 hexane:DCM. Following solvent exchange to hexane, the second fraction was concentrated and spiked with the internal standard (decachlorodiphenyl ether: Ultra Scientific, North Kingstown, RI).
Table 2. Detailed information on nest locations, ecoregion categories, sampling years, and egg numbers.

<table>
<thead>
<tr>
<th>Nest ID</th>
<th>Site Name</th>
<th>Town</th>
<th>State</th>
<th>Ecoregion: Urban (U)/Rural (R)</th>
<th>Sampling Year</th>
<th>Egg Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT-01</td>
<td>P.T. Barnum Bridge</td>
<td>Bridgeport</td>
<td>CT</td>
<td>U</td>
<td>2001</td>
<td>1</td>
</tr>
<tr>
<td>CT-02</td>
<td>Bayview Towers</td>
<td>Stamford</td>
<td>CT</td>
<td>U</td>
<td>2003</td>
<td>2</td>
</tr>
<tr>
<td>CT-03</td>
<td>West Rock Ridge</td>
<td>Hamden</td>
<td>CT</td>
<td>R</td>
<td>2006</td>
<td>1</td>
</tr>
<tr>
<td>MA-02</td>
<td>Braga Bridge</td>
<td>Fall River</td>
<td>MA</td>
<td>U</td>
<td>1999,2002</td>
<td>3</td>
</tr>
<tr>
<td>MA-03</td>
<td>Christian Science Center</td>
<td>Boston</td>
<td>MA</td>
<td>U</td>
<td>2002,2005</td>
<td>3</td>
</tr>
<tr>
<td>MA-04</td>
<td>Quincy Shipyard</td>
<td>Boston</td>
<td>MA</td>
<td>U</td>
<td>2003,2004</td>
<td>5</td>
</tr>
<tr>
<td>MA-05</td>
<td>Customs House</td>
<td>Boston</td>
<td>MA</td>
<td>U</td>
<td>2003,2005</td>
<td>2</td>
</tr>
<tr>
<td>MA-06</td>
<td>Ideal Box Company</td>
<td>Lawrence</td>
<td>MA</td>
<td>U</td>
<td>2003,2004</td>
<td>2</td>
</tr>
<tr>
<td>MA-07</td>
<td>Mount Sugarloaf</td>
<td>Deerfield</td>
<td>MA</td>
<td>R</td>
<td>2004</td>
<td>4</td>
</tr>
<tr>
<td>MA-08</td>
<td>U Mass Library</td>
<td>Amherst</td>
<td>MA</td>
<td>U</td>
<td>2003</td>
<td>1</td>
</tr>
<tr>
<td>ME-01</td>
<td>Verona Island Bridge</td>
<td>Verona</td>
<td>ME</td>
<td>U</td>
<td>2003</td>
<td>1</td>
</tr>
<tr>
<td>NH-02</td>
<td>Rattlesnake Cliff</td>
<td>Rumney</td>
<td>NH</td>
<td>R</td>
<td>1996,1999,2006</td>
<td>6</td>
</tr>
<tr>
<td>NH-05</td>
<td>Painted Walls</td>
<td>Albany</td>
<td>NH</td>
<td>R</td>
<td>2000,2001</td>
<td>3</td>
</tr>
<tr>
<td>NH-06</td>
<td>Owls Head</td>
<td>Benton</td>
<td>NH</td>
<td>R</td>
<td>2000,2002</td>
<td>6</td>
</tr>
<tr>
<td>NH-07</td>
<td>Holts Ledge</td>
<td>Lyme</td>
<td>NH</td>
<td>R</td>
<td>1999,2000,2003</td>
<td>3</td>
</tr>
<tr>
<td>NH-08</td>
<td>Frankenstein Cliff</td>
<td>Harts Location</td>
<td>NH</td>
<td>R</td>
<td>2001</td>
<td>3</td>
</tr>
<tr>
<td>NH-11</td>
<td>Russell Crag</td>
<td>Woodstock</td>
<td>NH</td>
<td>R</td>
<td>2002,2003</td>
<td>4</td>
</tr>
<tr>
<td>NH-12</td>
<td>Memorial Bridge</td>
<td>Portsmouth</td>
<td>NH</td>
<td>U</td>
<td>2006</td>
<td>1</td>
</tr>
<tr>
<td>RI-01</td>
<td>Fleet Bank</td>
<td>Providence</td>
<td>RI</td>
<td>U</td>
<td>2001,2005,2006</td>
<td>4</td>
</tr>
<tr>
<td>VT-01</td>
<td>Arrowhead Mountain</td>
<td>Milton</td>
<td>VT</td>
<td>R</td>
<td>2000,2002</td>
<td>3</td>
</tr>
<tr>
<td>VT-02</td>
<td>Snake Mountain</td>
<td>Addison</td>
<td>VT</td>
<td>R</td>
<td>2000,2004</td>
<td>3</td>
</tr>
<tr>
<td>VT-03</td>
<td>Mt Horrid</td>
<td>Rochester</td>
<td>VT</td>
<td>R</td>
<td>2000,2004,2006</td>
<td>3</td>
</tr>
<tr>
<td>VT-04</td>
<td>Deer Leap</td>
<td>Bristol</td>
<td>VT</td>
<td>R</td>
<td>2003,2005</td>
<td>2</td>
</tr>
<tr>
<td>VT-05</td>
<td>Hawk Rock</td>
<td>Newark</td>
<td>VT</td>
<td>R</td>
<td>2004,2006</td>
<td>2</td>
</tr>
<tr>
<td>VT-06</td>
<td>Burnt Mountain</td>
<td>Marshfield</td>
<td>VT</td>
<td>R</td>
<td>1996</td>
<td>1</td>
</tr>
<tr>
<td>VT-07</td>
<td>Rattlesnake Point</td>
<td>Salisbury</td>
<td>VT</td>
<td>R</td>
<td>2001</td>
<td>1</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------</td>
<td>-----------</td>
<td>----</td>
<td>---</td>
<td>------</td>
<td>---</td>
</tr>
<tr>
<td>VT-08</td>
<td>Sawyer Mountain</td>
<td>Fairlee</td>
<td>VT</td>
<td>R</td>
<td>2003</td>
<td>1</td>
</tr>
<tr>
<td>VT-09</td>
<td>Ryegate Quarry</td>
<td>Ryegate</td>
<td>VT</td>
<td>R</td>
<td>2006</td>
<td>1</td>
</tr>
</tbody>
</table>

^ State identification: CT=Connecticut; MA=Massachusetts; ME=Maine; NH=New Hampshire; RI=Rhode Island; VT=Vermont.

Urban nest sites are those nests on man-made structures, e.g., buildings and bridges, of which most occur in metropolitan areas. Rural nests are predominantly on natural cliffs, all of which are in rural (low human population) settings.

**Figure 6.** Distribution of sampled nests in Connecticut (CT) (3 eyries), Massachusetts (MA) (8 eyries), Maine (ME) (1 eyry), New Hampshire (NH) (12 eyries), Rhode Island (RI) (2 eyries), and Vermont (VT) (9 eyries).
Instrumental analysis of final extracts was similar to what has been reported previously (La Guardia et al., 2006), with minor modifications. Compounds of interest were separated by an Agilent 6890N gas chromatograph (GC) (Agilent Tech., Palo Alto, CA), using a 30-m DB-5HT column (0.25 mm i.d., 0.1 μm, J&W Scientific, Agilent Tech.). Ion fragmentation spectra for compound identification were produced by both electron ionization (EI) and electron-capture negative ionization (ECNI) (JMS-GC Mate II, JEOL, Peabody, MA). A pressure pulse split/splitless injector was used, with an injector temperature of 300°C and pressure of $3.4 \times 10^5$ Pa. Previous studies indicated only minimal thermal degradation of BDE-209 by this injection technique (La Guardia et al., 2007). EI mode (scan range 50 – 1000 m/z, scan time 0.30 s, electron energy 70 eV) was first employed to identify the PBDE congeners of interest (BDE-3, 7, 15, 17, 28, 47, 49/71, 66, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 201, 202, 203, 206, 207, 208 and 209). Native PBDE standards used in calibration mixtures were purchased from Wellington Laboratories (Ontario, Canada). The dominant ion clusters in EI mode are centered on the molecular ion ([M]$^+$) and the loss of two bromines ([M–Br₂]$^+$) (La Guardia et al., 2006). Initial column oven temperature was held at 90°C for 4 min, increased to 150°C at 30°C/min, then to 300°C at 10°C/min (held for 15 min), and to 350°C at 30°C/min (held for 15 min). Using the same GC program, ECNI-SIM was then employed for the quantification of target analytes, except for BDE-154, which co-eluted with PBB-153 and hence was quantified using EI. The predominant ions generated in ECNI spectra were 79 and 81 m/z for PBDEs and 35 and 37 m/z for chlorinated surrogate and internal standards. Deca-, nona-, and octa-congeners were further confirmed on a 15-m DB-5 column (0.25 mm i.d., 0.1 μm, J&W Scientific,
Agilent Tech.) in the EI mode and then quantified using ECNI. The initial column oven temperature was held at 90°C for 4 min, increased to 150°C at 30°C/min, to 300°C at 10°C/min (held for 7 min), and finally to 350°C at 30°C/min (held for 15 min).

2.3. QA/QC

Several procedures were employed to minimize and evaluate the potential for analyte loss, sample contamination and PBDE degradation. These included: PBDE spiking tests, analysis of procedural blanks, and examination of surrogate standard recoveries. Before extracting the authentic samples, spiking tests were conducted in order to appraise the recoveries of major PBDE congeners. Chicken eggs purchased from a local supermarket were used as a spiking matrix. After confirming that they were free of PBDEs, 2-g dry aliquots were spiked with 0.5 μg of BDE-28, -47, -99, -100, -153, -154, -183 and -209 (AccuStandard Inc., New Haven, CT). Five experimental groups, each consisting of five spiked samples, were analyzed as described above. The mean (± standard error) recoveries of individual PBDE congeners ranged from 74.9 (± 1.3) % for BDE-154 to 89.5 (± 2.2) % for BDE-209 (Figure 7). Very small amounts of BDE-207 and -206 (< 1% of BDE-209) were observed in two spiked samples, indicating possible minor BDE-209 degradation. Accuracy and Precision Control Charts (X-R Chart) (Newman 1995) for BDE-209 recoveries were developed (Appendix IV). One procedural blank was processed with every 10 authentic samples. BDE-99 was detected in 9 out of 12 blanks at trace concentrations. BDE-209 was detectable in a single blank, but at a non-quantifiable (S/N < 5) level. Recoveries of surrogate standard PCB-204 were 95.5 (± 1.0) % among all blanks and samples.
Figure 7. Mean recoveries of individual PBDE standards in spiking tests \((n = 25)\) (error bars represent one standard deviation).

2.4. Statistical analysis

The limits of quantification (LOQs) were defined as a signal of five times the noise level. For measurements below the LOQs, a regression probability plotting method was applied to assign values for statistical analysis (Newman 1995). As the condition and stage of the addled eggs varied, adjustment for moisture and lipid losses was necessary for valid interpretation of residue concentrations (Stickel et al., 1973). This was achieved through the estimation of the volume of each egg (Hoyt 1979). The final concentrations were expressed as ng/g fresh wet weight (ng/g ww), unless otherwise noted. All concentration values were corrected using surrogate PCB-204 recoveries. Non-normally distributed data were logarithmically transformed to approximate a normal distribution before being subjected to analysis of covariance (ANCOVA). Significant results were
investigated further by Scheffe’s posthoc analysis (SPSS 13.0, SPSS Inc.). Temporal trends of PBDE concentrations were examined with Linear Regression Analysis (SPSS 13.0), after log-transforming the residue data, followed by ANOVA. The level of significance was set at $a = 0.05$.

3. Results and Discussion

3.1. Concentrations and congener profiles

Of the PBDE congeners examined, 17 exhibited levels above the LOQ in at least 70% of all samples: BDE-47, -99, -100, -119, -138, -153, -154, -183, -197, -196, -201, -202, -203, -206, -207, -208 and -209; \( \sum \) PBDEs” is defined here as the sum of these 17 congeners. \( \sum \) PBDE concentrations in the 114 eggs ranged from 74.5 – 6610 ng/g ww, with a median of 440 (7660 ng/g lipid weight). Two eggs exhibited extremely high levels, 2670 and 6610 ng/g ww (47 400 and 72 000 ng/g lipid weight, respectively). These were collected from one of the most frequently occupied nesting sites in New Hampshire (NH-08), a cliff located in a state park (Figure 8). These concentrations rival the highest PBDE burdens reported in wildlife to date. Compared to other studies, U.S. peregrine eggs contained greater \( \sum \) PBDEs than eggs from Greenland (~ 100 ng/g ww), Norway (155 ng/g ww), and Sweden (230 ng/g ww) (Herzke et al., 2005; Lindberg et al., 2004; Vorkamp et al., 2005). \( \sum \) PBDE burdens were similar to those observed in some North American aquatic bird eggs, i.e., osprey from Chesapeake (176 – 725 ng/g ww) and North Delaware Bay (82 – 572 ng/g ww); Caspian tern from Washington State (340 ng/g ww) and San Francisco Bay (440 ng/g ww); herring gull from the Great Lakes (192 – 1440 ng/g ww) (Norstrom et al., 2002; Rattner et al., 2004; She et al., 2003; Toschik et
al., 2005). They were much higher than in eggs from European and Arctic aquatic birds (i.e., osprey and sea eagle from Norway (103 and 184 ng/g ww, respectively), and black guillemot from Greenland (2.6 ng/g ww)) (Herzke et al., 2005; Vorkamp et al., 2004). These observations may relate to the greater usage and release of PBDE flame retardants in North America. The falcon population in six New England states increased from 33 territorial pairs in 1996 to 87 in 2006, at a mean rate of 10.4% per year (USFWS unpublished data). Peregrine falcon productivity (young produced per territorial pair) averaged 1.62 during the period 1996-2000 and dropped slightly to 1.52 during the period 2001-2006. The mean productivity for the whole study period (1996-2006) was 1.56. This is within the range reported for other recovering peregrine populations (1.25 – 1.8) (US Fish and Wildlife Service, 1999), but slightly below the national productivity average (1.64) compiled for 2003, the first year of post-delisting monitoring under the Endangered Species Act (Green et al., 2006). Although current PBDE burdens may be insufficient to cause noticeable adverse effects at the population level, effects on individual peregrines cannot be excluded, as some nests (e.g., NH-08) exhibited extremely high PBDE concentrations.

PBDE congener profiles in peregrine eggs were dominated by BDE-153, followed by BDE-99, -183, -209, -197, -207, -154, -100 and -196; with lesser contributions from BDE-47, -208, -203, -201, -206, -202, -138 and -119 (Figure 9). Individual congener concentrations from each nest are listed in the Appendix III. This distribution differs dramatically from that reported in aquatic birds, where BDE-47 usually dominates (Law et al., 2006), but resembles that observed in European peregrines and terrestrial raptors elsewhere (Herzke et al., 2005; Lindberg et al., 2004; Vorkamp et al., 2005). Elevated
Figure 8. Median $\Sigma$PBDE and BDE-209 concentrations in each of the 35 nests examined. Error bars represent 25 and 75 percentiles.

Figure 9. Median PBDE congener profiles in urban ($n = 42$) and rural ($n = 72$) eggs. Error bars represent 25 and 75 percentiles. Urban nests contained greater concentrations of the highly brominated congeners.
contributions from the heavier congeners have also been observed in some mammals (e.g., red fox and grizzly bears) (Christensen et al., 2005; Voorspoels et al., 2006a). These findings reinforce the view that terrestrial animals may experience greater exposure to the heavier congeners, compared to aquatic organisms.

Although Octa-BDE constituted only 4.5% of the reported total (sum of Penta-, Octa- and Deca-BDE) 2001 North American PBDE demand (BSEF, 2003), BDE-183, the characteristic congener in technical Octa-BDE formulations, was the third most prominent congener in peregrine eggs. Aquatic organisms usually have been observed to contain minor BDE-183 contamination. This may relate to its very high $K_{ow}$ and large molecular size, which reduce bioaccumulation in such ecosystems. A recent study, however, indicated that BDE-183 had the highest biomagnification factor among the examined congeners (from tetra- to hepta-) in the passerine-sparrowhawk food chain (Voorspoels et al., 2007). The elevated BDE-183 concentrations in peregrines may therefore derive in part from its high biomagnification potential in terrestrial food chains. BDE-47 was a minor contributor (<2% on average) in peregrine eggs, as was the case in Chinese kestrels (Chen et al., 2007) and Swedish peregrine falcon eggs (Lindberg et al., 2004). Extensive biotransformation of BDE-47 in American kestrel nestlings has been demonstrated in a lab study after feeding a penta-mixture (Fernie et al., 2006). Though the concentration ratio of BDE-153 to -99 was 2.6 on average, similar to the ratios observed in European peregrines (2.2 – 2.4) (Herzke et al., 2005; Lindberg et al., 2004; Vorkamp et al., 2005), some eggs did contain greater amounts of BDE-99 than BDE-153. For example, BDE-99 concentrations were 1.2-3 times higher than BDE-153 in eggs from nests CT-02, MA-04, MA-08, NH-01 and NH-07. These patterns were closer to
those observed in some birds that feed primarily on terrestrial mammals or insects (i.e., Belgium little owl and great tit) (Dauwe et al., 2006; Jaspers et al., 2006). This might reflect dietary differences between some peregrines, from predominantly passerines to more doves. The latter may contain greater amounts of BDE-99 than -153. Other possibilities, such as the abundance of lighter congener sources near those nests, cannot be excluded.

3.2. Differences among ecoregions

Ecoregions are more relevant, in terms of explaining contaminant burdens, than political divisions such as states. Among the eggs examined, some were from urban environments, where the nests were located on high rise buildings or bridges. Most rural nests were located on natural cliffs. Concentrations and congener profiles were compared between these two subgroups using ANCOVA, which incorporated year as a covariate. To avoid pseudo-replication, a clutch mean was calculated if more than one egg was collected from a clutch in the same year. This clutch mean was then included as a single data point for statistical analyses. The concentration variance observed in this study was much smaller within clutches than among clutches, in agreement with other reports (Lindberg et al., 2004; Van den Steen et al., 2006a). \( \Sigma \)PBDE concentrations were not significantly different between urban (median: 570; range: 150 – 1910 ng/g ww) and rural eggs (median: 380; range: 75 – 3570 ng/g ww) \((p = 0.075)\). Congener patterns, however, were significantly different between the two subgroups (Figure 9). Both the BDE-209 concentrations and its contributions to \( \Sigma \)PBDEs (BDE-209%) were significantly higher in urban than rural eggs \((p < 0.005)\). The ratio H/L, describing the proportion of heavier congeners, was calculated as the summed concentration of heavier
congeners divided by the summed concentration of lighter congeners (i.e., \((\text{octa} + \text{nona} + \text{deca}) / (\text{tetra} + \text{penta} + \text{hexa} + \text{hepta})\)). Urban eggs had statistically higher H/L ratios than rural eggs \((p < 0.005)\). These findings point to elevated contributions by heavier congeners (especially deca-) in urban populations. Deca-BDE is extensively used in themoplastics and in textile backcoatings. Peregrines living in urban environments have more opportunities for exposure to such products. A previous study reported much higher BDE-209 concentrations in common kestrels living in a large city compared to sparrowhawks from outside of the urbanized zone (Chen et al., 2007). The hypothesis that more populated areas exhibit greater environmental levels of BDE-209 is supported by the significant correlation between median BDE-209 concentrations by nest and populations of the towns (US Decennial Census, 2000) where the nests were located (Figure 10). The Pearson product-moment correlation was highly significant \((p < 0.005; n = 34, r = 0.527)\), after exclusion of one extreme outlier (NH-08). Additionally, dietary habits differ between urban and rural populations. Urban peregrines may feed to a greater extent on resident birds, such as pigeons and starlings. Peregrines living in rural habitats may prey on a more diverse variety of migratory birds. A divergence in congener patterns, as a function of dietary differences, was also observed in British Columbian grizzly bears (Christensen et al., 2005). Bears consuming a higher proportion of terrestrial vegetation exhibited patterns dominated by heavier congeners, whereas those consuming salmon were dominated by BDE-47.

3.3. **Temporal trends**

Temporal changes in PBDE concentrations were examined from 1996 to 2006 (Figure 11). The opportunistic sampling strategy in this study could bias results and
subsequent data interpretation. For example, while the majority of nests had eggs collected for consecutive years, some were only sampled once. Nonetheless, ∑PBDE concentrations in peregrine eggs did not exhibit significant changes with time ($r = 0.135$, $p = 0.258$). Similarly, the concentrations of major individual congeners (i.e., BDE-153, -154, -99, -100, -183 and -197) exhibited non-significant temporal trends. In contrast, BDE-209 concentrations significantly increased ($r = 0.348$, $p < 0.005$), with a doubling time of 5 years (Figure 11B). The H/L ratio, representing the proportion of heavier congeners, also increased significantly over the study period ($r = 0.253$, $p < 0.05$). Additionally, separate trend analyses revealed a significant increase in BDE-209 levels.

![Figure 10](image.jpg)

**Figure 10.** Significant correlation between median BDE-209 concentrations by nest and the populations of towns where the nests were located ($n = 34$, $r = 0.527$, $p < 0.005$). Town population data were obtained from the US Decennial Census (2000). Nest NH-08 was identified as an extreme outlier in the Pearson product-moment correlation (SPSS 13.0) and thus was excluded from the analysis. Error bars represent 25 and 75 percentiles.
Figure 11. Temporal changes in median ∑PBDE (A) and BDE-209 (B) concentrations in peregrine eggs during the period 1996 – 2006. Error bars represent 25 and 75 percentiles.

in rural eggs, with a shorter doubling time of 3.7 years, whereas no significant trend was observed in urban eggs (p = 0.370). However, limited urban data points in earlier years (i.e., only one per year before 2001) may have compromised the analysis.

Previously, ∑BDE$_{47,99,100}$ concentrations in Great Lakes herring gull eggs were reported to have increased dramatically from 1981 to 2000, with doubling times ranging from 2.6 to 3.1 years (Norstrom et al., 2002). ∑BDE$_{153,154,183}$ also generally increased, but exhibited considerable variability. Other studies have reported exponential PBDE increases in eggs of various aquatic bird species from British Columbia (Canada) (1979 – 2002) (Elliott et al., 2005), and increases in fish and marine mammals around North America from the 1980s to 2000s, with varying rates (Ikonomou et al., 2002; Johnson-Restrepo et al., 2005; Lebeuf et al., 2004). These patterns, driven primarily by increases
in BDE-47 and -99 concentrations, were believed to result from the extensive usage of Penta-BDE on this continent. Some recent European data, in contrast, suggest decreases in PBDE concentrations from the late-1980s in birds and fish and from the late-1990s in human breast milk (Sellstrom et al., 2003). Because of their relatively high molecular weights and low vapor pressures, the more brominated congeners may escape more slowly from their host products than BDE-47. They tend to be absorbed on air-borne dusts, soils and sediments and less vulnerable to long-range transport. In addition, PBDEs have been reported to have lower biomagnification factors in some terrestrial food chains (i.e., up to 18 in passerine/rodent-raptor food chains) than aquatic systems (i.e., up to 204 in fish-shark food chains) (Johnson-Restrepo et al., 2005; Voorspoels et al., 2007). These factors may contribute to a slower increase in PBDE concentrations in terrestrial apex predators (i.e., birds of prey). This hypothesis was supported by a study on Greenland peregrine eggs, which reported a significant, but very slow increase in PBDE concentrations over a longer time scale (1986 – 2003) (Vorkamp et al., 2005). The unexpected short doubling time of BDE-209 concentrations in this study may result from the intensive applications of Deca-BDE in North America.

3.4. BDE-209 and potential biodegradation

In spite of BDE-209’s extreme hydrophobicity and substantial molecular size, which may hinder its bioaccumulation, it has been detected in wildlife with increasing frequency. BDE-209 was detectable in all eggs in this and the previously cited Greenland peregrine egg study (Vorkamp et al., 2005). Frequency of detection was 86% in Swedish peregrine eggs and 79.4% in Chinese terrestrial birds (Chen et al., 2007; Lindberg et al., 2004). Concentrations ranged from 1.4 – 420 ng/g ww in the present study (Figure 8).
The median concentration (26 ng/g ww or 480 ng/g lipid wt) was much higher than what has been observed in European birds (i.e., Swedish (82 ng/g lipid wt) and Greenland (11 ng/g lipid wt) peregrine eggs, Belgian buzzards (24 ng/g lipid wt) and sparrowhawks (17 ng/g lipid wt)), but comparable to those in Chinese kestrels (24 in muscle and 41 ng/g ww in liver) (Chen et al., 2007; Lindberg et al., 2004; Voorspoels et al., 2006b; Vorkamp et al., 2005). This follows the global demand pattern for Deca-BDE; i.e., greater amounts are consumed in both North America and Asia than Europe. Perhaps more important than where flame retardants and finished goods are produced is where they are used and discarded. North America is home to much of the world’s market for finished polymer products (Hale et al., 2002). These products will subsequently function as long-term sources for environmental releases. Exacerbating the situation in China and some other Asian countries is their role as a disposal site for obsolete PBDE-containing electronics.

In addition to BDE-209, eight nona- and octa-congeners were frequently detected in this study, but have rarely been reported in wildlife. Together with BDE-209, they constituted 16 – 57% of \( \sum \)PBDEs in urban eggs and 4.9 – 53% in rural eggs. BDE-197 (median 28 ng/g ww), -196 (13 ng/g ww) and -207 (20 ng/g ww) were the most dominant. Their concentration ratios (2:1:1.3) resembled what has been quantified in the technical Octa-BDE formulation DE-79 (2:1:1:1.1) (La Guardia et al., 2006). This may indicate exposure to such a commercial mixture. BDE-201, with a ratio of 1:28 to BDE-197 in DE-79 (La Guardia et al., 2006), had higher proportions (1:6.2) in the peregrine eggs. Another octa-congener BDE-202, detectable in 107 out of 114 peregrine eggs, was not reported in any of the technical mixtures in a recent compositional study (La Guardia et al., 2006). These observations suggest that these two congeners may originate from
debromination of BDE-209. Previous dietary BDE-209 exposure studies performed on rainbow trout and common carp suggested that BDE-202 was a dominant BDE-209 debromination product (Stapleton et al., 2006). A recent report on wild-caught fish from a wastewater receiving stream further indicated the biodegradation of BDE-209 to BDE-202 and -201 (La Guardia et al., 2007). Three nona-congeners (BDE-208, -207 and -206) were also candidate debromination products in both studies. Their relative abundances reported here (BDE-207 > -208 > -206), however, were different from those appearing in in vivo exposure studies in fish (BDE-208 > -207 > -206). Nonetheless, the patterns approximate those observed in a European starling BDE-209-exposure study (Van den Steen et al., 2006b). The congener distributions also deviate from those in technical Octa-BDE (BDE-207 > -206 >> -208) and Deca-BDE (-206 > -207 > -208) mixtures (La Guardia et al., 2006). Thus, the patterns observed in the U.S. peregrine eggs may originate from the direct accumulation from technical mixtures or via biodegradation of BDE-209. The above findings of high BDE-209 concentrations, short doubling time, and potential biodegradation in U.S. peregrine eggs, indicate wisdom in limiting unnecessary Deca-BDE release to the environment.

References


U.S. Fish and Wildlife Service. Final rule to remove the American peregrine falcon from the Federal list of endangered and threatened wildlife, and to remove the similarity or appearance provision for free-flying peregrines in the conterminous United States. Federal Register 1999, 64, 46541-46558.


Chapter III

Species-Specific Accumulation of Polybrominated Diphenyl Ether Flame Retardants in Birds of Prey from the Chesapeake Bay Region, USA
Species-Specific Accumulation of Polybrominated Diphenyl Ether Flame Retardants in Birds of Prey from the Chesapeake Bay Region, USA

Abstract. Compared to organochlorines, little is known about polybrominated diphenyl ether (PBDE) contamination of birds of prey breeding in the Chesapeake Bay region. This study examined and compared PBDE contamination in eggs of both piscivorous (i.e., osprey, double-crested cormorant and brown pelican) and terrestrial-feeding species (peregrine falcon) from this area. The level of human disturbance appeared to influence the level of PBDE exposure. For example, PBDE concentrations in osprey eggs collected from more densely human-populated locales exhibited greater levels than pelican and cormorant eggs from an offshore island. Fish-eating birds and peregrine falcons exhibited dissimilar PBDE congener distribution patterns. This suggests individual congeners may be subject to differences in bioaccumulation, biomagnification or metabolism in the aquatic and terrestrial environments. Biomagnification of PBDEs was studied in the Bay aquatic food chains for the first time. A biomagnification factor of 41 for the fish–osprey food chain was estimated, indicating substantial magnification potential for PBDEs. Hazard quotients, applied as a preliminary evaluation, indicated that PBDEs may pose a moderate hazard to ospreys and peregrines through impairment of pipping and hatching success.

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 breeding populations consisted of about 3500 pairs (Watts and Paxton, 2007). 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 occur in the Bay historically, but recently their populations have expanded here (e.g., Smith Island, MD). Several 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 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 well as reproductive courtship behaviors in adult kestrels (Fernie et al., 2005; Fernie et al., 2008). A Penta-BDE formulation, DE-71, has also been observed to reduce egg shell thickness (Fernie et al., 2009), and decrease pipping and hatching success in kestrels and cause sublethal effects (i.e., ethoxyresorufin-

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 (Figure 12). All eggs were nonviable and collected after the end of their normal incubation periods. 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 (Envirospe-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 minute; then increased to 350 at 4 °C /min and held for 1 minute. 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). The model has the form:

\[
Y_{predatory\ species} = BMF\left[F_1(X_1) + F_2(X_2) + \cdots + F_n(X_n)\right]
\]  

(1)

where \(Y\) = median PBDE concentration in predatory species, \(F_1 = \) fraction of item one in diet, \(X_1 = \) median PBDE concentration in item one, \(F_n = \) fraction of the nth item in diet, \(X_n = \) median PBDE concentration in the nth 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 effect contaminant concentrations below which no adverse effect is expected (PNEC or predicted no effect concentration) (Lam et al., 2005). 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, 2002). 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).
Figure 12. Distribution of peregrine falcon (PF), osprey (OS), brown pelican (BP) and double-crested cormorant (DCC) nests sampled in the Chesapeake Bay region.
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 quantifications (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 addled eggs varied, an adjustment of moisture and lipid losses was applied to better interpret residue levels (Chen et al., 2008). 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 posthoc analysis (SPSS 13.0). The level of significance was set at α = 0.05.

3. Results and Discussions

3.1. Concentration data and interspecies comparisons
Median $\Sigma$PBDE concentrations were 290 ng/g wet wt in ospreys, 182 in peregrine falcons, 28 in brown pelicans and 12 in double-crested pelicans. These levels were generally one to two magnitudes lower than $\Sigma$PCBs in the same species (Figure 13). In ospreys, $\Sigma$PBDE and $p,p'$-DDE concentrations were similar. 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 $\Sigma$PBDE levels ($p < 0.0001$). Though factors such as migration and food choices may contribute to inter-species variances, local exposure levels in their living habitats may play a role here. Piscivorous birds prefer to catch prey close to their nests, hence reducing energy consumption and time spent. Their body

![Figure 13](image.png)

**Figure 13.** Median PBDE, 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.
burdens may be greatly influenced by the contamination levels of local fishes. Therefore, PBDE concentrations in the bird eggs may track local exposure levels near their breeding sites. 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 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 recently 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. However, data concerning such differences are limited.

Peregrine falcons contained ΣPCB and ΣPBDE 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. High DDE burdens in peregrines may be sustained by their consumption of contaminated migratory birds. The correlation between DDE and $\sum$PBDE concentrations in peregrine eggs was not significant ($r = 0.067$, $p = 0.194$) (Figure 14). This suggests there may be different sources for these contaminants, e.g., DDE may be primarily contributed by migratory birds, whereas PBDE burdens may derive mostly from local exposure. In contrast, all fish-eating species exhibited significant correlations between DDE and PBDE burdens (Figure 15), suggesting common sources for various contaminants, e.g., local fishes. Therefore, our results indicate that diet and living habitat likely influenced the species-specific contamination patterns in the Bay birds.

### 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 (2008). Seven fish species were included in the BMF estimation, which cumulatively represented 91% of dietary items (Table 3). 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
Figure 14. Correlations between \( p,p' \)-DDE and PBDE concentrations in eggs of peregrine falcon \( (r = 0.067, p = 0.194) \), osprey \( (r = 0.954, p < 0.0001) \), brown pelican \( (r = 0.978, p < 0.0001) \), and double-crested cormorant \( (r = 0.595, p < 0.005) \).

was assigned to the remaining 9% of diet. The BMF for \( \Sigma \)PBDEs in the fish – osprey egg food chain was estimated to be 41, similar to \( \Sigma \)PCB (BMF = 43) and DDE (BMF = 34) values determined (Table 3). This indicated that PBDEs had similar biomagnification potential as PCBs and DDE in the studied aquatic system. 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 a ringed seal – polar bear food chain, where the BMF was less than 1 (Sørmo et al., 2006). This may be due to enhanced metabolic capacities in polar bears.

3.3. PBDE congener distribution patterns

Fish-eating birds and peregrines exhibited distinctly different PBDE congener distribution patterns (Figure 15). 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 ~5.9 and ~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 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 (Palma et al., 2002; Tittlemier et al., 2002). Therefore, in the aquatic piscivorous system, BDE-47 may be subject to greater
Table 3. Biomagnification factors (BMFs) of contaminants from fishes to Jams River osprey eggs.

<table>
<thead>
<tr>
<th>Species</th>
<th>Scientific Name</th>
<th>Percentage in Osprey Diet (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>PBDEs (ng/g wet wt)</th>
<th>PCBs (ng/g wet wt)</th>
<th>p,p'-DDE (ng/g wet wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel &amp; blue catfish</td>
<td><em>Ictalurus punctatus</em> and <em>Ictalurus furcatus</em></td>
<td>51.7</td>
<td>10.4</td>
<td>92.3</td>
<td>10.1</td>
</tr>
<tr>
<td>Gizzard shad</td>
<td><em>Dorosoma cepedianum</em></td>
<td>28</td>
<td>12.5</td>
<td>173</td>
<td>19.2</td>
</tr>
<tr>
<td>Atlantic croaker</td>
<td><em>Micropogonias undulatus</em></td>
<td>6.6</td>
<td>2.4</td>
<td>40.6</td>
<td>7.4</td>
</tr>
<tr>
<td>White Perch</td>
<td><em>Morone Americana</em></td>
<td>2</td>
<td>1.5</td>
<td>33.7</td>
<td>4.6</td>
</tr>
<tr>
<td>Stripped bass</td>
<td><em>Morone saxatilis</em></td>
<td>1.3</td>
<td>18.5</td>
<td>286.4</td>
<td>26.4</td>
</tr>
<tr>
<td>Hickory shad</td>
<td><em>Alosa mediocris</em></td>
<td>0.8</td>
<td>22.9</td>
<td>352</td>
<td>34.1</td>
</tr>
<tr>
<td>Largemouth bass</td>
<td><em>Micropterus salmoides</em></td>
<td>0.3</td>
<td>2.7</td>
<td>28.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td>9.3</td>
<td>10.4</td>
<td>92.3</td>
<td>10.1</td>
</tr>
<tr>
<td>Osprey egg</td>
<td><em>Pandion haliaetus</em></td>
<td></td>
<td>432</td>
<td>5082</td>
<td>448</td>
</tr>
</tbody>
</table>

BMF 41.4 44.3 35.2

<sup>a</sup> Fish contaminant data were from Virginia Department of Environmental Quality fish monitoring project (Hale unpublished data);
<sup>b</sup> Diet composition data were from Glass and Watts (2009).
Figure 15. Median PBDE congener distributions in eggs of peregrine falcon, osprey, brown pelican and double-crested cormorant.

Error bars represent 75 and 25 percentiles.
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 ~4 to ~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 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.

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 birds. Heavy molecular weight (959 Da), large molecular size, and high Log$K_{ow}$ (~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/total 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 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 (Söderstrom 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 ΣPBDEs. 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., ~0.5% of ΣPBDEs). 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 peregrines. DDE hazard was also evaluated, as it has traditionally been considered to be the most deleterious agent to bird populations. 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 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 (*Falco sparverius*), of 1800 ng/g wet weight. A PNEC of PBDEs was estimated by dividing this LOEL by an uncertainty factor of 10. As described in Table 4, HQs of DDE were 0.3 for osprey and 1.7 for peregrine, which indicated that DDE may still pose a moderate risk 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 1.6 and 1.0 for ospreys and peregrines, respectively (Table 4). This indicated that PBDEs may pose a moderate hazard to both species through impairment of pipping and hatching success. It was also suggested 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 ospreys 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 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. For example, synergistic effects were indicated on free thyroxine and EROD induction levels when rats were exposed to a mixture of BDE-47 and Witachlor 171P (technical chlorinated paraffins) (Hallgren and Darnerud, 2002). Additionally, some CYP1A inducers (i.e., coplanar PCBs) may promote the biotransformation of PBDEs in fish liver (Lebeuf et al., 2006). 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.

Table 4. Hazard quotients (HQs) of PBDEs and p,p'-DDE for ospreys and peregrine falcons.

<table>
<thead>
<tr>
<th></th>
<th>Osprey</th>
<th>Peregrine Falcon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LOEL (ug/g wet wt)</td>
<td>1.8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>PBDEs</td>
<td>PNEC (ng/g wet wt)</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>MEC (ng/g wet wt)</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>HQ</td>
<td>1.6</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td>LOEL (ug/g wet wt)</td>
<td>8.7&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>PNEC (ng/g wet wt)</td>
<td>870</td>
</tr>
<tr>
<td></td>
<td>MEC (ng/g wet wt)</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>HQ</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> LOEL associated with piping and hatching success;
<sup>b</sup> Data from McKernan et al., 2008;
<sup>c</sup> LOEL associated with 20% eggshell thinning;
<sup>d</sup> Data from Wiemeyer et al., 1988;
<sup>e</sup> Data from Peakall et al., 1976.
4. Conclusion

Diet and habitat may influence contamination patterns in various Chesapeake Bay bird species. Birds nesting in more populated areas are likely to be subject to greater PBDE exposure. Consumption of migratory birds may result in substantial DDE accumulation in peregrine eggs. However, their PBDE burdens may be more strongly influenced by exposure from more local sources. PBDEs exhibited substantial biomagnification in the James River fish–osprey food chain, with a calculated BMF of 41. As the first biomagnification report for Chesapeake Bay birds, the BMF 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 avian species, 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). Additionally, interactions between PBDEs and other contaminants (e.g., PCBs) may result in toxic effects that differ from those caused by PBDEs alone. 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.

References


Hallgren, S.; Darnerud, P.O. Polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and chlorinated paraffins (CPs) in rats – testing interactions and mechanisms for thyroid hormone effects. Toxicology 2002, 177, 227-243.


McKernan, M.A.; Rattner, B.A.; Hale, R.C.; Ottinger, M.A. Toxicity of polybrominated diphenyl ethers (DE-71) in chicken (Gallus gallus), mallard (Anas platyrhynchos), and American kestrel (Falco sparverius) embryos and hatchings. Environ. Tox. Chem. 2009, 28, 1007-1017.


Rattner, B.A.; McGowan, P.C. Potential hazards of environmental contaminants to avifauna residing in the Chesapeake Bay estuary. Waterbirds (Special Publication 1) 2007, 30, 63-81.


Watts, B.D.; Paxton, B.J. Ospreys of the Chesapeake Bay: population recovery, ecological requirements, and current threats. Waterbirds (Special Publication 1) 2007, 30, 39-49.

Chapter IV

A Global Review of Polybrominated Diphenyl Ether Flame Retardant Contamination in Birds
A Global Review of Polybrominated Diphenyl Ether Flame Retardant Contamination in Birds

Birds of prey feed high in the food webs. They can accumulate contaminants through bioaccumulation and biomagnification, making them particularly sensitive to environmental contamination. Birds of prey have long been considered valuable monitoring species for persistent organic pollutant (POP) contamination. Therefore, several studies have investigated PBDE contamination in wild birds. Most commonly studied species are those utilizing aquatic food webs, such as bald eagle, osprey, cormorant, gull and guillemot. Birds that exploit terrestrial food webs have been less frequently examined, e.g. peregrine falcon, sparrowhawk, kestrel, owl and buzzard. Insectivores, such as great tit, have also been used as monitoring species in Europe. Eggs have been most commonly examined, especially for long-term monitoring projects. Other studies examined bird tissues, when dead birds were available. A few others utilized plasma from living specimens. This review summarizes available PBDE studies in various bird species from around the world. To facilitate comparisons between studies, concentrations introduced throughout this review will be reported on lipid weight (ng/g lw) basis, unless otherwise noted. Several specific aspects will be emphasized, i.e., inter-region contamination differences, the extent of BDE-209 contamination, trophic biomagnification and temporal changes of PBDE contamination.

1. Summary of PBDE studies in birds of prey

1.1. Europe
Most European studies were conducted in the northern and western regions. The Baltic Sea is one of the earliest and most intensely studied areas. Guillemot (*Uria aalge*) eggs have been shown to be a good monitoring matrix for organohalogen contamination in this region (Bignert et al., 1995). They are one of the few bird species that are resident in the Baltic all year round. Several studies have reported PBDE concentrations in guillemot eggs from the Baltic Sea and north-western Europe. Sellstrom et al. (2003) reported that PBDE concentrations in the Baltic guillemot eggs peaked around late 1980s (1300 ng/g lw), and then decreased to below 100 ng/g lw in 2001. In samples collected in 2003, Jörundsdóttir et al. (2009) observed a concentration of 150 ng/g lw in eggs from Sora Karlso, Sweden. Concentrations were even lower in guillemot eggs from Iceland (52 ng/g lw), Faroe Islands (31 ng/g lw) and Norway (14 ng/g lw) (Jörundsdóttir et al., 2009). Furmar (*Fulmarus glacialis*) eggs collected from the Faroe Islands exhibited similar concentrations (21 ng/g lw) as guillemots from the same region (Fängström et al., 2005). Several other fish-eating species were studied in Norway. Osprey (*Pandion haliaetus*) and white-tailed sea eagle (*Haliaeetus albicilla*) eggs collected from 1992 – 2000 contained median PBDE concentrations of 1100 and 1900 ng/g lw, respectively (Herzke et al., 2005). Cormorant (*Phalacrocorax carbo*) tissues collected from England exhibited a median $\sum$PBDE concentration of 800 ng/g lw (Law et al., 2002).

Birds primarily exploiting terrestrial food webs were examined in Sweden, Greenland, Norway and Belgium. Swedish peregrine falcon (*Falco peregrinus*) eggs collected between 1987 and 1999 exhibited mean $\sum$PBDE concentrations of 2200 ng/g lw in the northern and 2700 in the southern populations (Lindberg et al., 2004). The mean BDE-209 concentrations were 80 and 86 ng/g lw in the two populations, respectively.
South Greenland peregrine falcon eggs collected between 1986 and 2003 exhibited a median concentration of 1900 ng/g lw for $\Sigma$PBDEs and 11 ng/g lw for BDE-209 (Vorkamp et al., 2005). A Norwegian study reported $\Sigma$PBDE concentrations of 1600 ng/g lw in peregrine falcon, 300 in merlin (Falco columbarius) and 500 in goshawk (Accipiter gentilis) eggs, whereas BDE-209 was rarely detected (Herzke et al., 2005). Median $\Sigma$PBDE concentrations were 3100 ng/g lw in sparrowhawk (Accipiter nisus), 1600 in barn owl (Tyto alba) and 60 in kestrel (Falco tinnunculus) livers, and 110 in little owl (Athene noctua) eggs that were collected from Belgium (Jaspers et al., 2005; 2006). BDE-209 was detected in a few specimens, but with levels generally lower than 100 ng/g lw.

Data were very limited from southern and eastern Europe. Also limited is the knowledge about the historical PBDE use patterns in these regions. Covaci et al. (2006) revealed a median PBDE concentration of 6.9 ng/g lw in comorant tissues from Romania, 1-2 orders of magnitude lower than those in piscivorous birds from U.K. and northern Europe. Van den Steen et al. (2009) used the eggs of great tit (Parus major), a residential passerine species, to monitor the organohalogen contamination in the European environment. The sampling sites were distributed in 14 different countries, including urban, suburban and rural areas. The $\Sigma$PBDE concentrations ranged from 4.0 – 136 ng/g lw. Concentrations were significantly higher in the urbanized sampling locations compared to other sites. This may indicate a heightened exposure in the urban environment. Highest concentrations were observed in a Spanish suburban area, which had intensive industrial activities. In general, the concentrations observed in the southern
European countries (e.g., Italy and Spain) were not significantly different from those from the northern part (e.g., Sweden, Finland and Norway).

1.2. North America

A monitoring program was performed by the Canadian Wildlife Service to investigate the distribution and trends of organohalogen pollutants throughout the Great Lakes from the mid-1970s (Norstrom et al., 2002). Eggs of the piscivorous herring gull (Larus argentatus) were used as biomonitoring matrices. This was particularly attractive as the adult population is resident year-around. In 2000, ΣPBDE concentrations ranged from 1800 in the eggs from Lake Erie to 16500 ng/g lw in those obtained near Green Bay. Highest concentrations were found in eggs from Lake Michigan nests, followed by those in proximity to Lake Ontario, Superior, Huron and Erie. This pattern follows the trends reported for lake trout from Lake Ontario (434 ng/g lw), Superior (392 ng/g lw), Huron (251 ng/g lw) and Erie (117 ng/g lipid) (Luross et al., 2002). This long-term monitoring work revealed a rapid increase in PBDE concentrations over the period of 1981–2000 in the Great Lake gull eggs (Norstrom et al., 2002). However, more recent studies suggested that post-2000 levels did not change significantly (Gauthier et al., 2008). PBDEs have also been determined in various marine and freshwater bird eggs from British Columbia, Canada (Elliott et al., 2005). Mean ΣPBDE concentrations were highest in great blue heron (Ardea herodias) eggs (7700 ng/g lw) collected in 2002 from the Fraser estuary. Eggs of osprey and double-crested cormorant (Phalacrocorax auritus) collected from 2000–2002 contained mean ΣPBDEs of 3400 and 960 ng/g lw, respectively. Bald eaglet (Haliaeetus leucocephalus) plasma has also been collected from southwestern British Columbia, Lake Superior and Santa Catalina Island (California, U.S.) (Mckinney et al.,...
2006; Dykstra et al., 2005). The mean levels in four British Columbia sites ranged from 1.78 – 8.49 ng/g wet weight, similar as those from Lake Superior (7.9 ng/g wet weight), but much lower than the burdens in California samples (30.9 ng/g wet weight). This was likely due to elevated urbanization in the latter area.

She et al. (2003) reported PBDE levels in eggs of several rail (Rallus longorostrus obsoletus) and tern species (Sterna caspia, Sterna forsteri and Sterna antillarum brownie) collected from the San Francisco Bay (U.S.). The median and maximum concentrations were 6200 and 62,400 ng/g lw, respectively. The median level in eggs was 20 times higher than that in fish (302 ng/g lw) and 3.6 times higher than that in harbor seal blubber (1700 ng/g lw) from the same area (Brown et al., 2004; She et al., 2002). Peregrine falcon eggs from California contained a mean \( \sum \)PBDE concentration of 7850 ng/g lw, similar as the seabirds from the San Francisco Bay (Holden et al., 2009). The mean BDE-209 concentration was 490 ng/g lw.

The Chesapeake Bay, in the mid-Atlantic U.S., provides a critical habitat for a vast number of resident and migratory bird species. The Bay supports one of the largest osprey breeding populations in the world (Watts and Paxton, 2007). Eggs have been collected for examination from various tributaries and estuary branches therein in 2001, 2002 and 2005 (Rattner et al., 2004; Chen et al., 2009). The median PBDE concentrations ranged between 1800 ng/g lw in eggs from York River and 11,000 ng/g lw in those from Baltimore Harbor and Patapsco River. High levels were frequently observed in the more human populated regions. As PBDEs are present in polymer and some textile products common in homes and workplaces, populated areas may contain proportionately more PBDE-treated products and in turn be sources for greater releases of PBDEs to the
environment. Another fish-eating species, the bald eagle, was also examined in the Chesapeake Bay (Chen et al. unpublished data). PBDE burdens in their eggs (median 17,200 ng/g lw, \(N = 7\)) were much higher than those in osprey eggs. Both species feed predominantly on catfish and shad species in the upper-estuarine areas of Chesapeake Bay (Glass and Watts, 2009; Markham and Watts, 2008). However, bald eagles are more opportunistic, also feeding on carrion, small mammals and other avian species (Markham and Watts, 2008). During the late fall and winter, bald eagles exhibit a dietary shift to more birds and mammals, as a result of a reduction in the availability of fish in shallow-water areas and the migration of winter-resident birds into the Bay (Watts et al., 2007). The predation on birds may result in an elevated position of eagles in the food web, and contribute to greater exposure. In addition to piscivorous birds, eggs from the terrestrial-feeding peregrine falcon were also examined from the Chesapeake Bay region, mostly from its southern half (Potter et al., 2009; Chen et al., 2009). The observed \(\Sigma\)PBDE concentrations ranged from 450 – 18,600 ng/g lw, with a median of 2300. BDE-209 was detectable in all eggs, with a median of 104 ng/g lw.

Chen et al. (2008) examined PBDEs in peregrine falcon eggs collected from nests that were distributed in six northeastern U.S states. The median concentration observed (7400 ng/g lw) was similar to that in California peregrine eggs, but exceeded those in peregrine eggs from the other sites reported to date (i.e. Sweden, South Greenland and Chesapeake Bay in the U.S.). BDE-209 was detectable in all eggs, with concentrations ranging from 20 – 5100 ng/g lw (median: 480). Urban and rural eggs contained similar \(\Sigma\)PBDE concentration, but different congener profiles. Urban eggs exhibited higher BDE-209 concentrations and greater percentages of other highly brominated congeners. A
significant positive correlation was observed between median BDE-209 concentrations by nest and human population densities of the towns in the vicinity of the nests. This supports the hypothesis that more populated areas exhibit greater environmental levels of BDE-209. A previous study has reported a decrease in air PBDE concentrations along a Canadian urban–rural transect (Harner et al., 2006). In addition, dietary habits differ between urban and rural peregrine populations. Peregrines living in rural areas may prey on a more diverse variety of migratory birds. Urban peregrines may feed to a greater extent on resident birds, such as pigeons and starlings. These residential prey species may be subject to elevated Deca-BDE exposure in the urban environment and further contribute to a heightened contamination in their predators.

1.3. Asia

ΣPBDE concentrations ranged from 320 – 2600 ng/g lw (median: 1400) in cormorant livers and 610 – 3300 ng/g lw (median: 930) in eggs collected from the Sagami River, Japan in 2000 (Watanabe et al., 2004). Various avian species from Japanese open sea, coastal and inland regions were examined for PBDEs (Kunisue et al., 2008). The coastal and inland sea birds accumulated higher concentrations (i.e., 530 ng/g lw in cormorant; 490 ng/g lw in jungle crow, Corvus macrorhynchos; and 290ng/g lw in black-tailed gull, Larus crassirostris) than the open sea species (i.e., 4.9 ng/g lw in northern fulmar; 10 ng/g lw in Laysan albatross, Diomedea immutabilis; and 100 ng/g lw in black-footed albatross, Diomedea nigripes). One goshawk specimen exhibited an extremely high concentration, 82000 ng/g lw. PBDE concentrations in Ardeid eggs from Hongkong, Xiamen and Quanzhou in South China were 140 – 1000, 30 – 550 and 140 – 380 ng/g lw, respectively (Lam et al., 2007). BDE-209 was detected in eggs from all three cities, with
concentrations up to 290 ng/g lw. This may indicate widespread occurrence of BDE-209 in the studied coastal region. Particularly high abundances of BDE-209 relative to $\Sigma$PBDEs were observed in the eggs of cattle egret (Bubulcus ibis) (> 30%) and Chinese pond heron (Ardeola bacchus) (> 70%). This was suggested to be a result of burgeoning electrical manufacturing industries in that region (Lam et al., 2007). Remarkable PBDE contamination was observed in the Pearl River Delta (PRD), a coastal region of South China, where rapid industrialization and intensive electronic waste (E-waste) recycling have occurred. It has been estimated that 50 – 70% of U.S. E-wastes generated have been exported to China, mostly South China, for recycling (Puckett et al., 2002). In the PRD region, for instance, approximately 145 million electronic devices were “recycled” in 2002, containing up to $2.61 \times 10^8$ kg of PBDEs (Martin et al., 2004). PBDE concentrations ranged from 23 – 14,000 ng/g lw in various waterbird species collected from an E-waste recycling region in Qingyuan County in the PRD (Luo et al., 2009a). The mean BDE-209 concentrations were 43.7, 46.3 and 530 ng/g lw in white-breasted waterhen (Amaurornis phoenicurus), common snipe (Gallinago gallinago) and slaty-breasted rail (Gallirallus striatus), respectively. Free-range domestic fowls (chickens and ducks) were collected from this same E-waste recycling site (Luo et al., 2009b). Chickens exhibited higher concentrations (5.7 – 4380 ng/g lw in muscle and 1.5 – 7897 in liver) than ducks (2.4 – 51 in muscle and 1.9 – 134 in liver). Both species exhibited unusual PBDE congener profiles, i.e., BDE-209 was the most abundant congener, followed by nona-BDEs (i.e., BDE-206, -207 and -208). Combined, these highly brominated congeners contributed 78-82% and 70-81% to the $\Sigma$PBDEs in chickens and ducks, respectively. These patterns
agreed well with those in grains and soils from the same region, and indicated a heavy Deca-BDE contamination due to E-waste recycling activities.

Various terrestrial species (i.e., sparrowhawk, kestrel, owl and buzzard) were collected from the capital city of China (Chen et al., 2007). Median PBDE levels in liver ranged from 50 ng/g lw in long-eared owl (*Asio otus*) to 7900 ng/g lw in common kestrel (*Falco tinnunculus*). The maximum observed was 40,900 ng/g lw in a kestrel specimen. BDE-209 was detected in the majority of specimens. Common kestrels exhibited some of the highest BDE-209 levels ever reported in wildlife (median/maximum: 1390/12200 ng/g lw). Common kestrels reside in the city year around. They were frequently observed in the urban center areas. There they normally roost on manmade structures (e.g., chimneys and towers) and on occasion incorporate synthetic materials such as plastics in their nests. The uptake of PBDEs may be direct via exposure to products or degradates, or via the food web via prey (i.e., mice and passerine birds) that previously may have contacted with these materials. While the concentrations were low relative to kestrels, BDE-209 was actually the predominant congener in buzzards, long-eared and scops owls. It also contributed up to 50% of $\sum$PBDEs in other species. In spite of various diet and migratory habits, those terrestrial raptors were all subjected to substantial Deca-BDE exposure. This may indicate extensive usage of Deca-treated products in urbanized areas of China. Examination of recent market demands suggests that far more Deca- than Penta-BDE usage occurs in Asia, especially compared to North America (BSEF, 2003).

1.4. Polar regions and other

While PBDE use and release is more prevalent in temperate areas of the Northern hemisphere, PBDE congeners have been detected in eggs of chinstrap (*Pygoscelis*
Antarctica) and Gentoo (Pygoscelis papua) penguins and south polar skua (Catharacta maccormicki) from the Antarctic (Yogui and Sericano, 2009). The migratory skua contained higher concentrations (146 ng/g lw) than the resident penguins (6.8 and 8.1 ng/g lw, respectively), which might be due to their migration to the northern hemisphere during the non-breeding season. Low PBDE concentrations (mean 3.1 ng/g lw) were also detected in Adélie penguin (Pygoscelis adeliae) eggs from the Ross Sea, Antarctica (Corsolini et al., 2006).

In the Arctic, PBDEs were also detected in Greenland black guillemots (Cepphus grille). The median PBDE concentrations were 46 ng/g lw in guillemot livers from southwestern Greenland, 26 ng/g lw in both livers and eggs from West Greenland, and 72 and 80 ng/g lw in livers and eggs from East Greenland, respectively (Johansen et al., 2004; Vorkamp et al., 2004a and b). Similar concentrations (60 ng/g lw) were observed in black-legged kittiwake (Rissa tridactyla) eggs collected from Lancaster Sound, Canandian Arctic (Braune and Simon, 2004). \( \sum \)PBDE concentrations in ivory gull (Pagophila eburnean) eggs from Canandian Arctic increased from 18.3 ng/g in 1976 to 45 in 2004 (Braune et al., 2003). Concentrations in thick-billed murres (Uria lomvia) and northern fulmars also increased from 2-4 ng/g lw in 1975 to 18-20 in 1998 (Braune et al., 2003). Two PBDE congeners, BDE-49 and -99, were detected in glaucous gull (Larus hyperboreus) liver and intestinal contents from Svalbard and Bjørnøya (Bear Island, Norway) (Herzke et al., 2003). The sum concentrations were 70 ng/g wet weight in intestinal contents and ranged from 27 – 450 ng/g lw (median: 54) in the liver. In another study from Bjørnøya, concentrations were 1400, 400 and 200 ng/g lw in the muscle of glaucous gull, little auk (Alle alle) and kittiwake (Rissa tridactyla), respectively (Herzke
et al., 2004). Similar concentrations (mean 1400 ng/g lw) were observed in plasma from Bjørnøya glaucous gulls collected in 2002 and 2004 (Verreault et al., 2004). BDE-209 was detected in 30% of plasma samples, with concentrations ranging from 200 – 1100 ng/g lw (mean: 410). The substantial BDE-209 burdens reported in gulls were believed to be due to overwintering in the North Atlantic Ocean and not from the arctic local breeding locations (Verreault et al., 2004). The degree of PBDE contamination was also examined in herring gull and great black-backed gull (Larus marinus) eggs from northern Norway (e.g., Alta, Kongsfjord, Sommarøy and Vardø) (Pusch et al., 2005). The concentrations were at the same magnitude as those in Bjørnøya gaulous gull, ranging from 500 – 700 ng/g lw.

The only southern hemisphere report available, except for the Antarctic studies mentioned above, was the Polder et al. (2008) examination of PBDEs in eggs of various bird species from South Africa. The concentrations were 7 – 40 ng/g lw in African darter (Anhinga rufa), 8.8 – 22 in reed cormorant (Phalacrocorax africanus), non-detection – 13 in cattle egret (Bubulcus ibis), 7.1 in one white-fronted plover (Charadrius marginatus), 19 in one little grebe (Tachybaptus ruficollis), 9.4 in one kelp gull (Larus dominicanus), 120 in one crowned plover (Vanellus coronatus), and 61 and 396 in two sacred ibis (Threskiornis aethiopicus) eggs (Polder et al., 2008). BDE-209 was detected in sacred ibis and crowned plover (2.6 – 9.7 ng/g lw). The PBDE concentrations in general were even lower than observed in some polar seabirds.

2. PBDE congener distribution patterns
Different bird species utilize different feeding strategies. Some feed primarily in freshwater or marine systems, with fish comprising the majority of their diet. Other species consume primarily terrestrial-based food items, e.g., passerine birds or terrestrial mammals. A few other species may feed more opportunistically, utilizing both terrestrial and aquatic items. For example, crowned plovers prey on both terrestrial and aquatic invertebrates. Principle component analysis (PCA) was applied to examine the relationships between the types of birds’ major diet (aquatic, terrestrial and aquatic/terrestrial) and the congener patterns observed in their tissues/eggs, based on available reports (Figure 16). The biplot of PCA clearly displays three clusters. The species in Cluster A consists primarily of those subsisting on aquatic prey. Their PBDE congener profiles were dominated by BDE-47, followed by BDE-99 and BDE-100. These have been reported to bioconcentrate in fish and other aquatic organisms (de Wit et al., 2002). BDE-183 and higher brominated congeners were rarely detected. Cluster B is comprised mostly of species feeding entirely or partially on elements of the terrestrial food web. BDE-153 usually was the most dominant congener, whereas BDE-47 mad a minor contribution to the \( \sum \)PBDEs. Congeners with bromines more than eight, particularly BDE-209, were more frequently detected in this cluster. Cluster C represents a very unusual congener pattern where BDE-209 was the predominant or second-most dominant congener. Remarkably, data included in this cluster were mostly from the Chinese studies (Chen et al., 2007; Lam et al., 2007; Luo et al., 2009a). The species included those feeding exclusively (e.g., long-eared owl, buzzard and common kestrel) or partially (e.g., slay breasted rail) on elements of the terrestrial food webs. This may suggest an elevated Deca-BDE exposure in some regions in China. For example, in a
Chinese E-waste recycling site, free-range poultry and wild birds had substantial accumulation of BDE-209, possibly due to their ingestion of contaminated soil, seeds or insects (Luo et al., 2009a; b). The percentages of BDE-209 in grain and soil samples were as high as 70% in this region (Luo et al., 2009b).

Food web magnification models proposed by Kelly et al. (2007) may be instructive in further illustrating the distinct congener distribution patterns between terrestrial and aquatic birds. 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 Log$K_{ow}$ higher than 8, which are absorbed at very slow rates, or for those with Log$K_{ow}$ less than 5, which are efficiently eliminated by respiration. 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. Additionally, BDE-47 is 7 to 8-fold more abundant than BDE-153 in the Penta-BDE formulations (La Guardia et al., 2006). This fact, plus a greater volatility and water solubility of BDE-47, makes it likely that higher amounts of BDE-47 enter the environment. For example, Ikonomou et al. (2002) reported a dominance of BDE-47 in surface water samples from the Fraser River (British Columbia, Canada). These may result in a dominance of the congener in fish and fish-eating birds. In the 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 
$\text{LogK}_{\text{ow}}$ of $\approx 4$ to $\approx 8$ and $\text{LogK}_{\text{oa}} > 8.2$ 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 terrestrial 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.

Congener patterns in the same species may shift as a result of diet change or elevated exposure. For example, although BDE-153 was the most dominant congener in both Chesapeake Bay and New England peregrine falcon eggs from the U.S., the median ratios of BDE-153/BDE-99 were different between these two populations, i.e. 1.7 vs. 3.5 (Chen et al., 2008 and 2009). The Chesapeake Bay peregrine falcons, especially those living in the shore islands, feed mostly on shorebirds. In contrast, the New England peregrines, especially those living in urban areas, feed primarily on terrestrial birds and hence may experience heightened exposure to more abundance of highly brominated congeners. Another study observed a recent shift in the relative abundances of BDE-99 and -153 in Great Lakes herring gull eggs (Gauthier et al., 2008). Percentages of BDE-209 and some
Figure 16. Biplot from the Principle Component Analysis of congener distribution patterns between aquatic and terrestrial birds worldwide. The A and T represent aquatic and terrestrial bird species, respectively. M represents the birds feeding in both aquatic and terrestrial food chains. The numbers following A/T/M were used to track the data from various studies. The data were from Braune et al. (2007); Chen et al (2007, 2008 and 2009); Dauwe et al. (2006); Elliott et al. (2005); Fängström et al. (2005); Gauthier et al. (2008); Herzke et al. (2005); Jaspers et al. (2006); Kunisue et al. (2008); Lam et al. (2007); Lindberg et al. (2004); Lundstedt-Enkel et al. (2006); Luo et al. (2009a); Polder et al. (2008); Rattner et al. (2004); She et al. (2003 and 2008); Vorkamp et al. (2005); Wan et al. (2008); and Yogui and Sericano (2009). An extreme outlier (M5) was from slasty-breasted rail collected from a Chinese E-waste recycling site (Luo et al., 2009a).
nona- and octa-BDEs were also increased in the gull eggs. This was suggested to be the result of both increasing application of Deca-BDE and a shift in the gull diet to a higher reliance of terrestrially derived food sources (Gauthier et al., 2008).

3. Inter-region comparison of PBDE contamination

3.1. $\Sigma$PBDEs

As terrestrial and aquatic birds exhibited distinctly different congener patterns, inter-region comparisons were performed by using separate datasets. Figure 17 shows the $\Sigma$PBDE concentrations in various aquatic birds that have been reported. The numbers indicated in the graph were mostly mean or median concentrations by species. The North American birds exhibited significantly higher concentrations compared to those from Europe and Asia (ANOVA, $p < 0.05$), in spite of species variation. For years in which data are available, the North American market represented the bulk of the world's Penta-BDE production, i.e., 95% in 2001 and 98% in 2003. Hence, the amounts of major congeners (e.g., BDE-47, -99 and -100) released to the North American environment and therefore readily available to the aquatic species would be expected to be substantially higher than elsewhere. Concentrations in some North American freshwater fishes and marine mammals were also among the highest in the world (Hale et al., 2001; Johnson-Restrepo et al., 2005). Figure 18 shows $\Sigma$PBDE concentrations in the terrestrial birds worldwide. The New England and California peregrine falcon eggs from the U.S. exhibited greater concentrations than observed in most other studies. However, the differences between regions were not statistically significant. Some elevated burdens
were also observed in several Chinese and European studies and may relate to point sources. Relatively few data in terrestrial birds may limit the inter-region comparison.

3.2. BDE-209

BDE-209 was more frequently observed in birds feeding on terrestrially based food webs than aquatic ones. Figure 19 shows the BDE-209 concentrations in the birds, according to previous reports. Highest concentrations were observed in Chinese kestrels and U.S. peregrine falcons. European birds contained significantly lower BDE-209 concentrations than those from the U.S. and China ($p < 0.05$), in spite of species variation. According to BSEF 2001 survey, North America and Asia consumed 44% and 41% of the world’s Deca-BDE production, respectively (BSEF, 2003). In Asia, PBDE application may primarily have been concentrated in its eastern part (e.g., China and Japan). The per capita Deca-BDE usage ($10^6$MT) and usage amount/territory area ($10^6$MT/km$^2$) were also higher in North America (46.3 and 991.9) and East Asia (15 and 1940) than those in Europe (10.4 and 745). However, the inter-region comparison may be skewed as some elevated Chinese levels were from samples collected near urban- or E-waste recycling-related point sources. For example, some waterbirds near an E-waste recycling site in south China even contained substantial amounts of BDE-209 (Luo et al., 2009). Atypical congener patterns have been observed in some Chinese birds (i.e., scops and long-eared owls), in which BDE-209 was the most dominant PBDE congener. These patterns indicated elevated exposure due to disproportionate presence of Deca-treated products in the big cities. Substantial contributions of nona- and octa-BDE cogeners (e.g., BDE-208, -207, -206, -202 and -201) were also observed in some Chinese birds and U.S. peregrine falcon eggs. For example, the sum of octa- and nona-BDEs contributed 40% of
Figure 17. \( \Sigma \)PBDE concentrations in birds feeding on the aquatic food web from various locations worldwide. Data are from Braune et al., 2007; Chen et al., 2009; Corsolini et al., 2006; Covaci et al., 2006; Elliott et al., 2005; Gauthier et al., 2008; Herzke et al., 2003 and 2005; Jaspers et al., 2006; Jorundsdottir et al., 2009b; Kunisue et al., 2008; Lam et al., 2007; Law et al., 2002; Luo et al., 2009; Lundstedt-Enkel et al., 2006; Polder et al., 2008; Rattner et al., 2004; Sellstrom et al., 2003; She et al., 2003; Vorkamp et al., 2004; Wan et al., 2008; Watanabe et al., 2004; and Yogui and Sericano, 2009.
Figure 18. ΣPBDE concentrations in terrestrially-feeding birds from various locations worldwide. Data are from Chen et al., 2007, 2008 and 2009; Herzke et al., 2005; Holder et al., 2009; Lindberg et al., 2004; Jaspers et al., 2005 and 2006; Kunisue et al., 2008; and Vorkamp et al., 2005 and 2009.
Figure 19. BDE-209 concentrations in birds collected around the world. Data are from Chen et al., 2007, 2008 and 2009; Holder et al., 2009; Jaspers et al., 2006; Kunisue et al., 2008; Lam et al., 2007; Lindberg et al., 2004; Luo et al., 2009; and Vorkamp et al., 2005.
ΣPBDEs in kestrels collected near Beijing (Chen et al., 2007) and 29% in the northeastern U.S. peregrine falcon eggs (Chen et al., 2008). Some of these congeners were suggested to be breakdown products from BDE-209.

4. PBDE biomagnification via food chains

Biomagnification of PBDEs has rarely been studied in the avian food chains. Voorspoels et al. (2007) determined PBDE biomagnification factors (BMFs) in three small terrestrial food chains. The mean BMFs were 17 in the passerine–sparrowhawk and 14 in the rodent–buzzard food chains. The BMFs for ΣPCBs were 20 and 40 in these two food chains, respectively. For the individual PBDE congeners (i.e., BDE-28, 47, 100, 99, 154, 153 and 183), the BMF increased from lesser to more brominated congeners with increasing logK_{ow} in the passerine–sparrowhawk food chain. In the same study, PCBs and PBDEs exhibited low (BMF = 3) and no biomagnification (BMF < 1) in the rodent–fox food chain, respectively. This may be due to a high biotransformation capability in fox. Biomagnification of PBDEs was also studied in the fish–osprey egg food chain from the James River, Virginia (U.S.) (Chen et al., 2009). The BMFs were determined based on a simple model that apportions the contamination contribution from several probable prey species. A BMF of 41 was determined for ΣPBDEs, similar to that for ΣPCBs (BMF = 43) and DDE (BMF = 34).

More biomagnification studies were performed in marine or terrestrial mammal food chains (Table 5). In the North Sea, BMFs for ΣPBDEs ranged from 15.6–53.5 in the fish–harbor porpoise and 10.6–36.5 in the fish–harbor seal food chains (Boon et al., 2002). In the former food chain, the mean BMFs for individual congeners increased from
for BDE-28 to 112 for BDE-153, with increasing logK_{ow}. Another study reported BMFs for \( \sum \)PBDEs ranging from 17.1 – 76.5 in the fish – harbor seal food chains from the coast of Maine (U.S.) (Shaw et al., 2009). Biomagnification was observed for each of BDE-28, -47, -99, -100, -153, -154 and -155, whereas BDE-49, -66 and -75 had BMFs less than 1, indicating possible biotransformation in harbor seals. In a marine foodweb of coastal Florida (U.S.), the BMFs for \( \sum \)PBDEs ranged from 14 – 74 in the fish – Atlantic sharpose shark, 39 – 204 in the fish – bull shark, and 29 – 150 in the fish – bottlenose dolphin food chains (Johnson-Restrepo et al., 2005). The mean BMFs were 31, 85 and 63 in these three food chains, respectively. Biomagnification was also studied in the Arctic regions. The BMFs ranged from 1.8 - 7.4 for BDE-47, 1 – 11 for BDE-99, 0.6 – 8.8 for BDE-100, 8.8 – 130 for BDE-153, 0.2 – 2.9 for BDE-154, and 1.9 – 9.0 for \( \sum \)PBDEs, in the Canadian Arctic ringed seal – polar bear food chains (Muir et al., 2006). The PBDE congeners generally exhibited lower BMFs than major PCB congeners (i.e., PCB-153, -180, and -194) except for BDE-153, which had a BMF 5.5-fold higher than that of PCB-153. In another Arctic study, PBDEs exhibited substantial biomagnification in the Svalbard (Norway) polar cod – ringed seal food chain (BMF = 155.2) (Sørmo et al., 2006). However, no magnification was observed for individual congeners or \( \sum \)PBDEs in the ringed seal – polar bear food chain, except for BDE-153 (BMF = 5.2) (Sørmo et al., 2006). This contrasts with the above mentioned Canadian Arctic study (Muir et al., 2006), and may indicate greater biotransformation capabilities in the Svalbard polar bears.

Trophic biomagnification was studied in a Canadian Arctic marine food chain for both PBDEs and PCBs (Kelly et al., 2008). The trophic biomagnification factors (TMFs)
were determined based on the correlations between chemical concentrations in each species and their trophic levels derived from nitrogen isotope values. TMFs for recalcitrant PCB congeners ranged from 2.9 – 11, indicating substantial trophic biomagnification (TMF > 1). Most PBDE congeners did not exhibit significant trophic magnification, i.e., TMFs not significantly different from 1, except for BDE-47, which had a TMF of 1.6. This study indicated that PBDEs may have lower trophic biomagnification potentials than the more recalcitrant PCB congeners. Similar methods were applied in another study (Mizukawa et al, 2009) to determine trophic biomagnification of PBDEs in a lower-trophic-level marine food web in Japan. The major congeners (including BDE-47, -99, -100, -154 and -153) all exhibited significant trophic biomagnification. This was contrary to what was reported by Kelly et al. (2008), and suggests that biomagnification potentials of PBDEs vary for various food chains.

5. Temporal trends

To date, most temporal trend studies in birds/eggs have been from locations in the Great Lakes, British Columbia, northeastern U.S., Baltic Sea, Greenland and Canadian Arctic (Figure 20). PBDE concentrations exhibited exponential increases in eggs of both herons and cormorants from British Columbia, with a doubling time of 5.7 years between 1979 and 2002 (Elliott et al., 2005). Exponential increases were also observed in Great Lakes herring gull eggs between 1981 and 2000 (Norstrom et al., 2002). The summed concentrations of BDE-47, -100 and -99 increased exponentially, with doubling times of 2.8 years for Lake Ontario, 2.6 years for Lake Michigan, and 3.1 years for Lake Huron. In contrast, the sum concentrations of BDE-154, -153 and -183 were increasing in
Table 5. Biomagnification factors (BMFs) of invidual PBDE congeners and ∑PBDEs in various food chains.

<table>
<thead>
<tr>
<th>Food chains</th>
<th>BDE-28</th>
<th>BDE-47</th>
<th>BDE-85</th>
<th>BDE-100</th>
<th>BDE-99</th>
<th>BDE-154</th>
<th>BDE-153</th>
<th>BDE-183</th>
<th>∑PBDEs</th>
<th>Reference</th>
</tr>
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<tr>
<td>passerine-sparrowhawk</td>
<td>4</td>
<td>10</td>
<td>25</td>
<td>20</td>
<td>24</td>
<td>21</td>
<td>27</td>
<td>17</td>
<td></td>
<td>Voorspoels et al., 2007</td>
</tr>
<tr>
<td>rodent-buzzard</td>
<td>12</td>
<td>17</td>
<td>14</td>
<td>22</td>
<td>12</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td>Voorspoels et al., 2007</td>
</tr>
<tr>
<td>rodent-fox</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
<td>Voorspoels et al., 2007</td>
</tr>
<tr>
<td>fish-harbor porpoise</td>
<td>7.8</td>
<td>24.5</td>
<td>37</td>
<td>72.1</td>
<td>84.2</td>
<td>161.5</td>
<td></td>
<td></td>
<td>33.3</td>
<td>Boon et al., 2002</td>
</tr>
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<td>4.8</td>
<td>24.4</td>
<td>5.5</td>
<td>45.8</td>
<td>11.2</td>
<td>193.8</td>
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<td></td>
<td>22.7</td>
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<tr>
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<td>16.2</td>
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<td></td>
<td></td>
<td>27</td>
<td>Shaw et al., 2002</td>
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<td>fish-bull shark</td>
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<td>2</td>
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<tr>
<td>ringed seal-polar bear</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td>4.6</td>
<td>Muir et al., 2006</td>
</tr>
<tr>
<td>polar cod-ringged seal</td>
<td>34.4</td>
<td>209</td>
<td>85.2</td>
<td>56.6</td>
<td>18.5</td>
<td></td>
<td></td>
<td></td>
<td>155.2</td>
<td>Sørmo et al., 2006</td>
</tr>
<tr>
<td>ringed seal - polar bear</td>
<td>0.16</td>
<td>0.4</td>
<td>0.23</td>
<td>0.29</td>
<td>0.25</td>
<td>5.2</td>
<td></td>
<td></td>
<td>0.41</td>
<td>Sørmo et al., 2006</td>
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general but varied in an erratic pattern. Therefore, the ratio of $\Sigma \text{BDE}_{154,153,183}$ to $\Sigma \text{PBDEs}$ decreased over time. It was concluded by the authors that most of the increases in $\Sigma \text{BDE}$ concentrations over the 20 years in the Great Lake ecosystem were associated with the Penta-BDE formulation, which has mainly been used as a flame retardant in polyurethane foam in North America (Hale et al., 2002). In a follow-up study, Gauthier et al. (2008) reported that the concentrations of BDE-47, -99 and -100 in Great Lakes gull eggs did not exhibit significant increases since 2000. By contrast, BDE-209 concentrations increased during the whole period of 1982 – 2006, with doubling times ranging from 2.1 – 3.0 years at different sites. The mean doubling times of octa- and nona-BDEs ranged from 3.0 – 11 and 2.4 – 5.3 years, respectively (Gauthier et al., 2008).

The reduction in rates of penta- and hexa-BDE contamination may result from the recent phasing-out of Penta- and Octa-BDE formulations. However, because many existing PBDE-treated products remain in use and have long service lives, releases from both in-service and discarded products may continue for decades. Therefore, a rapid decrease of PBDE concentrations in the North American environment may not occur in the near future. In the Canadian Arctic, PBDE concentrations in the thick-billed murres ($Uria lomvia$) and northern fulmar from Prince Leopold Island rapidly increased from 2-4 ng/g lw in 1975 to 18-20 ng/g lw in 1998 (Braune et al., 2003). Concentrations also increased exponentially in ringed seal ($Phoca hispida$) blubber from Holman Island (1981 – 2000) (Ikonomou et al., 2002a). Penta- and hexa-BDEs had doubling times of 4.7 and 4.3 years, respectively. Exponential increases in PBDE concentrations were also observed in beluga whales ($Delphinapterus leucas$) from the St. Lawrence Estuary, Canada between 1988 and 1999 (Lebeuf et al., 2004). Concentrations of tetra- (BDE-47, -49, and -66) and
penta-BDEs (BDE-99 and -100) increased with doubling times ranging from 2.0 – 2.9 years. Several other congeners (i.e., BDE-153, -154, and -183) also had doubling times less than 4 years in female whales (Lebeuf et al., 2004).

Temporal changes of PBDE concentrations were examined in northeastern U.S. peregrine falcon eggs (Chen et al., 2008). ΣPBDE concentrations increased from 1996 to 2006, but the trend was not significant during the study period. Similarly, the concentrations of major individual congeners (i.e., BDE-153, -154, -99, -100, -183 and -197) exhibited non-significant changes. In contrast to birds preying on aquatic species, for which burden changes were primarily driven by BDE-47, terrestrial raptor increases relied mostly on the more brominated congeners (i.e., BDE-153). However, because of their relatively high molecular weights and low vapor pressures, the more brominated congeners are released less readily from polymer products compared to BDE-47. They tend to sorb to a greater extent to air-borne dusts, soils and sediments and hence are less vulnerable to long-range transport. In addition, PBDEs have been reported to have lower biomagnification factors in some terrestrial food chains (i.e., up to 18 in the passerine/rodent-raptor food chains) than aquatic systems (i.e., up to 204 in fish-shark food chains) (31, 40). These factors may contribute to a slower increase in PBDE concentrations in terrestrial apex predators. Nonetheless, this study did observe a rapid increase in BDE-209 concentrations (doubling time = 5 years), perhaps due to continuing usage of Deca-BDE.

The chronology of PBDE contamination in Europe seems somewhat different from North America. In the guillemot eggs from the Baltic Sea, the concentrations of BDE-47 and -99 increased about 15-20 times from the early 1970s to the 1980s, peaking
Figure 20. Temporal changes of ΣPBDE concentrations were examined in (A) North America: great blue heron egg (Elliott et al., 2005), herring gull egg (Norstrom et al., 2002), beluga whale (Lebeuf et al., 2004), and peregrine falcon egg (Chen et al., 2008); (B) Europe: peregrine falcon egg (Vorkamp et al., 2005), guillemot egg (Sellström et al., 2003), and pike (Kierkegaard et al., 2004); and (C) Asia: northern fur seal (Kajiwara et al., 2004) and melon-headed whale (Kajiwara et al., 2008). Temporal changes of BDE-209 concentrations (D) were examined in peregrine falcon eggs from U.S. and Greenland (Chen et al., 2008; Vorkamp et al., 2009) and Great Lakes herring gull eggs (Gauthier et al., 2008).
around the mid- to the late-1980s, then rapidly declining during the remainder of the study period (Sellström et al., 2003). In the Swedish pike (1967 – 2000), PBDE concentrations exhibited an increase up to the mid-1980s, and then declined slowly since the late 1980s (Kierkegaard et al., 2004). PBDE concentrations in Swedish human milk also declined since 1998, after a rapid increase from 1992 to 1997 (Meironyte et al., 1999; 2001). The decreasing trends observed in European aquatic organisms and humans were likely driven by the reduced use and emission of PBDEs in Europe during the mid-to late-1980s. Since both Penta- and Octa-BDE formulations were banned in the European Union from August 2004, further declines in PBDE burdens in the aquatic environment may be expected in that continent. By contrast, in the south Greenland peregrine falcon eggs, PBDEs exhibited an overall slow increase during the entire period 1986 – 2003 (Vorkamp et al., 2005). In particular, BDE-209 concentrations increased significantly during that period.

Figure 21 shows the changes of the ratios ΣBDE (47, 99, 100)/ΣBDE (153, 154) in aquatic organisms (i.e., fish, marine mammal and piscivorous bird) from different regions. Swedish pikes exhibited a significant declining trend over time, different from the North American organisms all of which exhibited increasing patterns. These may agree well with the differences in PBDE usage patterns between North America and Europe. Continuous release of Penta-BDEs in North American environment led to the relatively rapid increase of lower brominated BDE congeners in wildlife, especially in the species with higher trophic levels, such as birds or marine mammals. In Europe, early cessation of Penta-BDE usage and shift to Octa-/Deca-BDE products may have resulted in the relatively increasing contribution by higher brominated congeners. However, to
date most North American temporal studies were performed before 2004 when the production of Penta- and Octa-BDE formulations ceased. Therefore, continuous monitoring would be important to track the on-going changes of environmental burdens in this continent.

![Graph showing temporal changes of ratio BDE (47, 99, 100)/BDE (153, 154) in gull egg (Norström et al., 2002; Gauthier et al., 2008), lake trout (Zhu et al., 2004), beluga whale (Lebeuf et al., 2004) and pike (Kierkegaard et al., 2004).]

**Figure 21.** Temporal changes of ratio BDE (47, 99, 100)/BDE (153, 154) in gull egg (Norström et al., 2002; Gauthier et al., 2008), lake trout (Zhu et al., 2004), beluga whale (Lebeuf et al., 2004) and pike (Kierkegaard et al., 2004).

Temporal studies on PBDEs in Asian wildlife are very scarce, especially for birds of prey. Analysis of northern fur seals (*Callorhinus ursinus*) from Japan revealed that \( \Sigma \)PBDE concentrations increased from 1972, peaking around 1991 – 1994, then decreased to about 50% in 1997 – 1998 (Kajiwara et al., 2004). Similarly, concentrations
in Japanese sea bass and gray mullet increased from 1986 to 1989, followed by a rapid
decrease after 1990 (Ohta et al., 2001). These patterns follow well the pattern of annual
PBDE market demands in Japan, which peaked around 1990 and then declined after that
(Kajiwara et al., 2004). A slightly different trend was reported by Kajiwara et al. (2008),
in which PBDE concentrations in melon-headed whales (Peponocephala electra) from
the Japanese coast increased significantly from 1982 to 2001/2002, but did not change
substantially between 2002 and 2006. This may suggest a recent PBDE input to the
Japanese coast regions, potentially from southeastern Asian countries. China is also an
important consumer of brominated flame retardants, due to its role as one of the world’s
largest manufacturers and consumers of textiles, plastics and electronic products. In
addition to be the largest exporter of electronics goods, China is also the largest consumer
of many electronic products (i.e., cellular devices) (www.etforecasts.com). However,
China currently lacks any specific regulations on PBDE production or use. Hence PBDE
burdens in the environment may be increasing in pace with the rapid economic
development. Ramu et al. (2006) reported that PBDE concentrations in finless porpoises
(Neophocaena phocaenoides) from China rapidly increased from 1990 to 2000. Analyses
of sediment cores collected from the Pearl River Delta, South China revealed rapid
increases of BDE-209 concentrations in the upper, more contemporary core layers (Mai
et al., 2005). This trend was suggested to be coincident with the growth of electronics
manufacturing capacities in that region.

6. Conclusion
PBDEs have been detected in the birds around the world, including those from the polar areas. North American birds generally exhibited greater burdens than birds from other regions. This was due to the disproportionately high PBDE demand in this continent, i.e. over half of total global PBDE demand, and 98% of Penta-BDE, in particular. Some high levels were also reported in Chinese birds. Though actual market demands are unavailable for China, its role as one of the world’s biggest manufacturers of textiles, plastics and electronic products may indicate that a large volume of brominated flame retardants have been consumed there. Consequently, both aquatic and terrestrial-feeding birds from North and South China frequently exhibited substantial accumulation of BDE-209. This may indicate elevated exposure in some regions, resulting from extensive applications of Deca-BDE or the releases from E-waste recycling activities.

Aquatic and terrestrial-feeding birds exhibited dissimilar PBDE congener distribution patterns. BDE-47 was normally the most dominant congener in aquatic birds of prey, where higher brominated congeners (particularly BDE-153) were more abundant in terrestrial species. This suggests individual congeners may be subject to differences in bioaccumulation, biomagnification or metabolism in the aquatic and terrestrial environments. Elevated BDE-209 concentrations were more frequently observed in terrestrial-feeding birds, indicating its heightened presence or bioavailability in such food chains. This also indicates that terrestrial birds of prey are preferred monitoring species to assess environmental contamination of Deca-BDE.

The temporal studies clearly indicate that regulations and voluntary actions by industries greatly affect the chemical releases and contamination. Due to the early
phasing-out of Penta- and Octa-BDEs in Europe and Japan, declines of PBDE concentrations have already been observed in birds of prey and other wildlife from those regions. Significant declines may not be realized in the near future in North America, as the voluntary actions were not taken by industries until the end of 2004. It may require decades for environmental burdens to diminish on this continent. Therefore, further monitoring will be essentially required. China is an important consumer of brominated flame retardants. However, its annual market demands remain unknown. Also lacking are regulations on the manufacturing and application of PBDEs. Available Chinese studies have centered on a limited number of regions. Particularly lacking are the temporal studies in Chinese wildlife. Therefore, more studies will be needed to examine the contamination and the trend in other economically prosperous areas in China. Deca-BDE is still in use. In spite of arguments as to its limited bioavailability, BDE-209 concentrations appear to be increasing in both aquatic and terrestrial bird eggs. Lab exposure studies have revealed the debromination of BDE-209 to less brominated and more bioavailable/bioaccumulative congeners (Stapleton et al., 2006; Van den Steen et al., 2006). Therefore, it would be wise to regulate the use of this chemical around the world and limit unnecessary releases to the environment.

References


Corsolini, S.; Covaci, A.; Ademollo, N.; Focardi, S.; Schepens, P. Occurrence of organochlorene pesticides (OCPs) and their enantiomeric signatures, and concentrations of polybrominated diphenyl ethers (PBDEs) in the Adélie penguin food web, Antarctica. Environ. Pollut. 2006, 140, 371-382.


Ikonomou, M.G.; Rayne, S.; Fischer, M.; Fernandez, M.; Cretney, W. Occurrence and congener profiles of polybrominated diphenyl ethers (PBDEs) in environmental samples from coastal British Columbia, Canada. Chemosphere 2002b, 46, 649-663.


Kaijawa, N.; Kamikawa, S.; Amano, M.; Hayano, A.; Yamada, T.K.; Miyazaki, N.; Tanabe, S. Polybrominated diphenyl ethers (PBDEs) and organochlorines in melon-headed whales, Peponocephala...


Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from

Mai, B.; Chen, S.; Luo, X.; Chen, L.; Yang, Q.; Sheng, G.; Peng, P.; Fu, J.; Zeng, E.Y. Distribution of
polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea.

Markham, A.C.; Watts, B.D. The influence of salinity on provisioning rates and nesting growth in bald

Martin, M.; Lam, P.K.S.; Richardson, B.J. An Asian quandary: where have all of the PBDEs gone? Mar.

McKinney, M.A.; Cesh, Lr.S.; Elliott, J.E.; Williams, T.D.; Garcelon, D.K.; Letcher, R.J. Brominated
flame retardants and halogenated phenolic compounds in North American west coast bald eagle

Meironyté, D.; Norén, K.; Bergman, Å. Analysis of polybrominated diphenyl ethers in Swedish human

Proceedings of the second international workshop on brominated flame retardants (BFR 2001), 2001,
303-305.

Mizukawa, K.; Takada, H.; Takeuchi, I.; Ikemoto, T.; Omori, K; Tsuchiya, K. Biocencentration and
biomagnification of polybrominated diphenyl ethers (PBDEs) through lower-trophic-level coastal marine

Muir, D.C.G.; Backus, S.; Derocher, A.E.; Dietz, R.; Evans, T.J.; Gabrielsen, G.W.; Nagy, J.; Norstrom,
R.J.; Sonne, C.; Stirling, I.; Taylor, M.K.; Letcher, R.J. Brominated flame retardants in polar bears
(Ursus maritimus) from Alaska, the Canadian Arctic, East Greenland, and Svalbard. Environ. Sci.


Verreault, J.; Gabrielsen, G.W.; Letcher, R.J.; Muir, D.C.G.; Chu, S. New and established organohalogen contaminants and their metabolites in plasma and eggs of galuocous gulls from Bear Island. Norwegian


Appendix I. Sample inventory, dietary compositions and migratory habits of the various bird species from Northern China.

<table>
<thead>
<tr>
<th>English Name</th>
<th>Scientific Name</th>
<th>N</th>
<th>Diet</th>
<th>Migratory Habits</th>
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<tbody>
<tr>
<td>Common Kestrel</td>
<td><em>Falco tinnunculus</em></td>
<td>6</td>
<td>Mainly small mammals, such as field voles and mice; other diet consists of small birds, lizards and insects</td>
<td>Remain mainly in Beijing area all year round</td>
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<tr>
<td>Eurasian Sparrowhawk</td>
<td><em>Accipiter nisus</em></td>
<td>11</td>
<td>Mainly small birds which contribute up to 99% of diet compositions; occasionally field voles and mice</td>
<td>Mainly migratory; usually stay in Beijing in the spring/autumn; over-winter in southeastern China and summer in the areas northern to Beijing Similar as <em>Accipiter nisus</em></td>
</tr>
<tr>
<td>Japanese Sparrowhawk</td>
<td><em>Accipiter gularis</em></td>
<td>6</td>
<td>Mainly small birds; occasionally some reptiles and insects</td>
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<tr>
<td>Little Owl</td>
<td><em>Athene noctua</em></td>
<td>6</td>
<td>Mostly small mammals, such as mice, voles, shrews, small rabbits, as well as insects, earthworms, snails, slugs and small fish, occasionally small passerines and vegetation</td>
<td>Resident in Beijing area</td>
</tr>
<tr>
<td>Scops Owl</td>
<td><em>Otus sunia</em></td>
<td>6</td>
<td>Mainly insects, spiders and small vertebrates</td>
<td>Mainly migratory; stay and breed in Beijing between April and October; winter in southern China Mainly migratory; over-winter in Beijing; breed in the northern areas (e.g., Mongolia or Russia) Migratory; over-winter in Beijing; breed in the areas northern to Beijing (e.g., Mongolia)</td>
</tr>
<tr>
<td>Long-eared Owl</td>
<td><em>Asio otus</em></td>
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<td>Mostly small mammals; the percentage of birds in the diet is usually low</td>
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<tr>
<td>Upland Buzzard</td>
<td><em>Buteo hemilasius</em></td>
<td>3</td>
<td>Mainly small ground mammals; occasionally small ground birds such as larks and pipits</td>
<td></td>
</tr>
<tr>
<td>Common Buzzard</td>
<td><em>Buteo buteo</em></td>
<td>3</td>
<td>Mainly small mammals (e.g., mice, voles, rats, rabbits); occasionally small birds, reptiles, amphibians and large insects</td>
<td>Migratory; over-winter in Beijing; breed in the areas northern to Beijing (e.g., Mongolia)</td>
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</table>
### Appendix II. Biological information related to the northeastern U.S. peregrine falcons (Falco peregrinus).

<table>
<thead>
<tr>
<th>Genus</th>
<th>Multiple subspecies of peregrines were bred in captivity during the 1970s-1990s and were the ancestors of the re-established peregrines restored to the Northeast U.S. None of original birds (captive breeders released or their F1 progeny) are known to be present locally in the wild today. Our contemporary peregrines descend from the later generations from those original birds. Therefore, geographically, they are in the range of Falco peregrinus anatum; genetically, they are a mixture of several ancestral subspecies acted on by natural selection over several generations.</th>
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<tr>
<td>Diet</td>
<td>Doves (i.e., rock dove, Columba livia; mourning dove, Zenaida macroura) constitute a dominant prey item for northeastern peregrines (15). Other major prey include blue jay (Cyanocitta cristata), common grackle (Quiscalus quiscula), European startling (Sturnus vulgaris), evening grosbeak (Coccothrautes vespertinus), killdeer (Charadrius vociferous), northern flicker (Colaptes auratus), red-winged blackbird (Agelaius phoeniceus), ring-billed gull (Larus delawarensis), short-billed dowitcher (Limnodromus griseus), and wood duck (Aix sponsa).</td>
</tr>
<tr>
<td>Migration</td>
<td>The northeastern peregrines migrate their first year down the Atlantic seaboard, passing through New Jersey, Maryland and Virginia, with some traveling as far south as Florida and Cuba. While adult birds (&gt;3 years of age) do not necessarily remain strictly within their breeding territories, they do appear to frequent the same region. They are likely stay close enough to periodically inspect their eyries during the non-breeding season.</td>
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</table>
## Appendix III.

Median and range (given in parentheses) of individual PBDE congener concentrations (ng/g wet weight) in the U.S. peregrine falcon (*Falco peregrinus*) eggs by nest.

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* nq = non-quantifiable (S/N < 5).
Appendix IV. Accuracy and Precision Control Charts (\( \bar{X} - R \) Chart) for BDE-209 recoveries in spiking tests

Shewhart Chart
VITA
DA CHEN