

# **Current-Use Flame Retardants in the Eggs of Herring Gulls (*Larus argentatus*) From the Great Lakes: Characterization, Trends and Degradation**

By

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## **ABSTRACT**

In the Laurentian Great Lakes, numerous currently-used organohalogen flame retardants (FR) were identified for the first time in herring gull eggs as a result from accumulation in parent birds and subsequent *in ovo* transfer during seasonal reproduction. Using eggs as biomonitoring tools, temporal and spatial trends of FR contaminants in annually collected eggs were reflective of chemical production and environmental release. Heavily used FRs (i.e. polybrominated diphenyl ethers) were first apparent in eggs collected in the 1980s and followed exponential increases until 2006. Some FRs (i.e. Dechlorane Plus) fluctuated over time, while others persisted more recently. Currently, brominated FRs are receiving considerable attention because of increasing usage and potential environmental availability and toxicity; thus it is prudent to monitor these substances in wildlife and key biomonitoring species such as Great Lakes herring gulls. Furthermore, increasing levels and/or changing patterns illustrate the increasing complexity of environmental contaminants that would classify (in a regulatory sense) persistent, bioaccumulative and inherently toxic.

## LIST OF CONFERENCE ABSTRACTS ASSOCIATED WITH THESIS

(Presenting author is underlined.)

Robert J. Letcher, Lewis T. Gauthier, Kim Fernie, D.V. Chip Wesloh and Soheila Shahmiri. 2005. Novel Brominated and Chlorinated Flame Retardants in Herring Gulls (*Larus argentatus*) and Peregrine Falcons (*Falco peregrinus*) From the Great Lakes. International Association for Great Lakes Research Conference, May 23-24, Windsor, Ontario, Canada. (Oral)

L.T. Gauthier, D.V.C. Weseloh, C.E. Hebert, R.J. Letcher. 2006. Current-Use and Emerging Brominated and Chlorinated Flame Retardant Contaminants in the Eggs of Herring Gulls (*Larus argentatus*) From the Great Lakes. 8<sup>th</sup> Annual Workshop on Brominated Flame Retardants, June 27-29, Toronto, Ontario, Canada. (Poster)

L.T. Gauthier, D.V.C. Weseloh, C.E. Hebert, R.J. Letcher. 2006. Temporal Trends in Current-Use Brominated Flame Retardants and Dechlorane Plus in Eggs of Great Lakes Herring Gulls (*Larus argentatus*). National Wildlife Research Centre Seminar Series, October 25th, Ottawa, Ontario, Canada. (Oral)

L.T. Gauthier, D.V.C. Weseloh, C.E. Hebert, R.J. Letcher. 2006. Temporal Trends in Current-Use Brominated Flame Retardants in Eggs of Great Lakes Herring Gulls (*Larus argentatus*). 17<sup>th</sup> Annual Meeting of Society of Environmental Toxicology and Chemistry (SETAC)-Europe, November 5-9, Montreal, Quebec, Canada. (Oral)

L.T. Gauthier, D.V.C. Weseloh, C.E. Hebert, R.J. Letcher. 2007. Temporal Trends of Decabromodiphenyl Ether (BDE-209) and Degradation Products in the Eggs of Herring Gulls From the Laurentian Great Lakes. 4<sup>th</sup> International Workshop on Brominated Flame Retardants, April 24-27, Amsterdam, the Netherlands. (Oral)

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L.T. Gauthier, D.V.C. Weseloh, C.E. Hebert, R.J. Letcher. 2007. Temporal Trends of Decabromodiphenyl Ether (BDE-209) and Degradation Products in the Eggs of Herring Gulls From the Laurentian Great Lakes. Ottawa-Carleton Chemistry Institute, OCCI Day, May 11, Carleton University, Ottawa, Ontario, Canada. (Poster)

L.T. Gauthier, D.V.C. Weseloh, C.E. Hebert, R.J. Letcher. 2007. Temporal Trends of Current-Use Brominated Flame Retardants in the Eggs of Herring Gulls (*Larus argentatus*) From the Laurentian Great Lakes of North America. 17<sup>th</sup> Annual Meeting of Society of Environmental Toxicology and Chemistry (SETAC)-Europe, May 20-24, Porto, Portugal. (Oral)

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## LIST OF ABBREVIATIONS

AOC	- area of concern
BAF	- bioaccumulation factor
BDE-209	- 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether
BFR	- brominated flame retardant
BMF	- biomagnification factor
BTBPE	- 1,2-bis(2,4,6-tribromophenoxy) ethane
CWS	- Canadian Wildlife Service
DBDPE	- decabromodiphenyl ethane
DCCO	- double crested cormorant ( <i>Phalacrocorax auritus</i> )
DCM	- dichloromethane
<i>p,p'</i> -DDT	- <i>bis</i> -2,2-(4-chlorophenyl)-1,1,1-trichlorethane
DP	- bis(hexachlorocyclopentadieno) cyclooctane or Dechlorane Plus®
DecaBDE	- commercial “deca-BDE” formulation
ECNI	- electron capture negative ionization
EI	- electron impact
ESI	- electrospray ionization
FR	- flame retardant
GC/MS-ECNI	- gas chromatography – mass spectrometry – electron capture negative ionization
GC/HRMS-EI	- gas chromatography – high resolution mass spectrometry – electron ionization
GPC	- gel permeation chromatography
HBB	- hexabromobenzene
HBCD	- hexabromocyclododecane
HEX	- hexane
HIPS	- high impact polystyrene
IJC	- International Joint Commission
IS	- internal standard
IUPAC	- International Union of Pure and Applied Chemistry
LC/MS(MS)	- liquid chromatography tandem mass spectrometry
MLOQ	- method limit of quantitation
MRM	- multiple reaction monitoring
NWRC	- National Wildlife Research Centre
OctaBDE	- commercial “octa-BDE” formulation
PBAE	- pentabromo allyl ether
PBB	- polybrominated biphenyl
PBBB	- pentabromobenzyl bromide
PBEB	- 2,3,4,5,6-pentabromoethyl benzene
PBDE	- polybrominated diphenyl ether
PBT	- 2,3,4,5,6-pentabromotoluene
PCB	- polychlorinated biphenyl
PentaBDE	- commercial “penta-BDE” formulation
PFK	- perfluorokerosine
POP	- persistent organohalogen pollutant

pTBX	- tetrabromo-p-xylene
RRF	- relative response factor
SD	- standard deviation
SE	- standard error
SIM	- selected ion monitoring
SRM	- standard reference material
TBAE	- 2,4,6-tribromo allyl ether
TBBPA	- tetrabromobisphenol A
TBCO	- 1,2,5,6-tetrabromocyclooctane
TBECH	- 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane
TMP	- 2,2',4-trimethylpentane
ww	- wet weight

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## CHAPTER 1

### General Introduction

Chemical contamination of the environment is a pervasive, insidious side effect of human population growth and technical development. Environmental monitoring programs have detected chemical contaminants for decades, only after long-event or long term usage, some chemicals have been classified as persistent organic pollutants (POPs). There has been an unbelievable widespread usage and environmental bioaccumulation of anthropogenic compounds such as *bis*-2,2-(4-chlorophenyl)-1,1,1-trichlorethane (*p,p'*-DDT), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) or other compounds including perfluoroalkyl compounds (PFCs).

Several classes of flame retardant (FR) chemicals exist as additives to a variety of products. More specifically, brominated flame retardants (BFRs; e.g., PBDEs), have or are becoming ubiquitous in the environment, and in the case of PBDEs have emerged as a new class of POP. Many additive FR chemicals are currently in use for which there is a dearth of information regarding their various toxicological and biological effects, as well as an enormous knowledge gap with respect to geographical and temporal distributions in the environment.

#### **1.1 Flame Retardants in General**

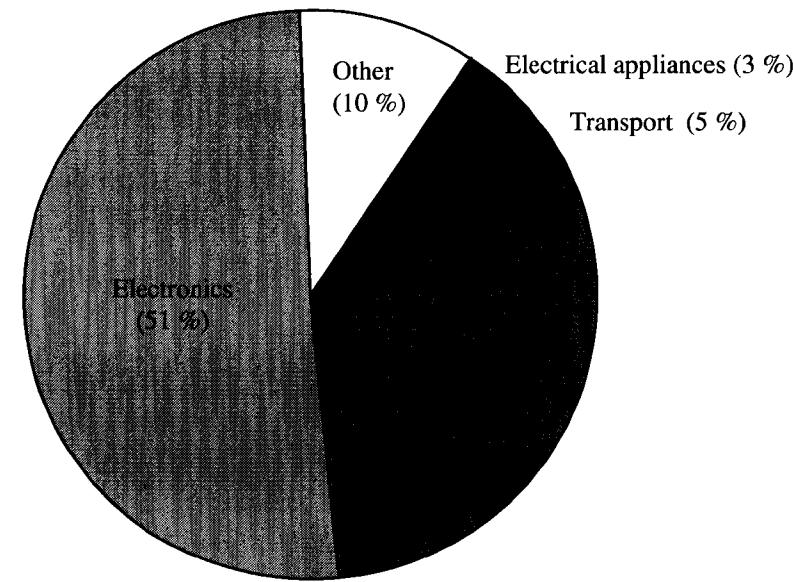
Several FR chemicals are applied as additives to mainly polymeric materials used in commercial products during or after manufacture, to adhere to stringent fire safety

regulations. Examples of products that contain FRs included many components of electronic devices, building materials, and textiles (Figure 1.1). During the twentieth century, new materials such as plastics and polyurethane foam/fiber-based materials began to replace traditional materials such as wood and metal. FRs interfere with the propagation of combustion at various stages of the process, e.g. during heating, decomposition, ignition or flame spread.

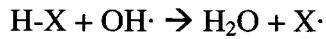
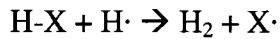
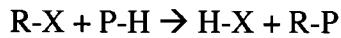
There are more than 175 different types of FRs used worldwide. FRs are a chemically diverse class of compounds that are aromatic, aliphatic or cycloaliphatic, where halogenated FRs are especially effective and pervasively used. Chlorinated FRs are mainly used in plastics and offer good light stability but compared to brominated flame retardants (BFRs), higher quantities are needed for achieving comparable flame retardancy. BFRs are currently the largest market group of FRs because of their low cost and high performance efficiency.

### **1.1.1. Mechanism of Flame Retardation**

The mechanism of flame retardancy by chlorinated and brominated substances occurs via a radical formation that subsequently quenches the combustion process in the gas phase (Equation 1.1). The exothermic processes are thus stopped and the system cools down in the absence of fuel, and thus fire is eventually suppressed.



**Figure 1.1.** The relative amounts of flame retardants used in different sectors. Data from Pijnenberg et al. (1995).



**Equation 1.1.** Mechanism of action for brominated and chlorinated FRs.

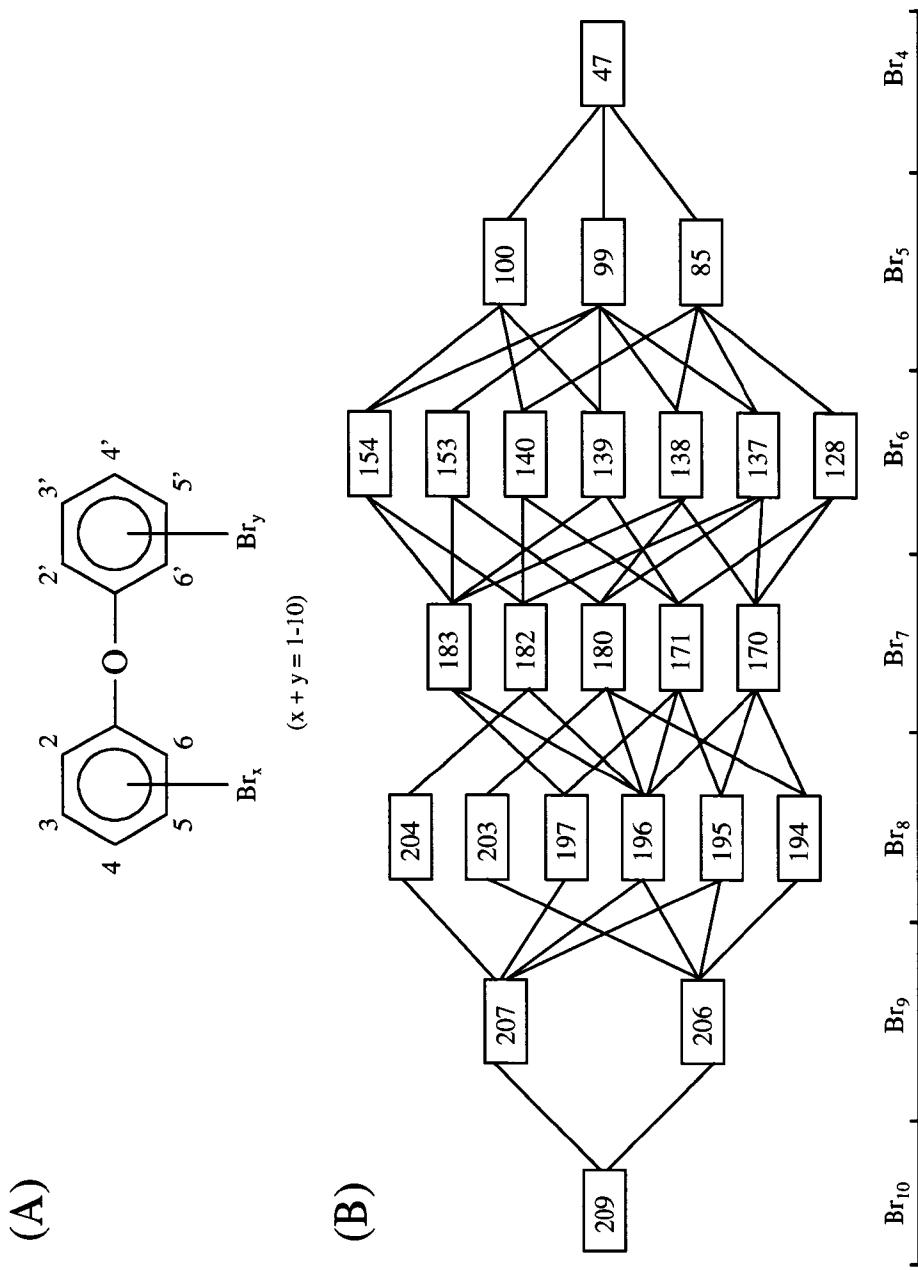
The highly-reactive OH· and H· radicals can react in the gas phase with other radicals, such as halogenated radicals (X·) bound to FR backbones (R) that result from flame retardant degradation in the polymer (P). Less reactive radicals, which decrease the kinetics of the combustion, are created. Ultimately, FRs will deprive the flame of oxygen and slow down or stop combustion.

## 1.2. Polybrominated Diphenyl Ethers in the Environment

Several formulations of PBDEs have been used as FR additives to industrial and household materials for nearly three decades. Structurally similar to PCBs, PBDEs contain one to ten bromine (instead of chlorine) atoms bound to two biphenyl backbones, which are bound by an ether linkage. Theoretically, PBDEs can occur in 209 different congener structures, and thus the systematic numbering scheme developed by Ballschmiter et al. (1991) for PCB congeners also was adopted for PBDEs. This numbering system was based on the arrangement of the chemical structures in ascending order of number of chlorine substituents and, with a homologue, in ascending order of the carbon ring numeration; for this purpose, an unprimed number was considered lower than the same number when primed. For PBDEs, the numerical naming system begins with an unprimed number closest to the ether linkage.

PBDE FRs are used in a variety of commercial and household products, such as polyurethane foam, which are then used in other products such as upholstered furniture. In fact, some polyurethane foam is treated with 10 to 30 wt % of PBDEs to make this material safe for homes. Formulations of this unique class of FR are also applied to polymers, which are used in electrical equipment, paints, textiles, and in automobiles and aircraft (de Boer et al., 2000). Three PBDE commercial technical mixtures currently exist, and are marketed as slightly different formulations, and in 2001 amounted to a total global market demand of approximately 67,300 metric tonnes (BSEF, 2006) (Table 1.1). PentaBDE formulations mainly consist of BDE-47, -99, and -100, as well as minor amounts of tri- to hepta-BDEs. The IUPAC PBDE names and corresponding structures associated with the present study can be found in Appendix 1 and Appendix 2, respectively, as well as Figure 1.2A. The commercial OctaBDE formulations consist mainly of BDE-153, BDE-154 and BDE-183, and four octa-BDE congeners. DecaBDE is composed of >97% of the fully brominated congener, BDE-209, with trace amounts of nona-BDE congeners (Hites, 2004) (Table 1.2).

PBDEs are not chemically bound to the products they are used in, and thus are prone to leaching into the environment. A main source of PBDEs in the environment is during the manufacturing process and when products containing PBDEs are disposed of in land fills. Aside from few natural products containing methoxylated and hydroxylated PBDE derivatives, PBDEs are present in the environment primarily due to human activity and



**Figure 1.2.** (A) Diphenyl ether 'backbone' and generalized PBDE substitution ( $x + y = 1$  to 10); (B) possible debromination pathway and potential intermediates stemming from BDE-209 and leading to the formation of BDE-47 (See Appendix 1 for corresponding IUPAC names and Appendix 2 for chemical structures of PBDE congener abbreviations).

have been detected in a variety of species worldwide. Evidence from many studies indicates that levels of certain PBDEs in biota around the world (including the Arctic regions) are increasing steadily and substantially over time (Hites, 2004). At present, PBDEs are the most extensively studied group of additive FRs and have been shown to be ubiquitous environmental contaminants that bioaccumulate in the tissues of wildlife and humans (Hites, 2004). Specifically for birds and bird eggs (Table 1.3), PBDE compounds have been found in several studies around the world in top predator birds.

Physio-chemical properties of a chemical determine persistence and bioaccumulation in the environment. PBDEs have various hydrophobic properties and tend to concentrate on particulate matter and in the tissues of biota (de Boer et al., 2000). In all levels of food webs, from plankton and fish to birds and mammals, PBDEs have been found in various tissues (de Wit, 2002, Hites, 2004). PBDEs are inherently lipophilic and will interact with fatty tissues in an organism: such lipophilicity can be defined by  $\log K_{ow}$  (octanol-water partition coefficient), which can be measured for a chemical and for PBDEs ranges between 4.3 and 10, depending on the number of bromines in a congener. Compounds that have a  $\log K_{ow} > 5$ , are classified as bioaccumulative (Table 1.4); tetra- and penta-BDEs have estimated  $\log K_{ow}$  of 5.9-6.2 and 6.5-7.0 respectively. With higher degrees of bromination,  $\log K_{ow}$  values also increase; for octa-BDEs and BDE-209,  $\log K_{ow}$  values are 8.4-8.9 and 10, respectively (Darnerud et al., 2001b).

**Table 1.1.** Major BFR volume estimates (metric tonnes) by region in 2001 (BSEF, 2006).

BFR	TBBPA	HBCD	DecaBDE	OctaBDE	PentaBDE	$\sum$ PBDEs	$\sum$ BFRs
Americas	18,000	2,800	24,500	1,500	7,100	33,100	53,900
Europe	11,600	9,500	7,600	610	150	8,360	29,460
Asia	89,400	3,900	23,000	1,500	150	24,650	117,950
Other	600	500	1,050	180	100	1,330	2,430

**Table 1.2.** The general compositions of PBDE-based flame retardant commercial formulations given in percent of PBDE congeners present (WHO, 1994).

Product	PBDE Congener Percent						
	tetra-	penta-	hexa-	hepta-	octa-	nona-	deca-
PentaBDE	24 - 48	50 - 60	4 - 8				
OctaBDE			10 - 12	44	31 - 35	10 - 11	< 1
DecaBDE					< 3	97 - 99	

**Table 1.3.** Current references on PBDE contaminants in bird eggs from around the world.

Bird species	Location	Article Reference
Herring gull ( <i>Larus argentatus</i> )	N. Norway, Svalbard, Great Lakes	(Knudsen et al., 2006a; Norstrom et al., 2002)
Peregrine Falcon ( <i>Falco peregrinus</i> )	South Greenland	(Herzk et al., 2005; Lindberg et al., 2004; Sellstrom et al., 2004; Vorkamp et al., 2005)
Atlantic Puffin ( <i>Fratercula arctica</i> )	N. Norway, Svalbard,	(Knudsen et al., 2006a)
Black-legged kittiwakes ( <i>Rissa tridactyla</i> )	N. Norway, Svalbard,	(Knudsen et al., 2006a)
Glaucous gull ( <i>Larus hyperboreus</i> )	Norwegian Arctic	(Verreault et al., 2005a; 2005b; 2006; 2007)
Baltic guillemot ( <i>Uria aalge</i> )	Baltic Sea, Greenland	(Lundstedt-Enkel et al., 2006; Sellstrom et al., 2003b); (Sellstrom et al., 2004)
Ivory gull ( <i>Pagophila eburnea</i> )	Canadian Arctic	(Braune et al., 2007)
White-tailed eagle ( <i>Haliaeetus albicilla</i> )	Norway	(Herzk et al., 2001)
Golden eagle ( <i>Aquila chrysaetos</i> )	Norway	(Herzk et al., 2001)
Merlin ( <i>Falco columbarius</i> )	Norway	(Herzk et al., 2001)
Little owl ( <i>Athene noctua</i> )	Belgium	(Jaspers et al., 2004)
Heron ( <i>Ardea cinerea</i> )	UK, Canada, China	(D'Silva et al., 2004; Elliot et al., 2005)
Bald eagle ( <i>Haliaeetus leucocephalus</i> )	Canada	(McKinney et al., 2006)
Great tit ( <i>Parus major</i> )	Belgium	(Van den Steen et al., 2006)
Little egret ( <i>Egretta garzetta</i> )	China	(Lam et al., 2007)
Black-crowned night heron ( <i>Nycticorax nycticorax</i> )	China	(Lam et al., 2007)
Northern fulmar ( <i>Fulmarus glacialis</i> )	Faroe Islands	(Fangstrom et al., 2005; Karlsson et al., 2006)
Adelie Penguin ( <i>Pygoscelis adeliae</i> )	Antarctica	(Corsolini et al., 2006)
Least Tern ( <i>Sternula antillarum</i> )	USA	(She et al., 2004)
Fosters Tern ( <i>Sterna forsteri</i> )	USA	(She et al., 2004)
Caspian Tern ( <i>Hydroprogne caspia</i> )	USA	(She et al., 2004)

**Table 1.4.** Criteria defining persistence, bioaccumulation and toxicity (P, B and T) regulations in Canada.

	Persistence	Bioaccumulation	Toxicity <sup>(1)</sup>	Protection goals and risk management
Canada Toxic Substances Management Programme (TSMP)	Half-life in Air >2 days Water >6 months Sediment >1 year Soil >6 months	BAF or BCF > 5000 or log $K_{ow}$ > 5	Toxicity according to Canadian EPA	Risk assessment: If toxic and P and B and primarily anthropogenic, then virtual elimination
Canadian Domestic Substances List (DSL)	Half-life in Air >2 days Water >6 months Sediment >1 year Soil >6 months	BAF or BCF > 5000 or log $K_{ow}$ > 5	Inherently toxic <sup>(2)</sup>	If inherently toxic and P or B : screening level risk assessment But even if P & B no virtual elimination unless determined by risk assessment

(1) For marine environment risk assessments, half-life data in freshwater and freshwater sediment can be overruled by data obtained under marine conditions.

(2) The definition of "inherently" toxic to non-human organisms is still under consideration by Environment Canada

### **1.2.1. Production Phase-out Legislation on PBDEs - Current Status**

The PentaBDE and OctaBDE commercial mixtures were widely used until recently, but strict regulations were imposed on commercial usage, and in 2004, were withdrawn for commercial usage in Europe. These PBDE products are also currently facing legislative regulation and restriction around the world, including North America (Canada Gazette, 2006). For example, in Canada, PentaBDE and OctaBDE mixtures were voluntarily phased out of use in 2006 and are no longer available on the commercial market. The increasing regulation and phasing out of PentaBDE and OctaBDE mixtures has been in response to persistence and bioaccumulation in the environment, and potential toxic characteristics of some individual congeners such as 2,2',4,4'-tetraBDE (BDE-47) and 2,2',4,4',5-pentaBDE (BDE-99) (see Appendix 2). In addition, suppliers and users of PentaBDE and OctaBDE have confirmed that given the regulatory climate, customer demand for PBDE-free products, the availability of cost-effective alternatives, and the fact that PentaBDE and OctaBDE were not available in the market after 2005, it was not technically or economically viable to continue using PentaBDE and OctaBDE commercial mixtures (Canada Gazette, 2006) (Table 1.1, Table 1.2). In contrast, presently there are no restrictions worldwide on the DecaBDE commercial mixture, which largely dominates the demand and use of PBDEs as an additive FR material in the global market, e.g., 56,400 tonnes in 2001 (BSEF, 2006) (Table 1.1, Table 1.2).

### **1.2.2. PBDE Degradation and Debromination**

The continued use of BDE-209 is highly controversial as it has been shown to persist and bioaccumulate in the tissues of aquatic feeding wildlife at low to non-detectable levels

(e.g. ppb/ppt). Contrary to congeners present in the PentaBDE and OctaBDE technical mixtures, it is assumed that BDE-209 is not easily absorbed through the gut and subsequently has low bioavailability because of its high molecular weight (959 amu) and hydrophobic characteristics ( $\log K_{ow} = 10$ ) (IPCS, 1994). Based on these characteristics, DecaBDE does not appear to fit traditional persistent, bioaccumulative and toxicity (PBT) criteria (Table 1.4).

At this time, there is considerable uncertainty and controversy regarding the extent of DecaBDE degradation. However, very recent studies have reported quantifiable levels of more highly brominated PBDE congeners such as hepta- to nona-BDEs and BDE-209 in the eggs of top predator avian species (Herzk et al., 2005; Knudsen et al., 2006a; Lindberg et al., 2004; Verreault et al., 2007; Vorkamp et al., 2005).

It is also unclear at this time what potential physiological damage might derive from the metabolic breakdown products of DecaBDE. There is increasing experimental evidence that PBDE exposure is detrimental to wildlife health. For example, whole organism studies with fish and birds exposed to individual congeners (e.g., BDE-47, -99 and -209) and PentaBDE mixtures, might impact structures that are similar to estrogen and/or thyroid hormones and are showing an increasing array of effects including modulation of liver enzyme activity, thyroid hormone immunotoxicity and neurological development (Birnbaum and Staskal, 2004; Darnerud et al., 2001a; Kierkegaard et al., 2006). Furthermore, there are several recent reports showing that BDE-209 is unstable in the environment. BDE-209 has been shown to metabolically degrade in biota (e.g. fish, rats

and birds) (Huwe and Smith, 2007; Stapleton et al., 2006a; Van den Steen et al., 2007a) or undergo abiotic photocatalytic degradation (Ahn et al., 2006; Bezaires-Cruz et al., 2004; Soderström et al., 2004) to lower brominated congeners. A postulation that continues to be controversial is that BDE-209 degradation leads to sequentially less brominated PBDE congeners, and ultimately to highly bioaccumulative and potentially more toxic congeners such as BDE-47, -99 and -100 (Kuriyama et al., 2007a; Muirhead et al., 2006) (Figure 1.2).

### **1.3. Non-PBDE Flame Retardants**

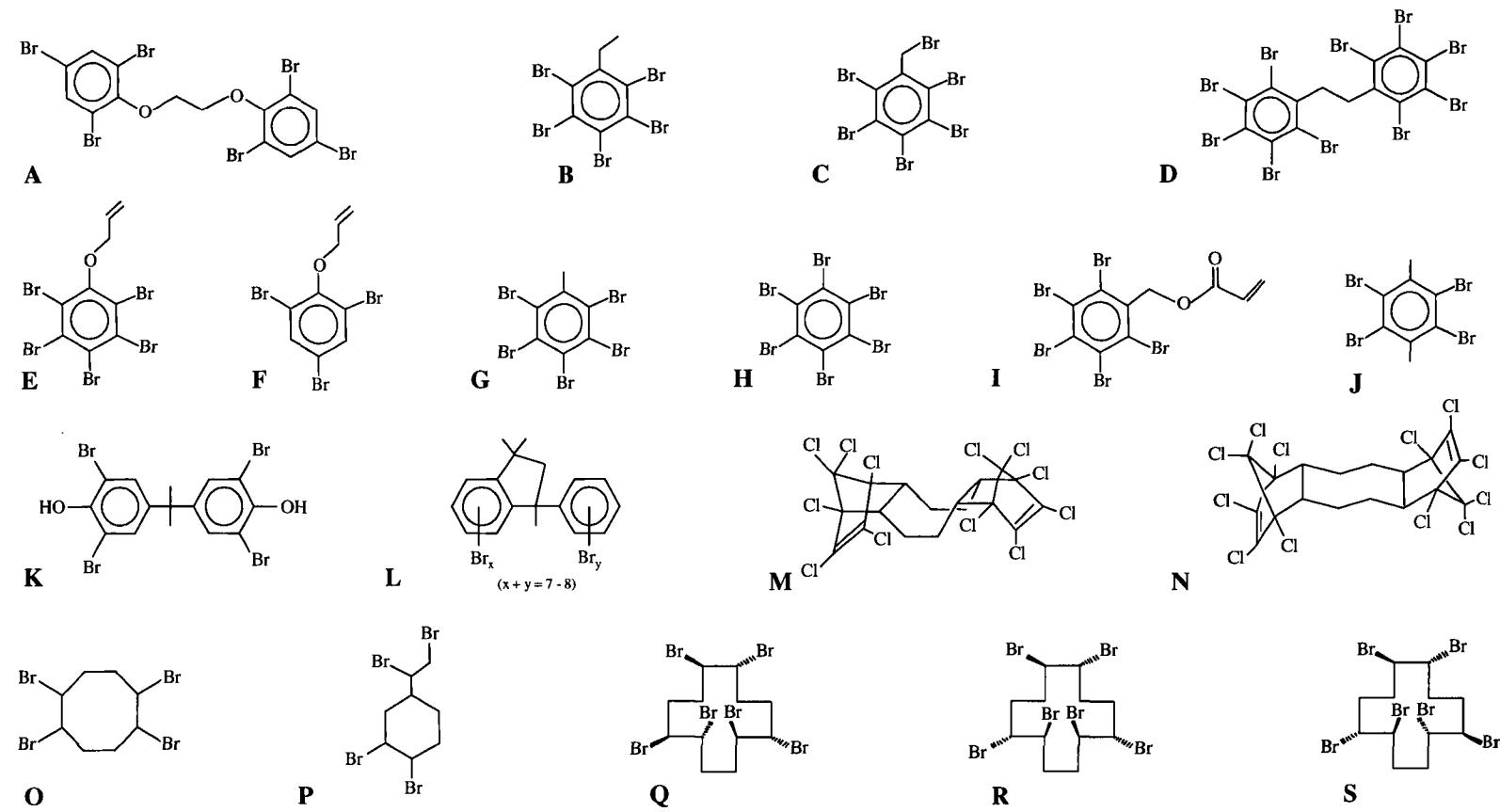
There are recent and increasing phase-outs of commercial usage of PentaBDE and OctaBDE technical mixtures by the FR industry (Canada Gazette, 2006; Tullo, 2003), which more than likely will be replaced by non-regulated FRs. High production volume FRs that are currently in use, not regulated, and have recently been receiving more attention as environmental contaminants include the DecaBDE mixture,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomers of hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) (Figure 1.3). However, there are approximately 75 different non-PBDE bromine-based compounds in production and commercial use as additives to polymeric products in need of flame retardancy (Birnbaum and Staskal, 2004). The chemical structures of some common and very popular current-use, additive non-PBDE FRs are found in Figure 1.3.

With the verification of recent regulatory guidelines on commercial PentaBDE and OctaBDE products, no technical or economic impact on the FR industry is expected from the proposed prohibitions on PentaBDE and OctaBDE use (Canada Gazette, 2006).

Global consumption of the major, high production volume, FR chemicals exceeds 300,000 metric tonnes per year, although this figure has decreased slightly from 2002 to 2003 (BSEF, 2006). This exemplifies the likelihood of alternative FR as replacements coming into commercial heavy use. For example, Chemtura, the major BFR player in the BFR industry, has announced that they will replace the OctaBDE mixture with 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) (Chemtura, 2004). Similarly, decabromodiphenyl ethane (DBDPE) is marketed as a replacement and alternative for the DecaBDE commercial mixture (Chemtura, 2004) and is favourable because it does not produce any polybrominated dibenzo-p-dioxins, which are known to have a variety of toxic effects including liver toxicity and death in experimental animals (EHC, 1998).

### **1.3. 1. Non-PBDE FRs in the Environment**

Based on P, B and T criteria introduced earlier (Table 1.3), several of the non-PBDE FRs (Figure 1.3) have physio-chemical properties that render them likely candidates for persistence and bioaccumulation in the environment. Since many physio-chemical properties are not currently publicly available for some current-use FRs, their base chemical structure, in relation to FRs presently known as environmental contaminants (i.e. PBDEs), provides some evidence to their potential occurrence. Nonetheless, the currently available data describing key (known) characteristics of potential persistent and bioaccumulative non-PBDE FRs is summarized in Table 1.5.



**Figure 1.3.** Chemical structures of non-PBDE flame retardants currently in commercial production: A, 1,2-bis-(2,4,6-tribromophenoxy) ethane (BTBPE); B, pentabromoethylbenzene (PBEB); C, pentabromobenzyl bromide (PBBB); D, decabromodiphenyl ethane (DBDPE); E, pentabromo allyl ether (PBAE); F, 2, 4, 6-tribromo allyl ether (TBAE); G, pentabotoluene (PBT); H, hexabromobenzene (HBB); I, pentabromobenzyl acrylate (PBBA); J, tetrabromo-p-xylene (pTBX); K, tetrabromobisphenol A (TBBPA); L, octabromo-1,3,3-trimethyl-1-phenyl indane (BTMPl); M, *syn*-Dechlorane Plus (*syn*-DP); N, *anti*-Dechlorane Plus (*anti*-DP); O, 1,2,5,6-tetrabromocyclooctane (TBCO); P, 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (TBECH); Q/ R/S, alpha-, beta- and gamma-hexabromocyclododecane ( $\alpha$  -,  $\beta$ -, and  $\gamma$ -HBCD) respectively. The hydrogen atoms have been omitted for simplicity.

Both BTBPE and DBDPE have been reported in environmental samples (Table 1.3). Specifically for birds' eggs, BTBPE has been reported in the eggs of glaucous gulls from the Norwegian Arctic (Verreault et al., 2007) and northern fulmars from the Faroe Islands (Karlsson et al., 2006), as well as in a variety of other biotic and abiotic environments (Table 1.6). There are rare occurrences of DBDPE in the biotic and abiotic environments. DBDPE has been previously reported in the environment and has been detected in a range of media such as human plasma, tree bark and sediment (Table 1.3). There are only two reports of the FR PBEB in environmental samples (Hoh et al., 2005; Lee et al., 2002), and very few on PBT and HBB (Table 1.3).

HBCD isomers are brominated aliphatic cyclic hydrocarbons used as FRs in a variety of materials (Alaee et al., 2003). HBCD technical mixtures consist of three isomers (Figure 1.3) and are classified as a high volume production FR (Table 1.1) (Alaee et al., 2003). The three isomers of HBCD exhibit similar pathways of entering the environment as PBDEs. HBCDs were first detected in fish and sediment samples from the river Viskan in Sweden (Sellstrom et al., 1998). Since then, their presence has been reported in a wide variety of biota and abiotic environmental samples (Covaci et al., 2006)(Table 1.3). Not many studies have examined contaminant levels of HBCDs in avian species. Reports of HBCDs in the eggs of top predator avian species are rare and include peregrine falcons from Sweden (Lindberg et al., 2004), common guillemots from areas of the Baltic Sea (Sellstrom et al., 2004).

**Table 1.5.** Summary of key (known) physio-chemical characteristics describing current-use non-PBDE FRs for the present study and their potential to persist and bioaccumulate in wildlife and humans.

Abbreviation	Structure (Figure 1.3)	MW (g/mol)	molecular Formula	melting point (°C)	$\log K_{ow}$	water solubility ( $\mu\text{g/L}$ $\text{H}_2\text{O} @ 20^\circ\text{C}$ )	Vapour pressure (mm Hg)
BTBPE	A	688	$\text{C}_{14}\text{H}_8\text{Br}_6\text{O}_2$	223-225	3.14	0.0002	$7.5 \times 10^{-7}$
PBEB	B	500	$\text{C}_8\text{H}_5\text{Br}_5$	n/a	7.5	n/a	n/a
PBBB	C	565	$\text{C}_7\text{H}_2\text{Br}_6$	178-181	n/a	n/a	n/a
DBDPE	D	959	$\text{C}_{14}\text{Br}_{10}\text{H}_4$	70	11	n/a	n/a
PBPAE	E	528	$\text{C}_9\text{H}_4\text{Br}_5\text{O}$	n/a	n/a	n/a	n/a
TBPAE	F	368	$\text{C}_9\text{H}_6\text{Br}_3\text{O}$	n/a	n/a	n/a	n/a
PBT	G	486	$\text{C}_6\text{Br}_5\text{CH}_3$ ,	285-286	7	insoluble	n/a
HBB	H	551	$\text{C}_6\text{Br}_6$	327	6.1	0.0001	$1.6 \times 10^{-8}$
PBBA	I	556	$\text{C}_{10}\text{H}_4\text{Br}_5\text{O}_2$	n/a	6.9	n/a	n/a
pTBX	J	422	$\text{C}_8\text{H}_6\text{Br}_4$	247	n/a	n/a	n/a
BTMPI	L	857	$\text{C}_{18}\text{H}_{12}\text{Br}_8$	n/a	n/a	n/a	n/a
DP	M/N	648	$\text{C}_{18}\text{H}_{12}\text{Cl}_{12}$	350	9.3	0.044 - 0249	0.006
TBCO	O	428	$\text{C}_8\text{H}_{12}\text{Br}_4$	n/a	n/a	n/a	n/a
TBECH	P	428	$\text{C}_8\text{H}_{12}\text{Br}_4$	70-75	n/a	n/a	n/a
HBCD	P,Q,R	641	$\text{C}_{12}\text{H}_{18}\text{Br}_6$	175-195	5.6	0.0034	$4.7 \times 10^{-7}$

**Table 1.6.** Compilation of what is presently documented in the literature concerning the occurrence of non-PBDE FRs (Figure 1.3) in the environment and in humans.

Non-PBDE FR	Type of Media	Location	References
PBEB	Particulate air	U.S.A., Great Lakes, UK	(Hoh et al., 2005; Lee et al., 2002)
HBB	glaucous gulls, air, sediment, human adipose tissue and fish	Great Lakes, Norwegian Arctic, Japan	(Verreault et al., 2007; Watanabe et al., 1986b; Yamaguchi et al., 1988b; Japanese Governemnt, 2001)
PBT	glaucous gulls, sediment, sewage sludge and air	Great Lakes Canada, Norwegian Arctic, Sweden.	(Gouteux et al., 2006; Hoh et al., 2005; Hyotylainen and Kartonen, 2002; Mattsson et al., 1975; Schwarzbauer et al., 2001; Verreault et al., 2007)
BTBPE	Particulate air, sediment, tree bark, workplace air, fish, bird eggs (herring gulls, Northern Falmers, glaucous gull), human plasma, and dust	U.S.A., Great Lakes, Feroe Islands (Denmark), Lake Winnipeg (Canada), Norwegian Arctic.	(Hoh et al., 2005; Hoh and Hites, 2005; Julander et al., 2005b; Karlsson et al., 2007; law et al., 2006; Pettersson-Julander et al., 2004; Qiu et al., 2007; Sjödin et al., 2001; Verreault et al., 2007; Zhu and Hites, 2006)
DBDPE	Air, dust, human plasma, sewage sludge, sediment, tree bark	Sweden, Netherlands, Great Lakes, U.S.A.	(Julander et al., 2005b; Karlsson et al., 2007; Kierkegaard et al., 2004; Pettersson-Julander et al., 2004; Zhu and Hites, 2006)
HBCDs	glaucous gulls, porpoises, fish, air, dust, sediment, soil, sewage sludge, birds, humans	Globally	(Covaci et al., 2006)
DP	sediment, fish, tree bark, zooplankton, mussels	Great Lakes, Lake Winnipeg (Canada)	(Hoh et al., 2006; Qiu et al., 2007; Tomy et al., 2007c)

The *syn*- and *anti*-stereoisomers of bis(hexachlorocyclopentadieno)cyclooctane, or more commonly known as Dechlorane Plus (DP) (Figure 1.3 M/N), is a highly chlorinated flame retardant. DP was introduced as a substitute for Dechlorane (also called Mirex) by Hooker Chemical (now known as OxyChem) in the mid-1960s. This is the only chlorinated flame retardant in current production and usage (Weil and Levchik, 2004). Dechlorane Plus was recently identified in ambient air, fish and sediment from the Great Lakes (Hoh et al., 2006; Qiu et al, 2007). The DP isomers were also detected in archived fish from Lake Erie, which suggests that this compound is widely bioavailable and bioaccumulates in Great Lakes food webs (Table 1.3).

Global production volumes for many of the current-use, non-PBDE FRs are not available publicly. However, several countries have imposed inventory update rules requiring that FR producing industries relinquish FR production volume estimates. BTBPE falls under the U.S. EPA Inventory Update Rule and Great Lakes Chemical produced 45 to 22,500 metric tonnes of BTBPE from 1986 to 1994, but production decreased to 450-4500 metric tonnes per year after 1998.

#### **1.4 The Laurentian Great Lakes of North America**

The Laurentian Great Lakes (Figure 1.4) represent the single largest body of fresh water in the world, and cover an area of approximately 244,000 km<sup>2</sup> (Assel et al., 1983). The human population living on and around the Great Lakes is in the order of several tens of millions of people, and thus the urban, agricultural and industrial inputs of anthropogenic

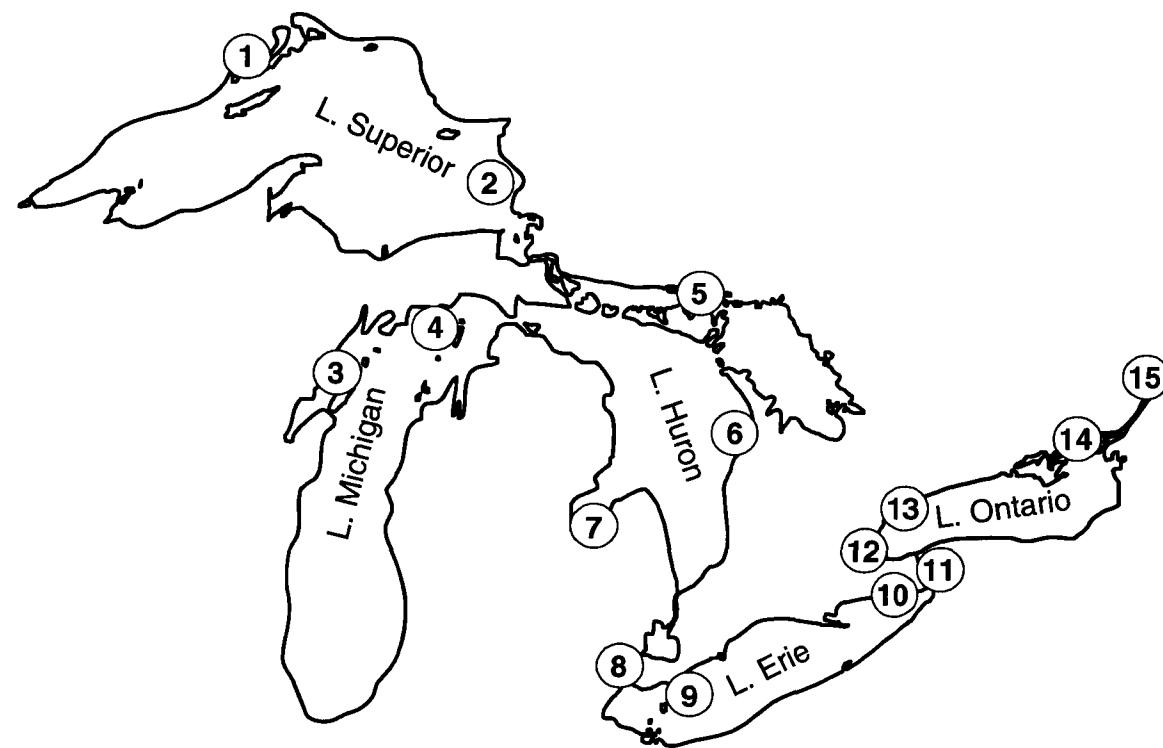
compounds into the aquatic environment is substantial. The U.S.- Canadian International Joint Commission (IJC) has identified 43 areas of concern (AOCs) around the Great Lakes; environments in which pollution currently is severe enough to pose a substantial risk to human and wildlife health.

### **1.5. The Great Lakes Herring Gull and its Egg**

In the Laurentian Great Lakes basin, herring gulls are primarily piscivorous but they also consume a wide variety of other food types including human garbage, small mammals, invertebrates, songbirds, amphibians, and vegetation (Ewins et al., 1994b; Fox et al., 1990; Hebert et al., 1999b). Gulls are exposed to POPs via their aquatic environment and food web, making them an ideal avian species for POP biomonitoring. The herring gull was selected as one of the Canadian Wildlife Service's (CWS) primary Great Lakes monitoring species for several reasons (Hebert et al., 1999a):

- (1) it primarily consumes fish, thereby occupying a high trophic level;
- (2) the adult is a year-round Great Lakes resident;
- (3) it nests in colonies facilitating population assessments; and
- (4) it has a holarctic distribution, allowing geographic comparisons.

A review of the silver anniversary of the CWS Great Lakes Herring Gull Monitoring Program (GLHGMP) is provided by Hebert et al. (1999). Initial studies using this program were conducted in response to observations of breeding failure in colonial fish-eating water birds in the region (Hebert et al., 1999a). Currently, archived tissue samples



**Figure 1.4.** Annually monitored CWS herring gull colonies in the Laurentian Great Lakes: (1) Granite Island, Lake Superior; (2) **Agawa Rocks, Lake Superior**; (3) Big Sister Island, Green Bay, Lake Michigan; (4) **Gull Island, Lake Michigan**; (5) Double Island, North Channel, Lake Huron; (6) **Chantry Island, Lake Huron**; (7) **Channel-Shelter Island, Saginaw Bay, Lake Huron**; (8) **Fighting Island, Detroit River**; (9) Middle Island, Lake Erie; (10) Port Colbourne, Lake Erie; (11) **Niagara River (above the falls)**; (12) Hamilton Harbour, Lake Ontario; (13) **Leslie St. Spit, Toronto Harbour, Lake Ontario**; (14) Snake Island, Lake Ontario; (15) Strachan Island, St. Lawrence River. Bold text and arrows mark the seven colonies selected for the current study.

from the National Wildlife Research Centre's (NWRC) specimen bank provide an invaluable function in reconstructing the occurrence of toxic contaminants in the Great Lakes Herring Gulls from fifteen annually monitored colonies (Figure 1.4).

Because the herring gull occupies a high trophic position in the Great Lakes, POP contaminant concentrations in their tissues are found at much greater concentrations than in organisms occupying lower trophic levels, or in water and sediment (Norstrom et al., 1978). For example, concentrations of PCBs in herring gull eggs are approximately  $10^7$  times greater than in water and 50 times greater than in fish (Norstrom et al., 1978). The GLHGMP has annually provided information concerning levels of environmental contaminants in herring gull eggs since 1974, making it one of the longest running biomonitoring programs in the world (Hebert et al., 1999a).

## **1.6 Thesis Objectives**

Very little information exists on current-use FRs in the environment and biota surrounding the Great Lakes basin. It is hypothesized that with recent FR production phase-out/regulation of PentaBDE and OctaBDE commercial mixtures, heavy legislative pressure for the use of alternative, will result in greater environmental bioavailability of non-PBDE FRs. The objectives of the current thesis are:

- (i) Survey, identify/characterize, and quantify as comprehensively as possible in Great Lakes herring gull eggs all potential flame retardant additives that are presently in commercial production and/or usage for which reference

standards or technical mixtures are available. Qualitatively assess the spatial distribution of the above FRs, and their degradation products, in gull eggs collected at selected colonial sites spanning the Laurentian Great Lakes (addressed in Chapter 3).

- (ii) Depending on the current-use FRs identified, and regardless of the source or origin, the study design will assess the temporal changes and fluctuations in the current-use FRs in the eggs of herring gulls from selected colonies on all five Laurentian Great Lakes (addressed in Chapters 4 and 5).

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## CHAPTER 2

### Materials and Methods

#### **2.1. Herring Gull Egg Sample Collection**

##### **2.1.1 Colony Locations on the Laurentian Great Lakes**

Of the 52 major herring gull colonies on the Great Lakes (Morris et al., 2003), the 15 sites illustrated in Figure 1.4 were selected for the GLHGMP to best represent the spatial distribution of herring gull colonies on all five lakes. Many of these sites were selected to represent densely urbanized/industrialized areas, while others were selected as reference sites located in remote regions. The present study selected seven colonies using a similar rationale, although some influence was paid to PBDEs levels previously reported (Norstrom et al., 2002). Four colonies were chosen in close proximity to designated AOCs: Channel-Shelter Island (Lake Huron), Fighting Island (Detroit River), Niagara River (above the falls), and Toronto Harbour (Lake Ontario). In addition, two colonies, Gull Island (Lake Michigan), and Agawa Rock (Lake Superior) represented reference sites for the present FR temporal and spatial trends study.

##### **2.1.2. Egg Sample Processing and Storage**

As early as 1965, adult herring gulls were collected for contaminant analysis. However, from 1972 and onwards the favoured tissue for analysis has been eggs for several reasons (Mineau et al., 1984). The lipid content of an egg is less variable than that of most other tissues. For the eggs that are laid, lipid content will be maintained within a range of values that ensures the proper development of the embryo. Other tissues, e.g. liver, will

fluctuate more in lipid content because they will more directly reflect food availability/investment of resources in reproduction. Eggs can be easily collected with little disturbance to the colony. A number of studies (Herman et al., 1969; Vermeer and Reynolds, 1970) have shown the similarity between contaminant burdens of eggs and bodies of female birds. All egg samples were collected annually in late April to early May, where  $n = 10$  to 13 eggs per site according to a strictly defined protocol (Elliot, 1985). In the laboratory, each egg was weighed, measured and the contents emptied into a chemically clean container and then homogenized. Aliquots of the individual eggs were then pooled on an equal wet weight (ww) basis. The egg homogenate individuals and pools from the colonial sites were stored at -40 °C prior to chemical analysis.

### **2.1.3 Egg Pools - Rationale and Validation**

The high cost of sample analysis for organic contaminants required a strategy of not analysing individual samples every year. Such a strategy was brought forward in 1986 and incorporated analysis of pools into the GLHGMP. The strategy required that eggs from each colony monitored were pooled and the pool analysed. To ensure that there was no change in the variation associated with each colony, all the eggs from all the colonies in one of the Great Lakes were individually analysed every fifth year. Thus, over a five year period all colonies would be analysed as individuals (Elliot, 1985; Mineau et al., 1984; Turle and Collins, 1992). Any differences between the means of individual analyses and those of pooled samples are generally less than the normal analytical variation (Turle and Collins, 1992). Having said this, pooled egg homogenates were

selected for the present study in order to effectively represent the levels and trends of current-use FRs in and around the Laurentian Great Lakes.

## **2.2. Chemicals and Standards**

All PBDE congeners and HBCD isomer ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCD, and  $^{13}\text{C}_{12}$ -labeled  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCD) standards (>98% purity) were purchased from Wellington Laboratories (Guelph, ON, Canada) or available from the National Institute of Standards and Technology (Gaithersburg, MD, U.S.A.), which included: BDE-17, -25, -28, -30, -47, -49, -54, -66, -71, -75, -77, -85, -99, -100, -116, -119, -138, -139, -140, -153, -154, -155, -156, -170, -171, -179, -180, -181, -183, -184, -190, -191, -194, -195, -196, -197, -201, -202, -203, -205, -206, -207, -208, and -209 (see Appendices 1 and 2 for full chemical names and structures to which these abbreviations pertain), as well as PBEB, HBB, BTBPE and DBDPE. PBBB, PBAE, TBAE, PBBA, pTBX, TBCO, TBECH were all available from Sigma-Aldrich. Technical-grade DP was purchased form Cambridge Isotope Laboratories (Cambridge, MA, USA). The solvents and chromatographic materials were all of pesticide analysis grade.

## **2.3. Contaminant Extraction**

Briefly, approximately 3 g ww of fresh egg homogenate were retrieved frozen from the CWS specimen archives. Samples were thawed to room temperature and ground with anhydrous sodium sulphate, and then extracted with 175 mL of 50:50 dichloromethane:hexane (DCM:HEX). Internal standards for quantification were spiked to the head of the extraction column, namely BDE-30, BDE-156 as well as  $^{13}\text{C}_{12}$ -labeled-

$\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCD isomers. The extract was then concentrated to 5 mL and a 10 % portion of the eluant was used for gravimetric lipid determination. The sample was then completed to 6.4 mL with 50:50 DCM:HEX, after which lipids were removed by GPC (Norstrom and Simon, 1986) using 50:50 DCM:HEX. Final sample cleanup was performed with 12 mL of 15:85 DCM:HEX using 6 mL, 0.5 g silica (SiOH), Bakerbond disposable solid-phase extraction cartridges (VWR International, Mississauga, ON, Canada). The final volume of the sample extract was accurately reduced to 200  $\mu$ L in TMP.

## 2.4. Determination of Contaminants

### 2.4.1. PBDEs and non-PBDE FRs

Sample fractions were analyzed using an Agilent 6890 gas chromatograph equipped with an Agilent 7683 automated injector and coupled to an Agilent 5793 mass spectrometer working in electron capture negative ionization mode (GC/ECNI-MS). The analytical column was a 15 m  $\times$  0.25 mm  $\times$  0.10  $\mu$ m DB-5 HT fused-silica column (J & W Scientific, Brockville, ON, Canada). A volume of 1  $\mu$ L was introduced to the injector operating in pulsed-splitless mode (injection pulse at 25.0 psi until 0.50 min; purge flow to split vent of 96.4 mL/min to 2.0 min; gas save flow of 20 mL/min at 2.0 min), with the injector held at 240 °C. The GC oven ramping temperature program was as follows (Wellington Laboratories, 2006): initial 100 °C for 2.0 min, 25 °C/min. until 260 °C, 1.5 °C/min until 280 °C, 25 °C/min until 325 °C and hold for a final 7.0 min. The GC to MS transfer line was held at 280 °C, ion source temperature was 200 °C, and the quadrupole temperature was 150 °C.

Quantification of all BDE congeners and current use FRs was achieved via SIM mode for isotopic bromine anions (*m/z* 79 and 81). The *syn*- and *anti*-DP isomers were chromatographically resolved under the same temperature ramping parameters, except isotopic bromine was monitored for the internal quantification standard (BDE-30) while DP (MW 648) isomers were monitored using a separate mass window monitoring the [M + 4]<sup>+</sup> and [M + 6]<sup>+</sup> isotopic chlorine anions (Hoh et al., 2006; Zhu and Hites, 2006).

#### 2.4.2. Isomer-specific HBCD ( $\alpha$ -, $\beta$ -, and $\gamma$ -HBCD)

Pooled herring gull egg extracts were further analysed by LC-electrospray-tandem quadrupole MS (LC/MS(MS)) for HBCD isomers. Quantification of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCD using corresponding <sup>13</sup>C<sub>12</sub>-labeled internal standard permitted for the correction of any matrix-dependent, ionization suppression/enhancement that may have occurred. A solvent transfer from isoctane to methanol was necessary for LC/ESI-MS(MS) analysis. All samples were reduced under nitrogen to dryness, reconstituted in 500  $\mu$ L HPLC-grade methanol, and filtered using Acrodisc LC 13 mm syringe filters (PALL, Mississauga, ON, Canada) with 0.20  $\mu$ m polyvinylidene fluoride (PVDF) membrane. A Waters Alliance 2695 HPLC Pump system (Waters, Mississauga, ON, Canada) was equipped with a Symmetry C<sub>18</sub> reverse phase column (part no. WAT058965) having dimensions 100  $\times$  2.1 mm, 3.5  $\mu$ m. At ambient temperature of about 23 °C, the gradient mobile phase used was water (A), methanol (B), and acetonitrile (C), at a flow rate of 250  $\mu$ L/minute. Initially, the solvent composition was 40/40/20 A/B/C (%) held for 3.00 min, followed by 60/40 B/C for 6.50 min and finally returning back to initial conditions 40/40/20 A/B/C,

held for 8.00 min to allow for equilibration. The total run time was 17.50 min. Mass spectral analysis was achieved via a Waters Micromass Ultima ESI-MS(ESI) operating in the ESI(-) mode. The source parameters were as follows: ionspray voltage -4000 V; curtain gas flow 25 a.u. (arbitrary units); sheath gas flow 35 a.u.; turbo-gas flow and temperature 30 a.u. and 500 °C, respectively. For the determination of α-, β-, and γ-HBCD, the [M-H]<sup>-</sup> fragment to Br<sup>-</sup> transition *m/z* 640.8 to 79.2 was accomplished via the multiple reaction monitoring mode (MRM) (Budakowski and Tomy, 2003).

## 2.5. Structure Confirmation-PBDEs and non-PBDE FRs

Structural confirmation of the current-use FRs was accomplished by GC-HRMS using a VG AutoSpec system with a double focusing-magnetic sector mass analyser, and operated in the electron ionization (EI) mode. The ionization energy was 70 eV, and for which the instrument was operated at a mass resolution of 10,000 or greater. A DB-5 fused-silica column with dimensions 30 m × 0.25 mm × 0.25 μm was used for separation. A 1 μL sample was introduced into the injection port working in splitless mode at 260 °C. The oven temperature program (Norstrom et al., 2002) was 100 °C initially, held for 3 min; 20 °C/min. until 180 °C then 5 °C/min. until 325 °C; final hold time was 4 min. A total of 8-10 ions were monitored for the FRs using SIM mode, which consisted of the molecular ions and most abundant fragments. Isotopic molecular ions of PBEB (PFK lock mass 492.969) were observed by *m/z* [M + 2]<sup>+</sup> 497.6288, [M + 4]<sup>+</sup> 499.6267, [M + 6]<sup>+</sup> 501.6247, and [M + 8]<sup>+</sup> 503.6227; of which the most abundant fragment was a loss of a methyl, revealing the corresponding isotopic fragment ions for [C<sub>7</sub>H<sub>2</sub>Br<sub>5</sub>]<sup>+</sup> of *m/z* 482.6053, 484.6032, 486.6012, and 488.5992, respectively. The molecular ion of HBB

was not as abundant as the fragment ion with the loss of bromine. The isotopic  $[C_6Br_5]^+$  fragment ions for the structural confirmation of HBB were  $m/z$  469.5969, 471.5949, 473.5928, and 475.5908. A PFK lock mass of  $m/z$  480.976 was used for HBB. PBT was identified by monitoring the four most abundant, isotopic ions of the molecular ion  $[C_7H_3Br_5]^+$ : 483.6131, 485.6111, 487.6090, 489.6070 (PFK lock mass, 480.969). Quantification of PBT was achieved by monitoring the internal standard, BDE-30, as a second function: 405.8027 and 407.8006 for  $[C_{12}H_7Br_3O]^+$  (PFK lock, 404.976) and 245.9680 and 247.9661 for  $[C_{12}H_7BrO]^+$  (PFK lock mass, 280.982). The fragment pattern of BTBPE showed an absence of the molecular ion in both the authentic reference standard and egg homogenates; however, the isotopic pattern of a very abundant fragment associated to three bromine atoms  $[C_8H_6Br_3O]^+$ . Verification of the presence of BTBPE in herring gull eggs was accomplished via corresponding retention time and mass spectral ions of this fragment:  $m/z$  355.8041, 357.8021, 359.8001, and 361.7982. The PFK calibration gas lock mass was  $m/z$  380.9760.

Several flame retardant chemicals currently under study were not present in the current herring gull egg homogenates from any of the sites. However, to confirm the presence (or absence) via GC/HRMS-EI, the following ions were monitored: PBBB  $m/z$  564.5289, 566.5268, 568.5248, and loss of bromine:  $m/z$  483.6126, 485.6105, 487.6085 and 489.6065. PBAE was also not detectable but ions  $m/z$  526.6138, 528.6118 and fragment  $[M-Br]^+$  446.7054, 448.7033, 450.7013 were monitored. Similarly, for TBAE, ions monitored were  $m/z$  369.8027, 371.8007 and  $[M-Br]^+$  290.8843 and 292.8824 and ions  $m/z$  404.6942, 406.6922, 408.6902 and  $[M-2Br]^+$  396.7892, 398.7872 for PBBA. The

ions selected for monitoring pTBX were *m/z* 419.7183, 421.7162, 340.7999 and 342.7979. Although both TBCO and TBECH have distinctively unique structures, they both contain the same molecular weight primary fragment loss of bromine. For TBCO and TBECH, analysis was performed at Wellington Laboratories. The ions monitored were *m/z* 425.7652, 427.7632, 429.7612 and 346.8469 and 348.8448 for the [M-Br]<sup>+</sup> fragment. The PFK calibration gas lock mass was *m/z* 380.976 and 480.976 or 330.979 depending on the molecular weight of the above target compounds.

## 2.6. Quality Control and Assurance

Method limits of quantification (MLOQ) were based on the criterion that an analyte response must be 10 times the standard deviation of the noise. For an analyte to be detectable but not quantifiable, the analyte response must be at least 3 times the standard deviation of the noise. Based on samples that had the lowest concentration levels, the MLOQs were estimated by calculating the proportional concentration adjusted to a S/N = 10. In general, the MLOQ for all PBDEs were about 0.05 and 0.1 ng/g ww, excluding BDE-209 and DBDPE for which the MLOQ was about 0.5 ng/g ww and 3.0 ng/g ww, respectively, due to analytical degradation and instability of these highly brominated compounds. Where analytical results were below the MLOQ, a randomly-generated value between zero and the appropriate MLOQ was assigned for statistical analysis purposes. The recovery efficiencies based the BDE-30, -156, and -205 internal standards (IS) ranged from 90 ± 10 %. Little difference in recovery efficiencies were observed for the three ISs, and thus quantification of PBDEs and non-PBDE FRs were based on the iron response of BDE-30. A method blank was included in each sample block

(homogenates from seven locations), due to the likelihood that PBDEs under investigation may have been present in materials used for extraction and analysis. Background presence of BDE-47, -99 and -100 were frequently observed, although levels were less than 1% of contaminant levels reported in samples.

To assess reproducibility (precision) of analyses, a standard reference material (SRM) of double-crested cormorant (*Phalacrocorax auritus*) (DCCO) egg homogenate was used. In 2003, CWS collected 160 individual eggs from double-crested cormorant (DCCO) nests at the Scotch Bonnet Island colony (Lake Ontario), and combined and homogenized to generate a very large sample pool. The DCCO SRM was chosen for the present study since it is reflective of recent, naturally-contaminated PBDEs and other BFRs in a top predator avian species. Along with PCBs and several organochlorine pesticides, 14 PBDE congeners (BDE-17, -28, -47, -49, -66, -85, -99, -100, -138, -153, -154, -183 and -190) including BDE-209 were recently assessed in the DCCO SRM. Although many of the current-use FRs that we describe in this study were not previously analysed in this DCCO SRM, in cases where a non-PBDE FR was quantifiable (HBB, BTBPE or PBT were not detected in DCCO SRM) the precision was assessed. An aliquot of DCCO SRM was analysed with every batch of seven herring gull egg pool samples. For the 14 major PBDE congeners, and other PBDE congeners, and quantifiable non-PBDE BFRs and DPs, good analysis reproducibility was shown by a mean concentration ( $n = 12$  replicates among sample batches) with a variance within 5% RSD. The only current-use, non PBDE FR detected in the egg SRM was DP.

## 2.7 Data Analysis

Doubling times for PBDEs (Chapter 4) measured at each site were calculated using all 15 years spanning 1982 to 2006 ( $n=15$  time points); excluding Fighting Island (1982 to 2005). Chantry Island, Lake Huron (1995 to 2006), was not included in this analysis to maintain time trend consistency among sites. Doubling times were determined (six sites) using the rate of change (slope) of a curve fit from a non-linear, exponential growth regression model using non-transformed PBDE concentration data (Microsoft Excel, data analysis package). In determining the rate of change for various PBDE concentrations in eggs from six colonial sites, the statistical tests for Spearman rank correlation coefficients ( $r_s$ ) and significance ( $p=0.05$ ) were determined using Statistica® (StatSoft, 2005, Tulsa, OK, U.S.A.).

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## CHAPTER 3

### Identification of Current-Use Flame Retardants in the Eggs of Herring Gulls (*Larus argentatus*) from the Laurentian Great Lakes

#### 3.1 Introduction

Several flame retardant (FR) chemicals are used as additives to mainly polymeric materials in commercial products to adhere to stringent fire safety regulations. However, some FRs have faced increased regulation by governments and agencies worldwide due to their potential toxicity and environmental presence (Alaee et al., 2003). One such class of FRs are the PBDEs, which are, at present, the most extensively studied group of additive FRs that have been shown to be ubiquitous environmental contaminants and bioaccumulate in the tissues of wildlife and humans (Hites, 2004). In particular for birds, there are a growing number of reports on PBDEs in top predators (Knudsen et al., 2006a; McKinney et al., 2006; Sellstrom et al., 2004; Verreault et al., 2007) (Table 1.3).

With increasing regulation and phasing-out of production of the commercial usage for some BFR technical mixtures by members of the FR industry (Tullo, 2003), some technical mixtures may likely be replaced by those non-regulated. There are numerous different bromine-based compounds in production and commercial use as additives to polymeric products today (Birnbaum and Staskal, 2004). Two such compounds are BTBPE and DBDPE, both marketed as replacements and alternatives for some PBDE

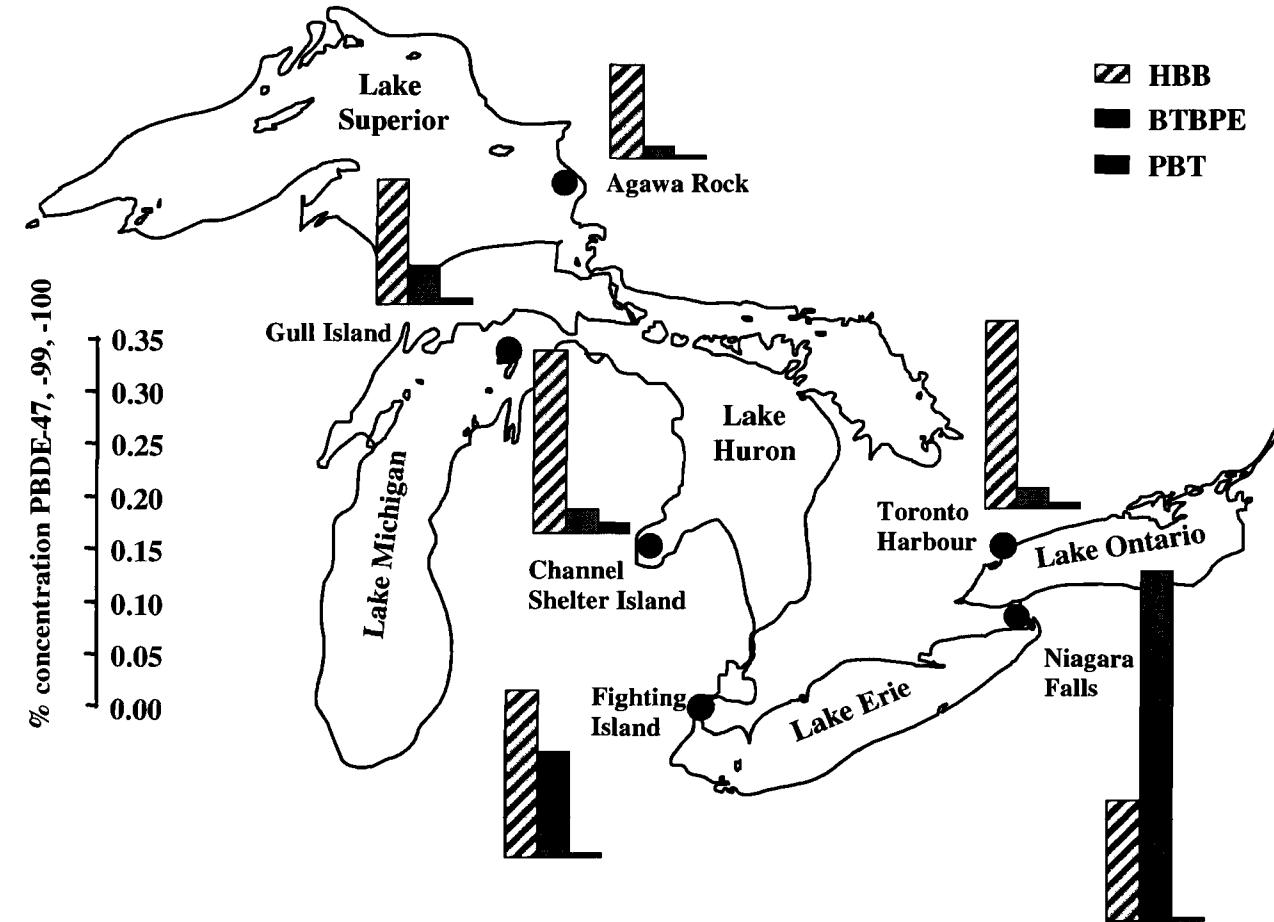
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Gauthier, L. T.; Hebert, C. E.; Weseloh, D. V. C., and Letcher, R. J., 2007. Current-Use Flame Retardants in the Eggs of Herring Gulls (*Larus argentatus*) From the Laurentian Great Lakes. *Environ.Sci.Technol.*, **41**, 4561-4567.

technical mixtures. An increasing number of reports are available on the presence of these BFR alternatives in the environment (Table 1.4). The objective of the present study was to survey, identify/characterize, and quantify as comprehensively as possible in Great Lakes herring gull eggs, (1) all PBDE congeners (mainly hepta- to nona-BDEs and BDE-209) that were not reported in a spatial and temporal assessment of PBDEs from 1981 to 2000 (Norstrom et al., 2002), (2) BDE congeners that are likely debromination products of BDE-209, (3) all non-PBDE BFRs, and (4) DP isomers. A further objective was to qualitatively assess the spatial distribution of all of the above FRs in gull eggs collected at selected colonial sites spanning the Laurentian Great Lakes.

### **3.2 Results and Discussion**

The present hypothesis is that with recent regulations/phasing-out of the PentaBDE and OctaBDE commercial mixtures, several current-use and non-BDE FRs, BDE-209, several hepta- to nona-brominated PBDE congeners would be present in the eggs of colonial herring gulls from the Laurentian Great lakes. Of the 17 non-PBDE FRs monitored, five were quantifiable in the egg pools from six colonies collected in 2004. Also present were DP isomers as well as BDE-209 and up to 17 hepta- to nona-BDE congeners that were not monitored for and thus not detected previously in the eggs of Great Lakes herring gulls assessed from 1981 to 2000 (Norstrom et al., 2002). The data discussed in this chapter is from six herring gull colonies across the Great Lakes (Figure 3.1). A seventh reference colony was later added and will be discussed in Chapter 4 and Chapter 5.



**Figure 3.1.** The concentration ratios of HBB, PBT and BTBPE relative to the sum of dominant PBDE (BDE-47, -100 and -99) congeners (Table 3.1) in herring gull eggs from six representative Great Lakes herring gull colonies.

### 3.2.1 Pentabromethylbenzene

PBEB was investigated in herring gull egg pools and was considered of high interest upon the discovery of this compound in ambient air around the Laurentian Great Lakes (Hoh et al., 2005). The chemical structure of PBEB (Figure 1.3B) is comparable to the primary structures of many other FRs already identified in the present study. Namely containing a phenyl ring ‘backbone’, while combined with a certain degree of bromination, PBEB chemical structure is very similar to PBT and HBB, both of which were also identified in herring gull eggs as well (see Figure 3.1, Sections 3.2.2 and Section 3.2.3). Based on the presence of PBT and HBB, it was hypothesized that PBEB was also bioaccumulative and present in Great Lakes biota.

Analysis of existing herring gull egg homogenate extracts collected in 2004, the presence of PBEB was not confirmed in any samples by analysis using GC/HRMS-EI. An absence of mass spectral bromine fragment response for PBEB was also observed in the procedural blank included in the temporal assessment, when analysed by GC/MS-ECNI. However, the GC/HRMS-EI mass chromatogram revealed a response for PBEB in method blank at comparable abundances to those for the sample extracts. Interestingly enough, PBEB was detected in the solvent (isooctane) that the sample extracts were transferred into prior to analysis (Chapter 2) and is likely the main contributor to the response originally thought to be in the herring gull egg pools. This provides evidence that PBEB, although it is not reported to be produced in North America, is present in materials used in or imported into North America.

Further spatial analysis of non-PBDE FRs revealed that the occurrence of the compound containing bromine that bromide responsive and eluted coincidentally at the retention time for PBEB was present at all six colonies in concert with several PBDE congeners. Elevated levels were observed for the Channel-Shelter Island colony. This led to the hypothesis that an unknown PBDE, not included in the 43 congeners assessed for (Chapter 2, Appendix 1), was present in the pooled herring gull egg homogenates. It was not possible to obtain a full-scan mass chromatogram of this GC peak previously assigned as PBEB; however, SIM analysis of the pooled egg extracts later revealed several characteristic ions pertaining to a PBDE were observed for the GC peak eluting with the same retention time as PBEB. The structural identity of this potential PBDE could not be determined; however it could be categorized as to its degree of bromination, via fragment ions characteristic to a tri- or tetra-brominated PBDE:  $m/z$  405, 245 for the molecular ion and [M or M-Br]<sup>-</sup> and [M-2Br or M-3Br]<sup>-</sup> fragments, respectively.

There are few possibilities that may explain the likely origin of this unknown tetra-BDE. La Guardia et al. (2006) published a report detailing the congener composition of the three widely-used technical FR mixtures. In this study, the authors noted an unknown tetra-BDE that eluted shortly after BDE-28 in the commercial DE-71 technical mixture (Great Lakes Chemical, West Lafayette, IN, U.S.A)(La Guardia et al., 2006). Given the circumstances of wide-spread commercial usage and application of this PBDE technical mixture (mainly in North America), as well as the ubiquitous environmental detection of various PBDE congeners, it could be construed that the unknown tetra-BDE identified in the present herring gull egg pools, is of DE-71 technical mixture in origin.

In the event that this unknown tetra-BDE does not originate from a technical mixture, the presence could also be explained by the fact that herring gulls may be capable of several levels of PBDE debromination from congeners of higher degrees of bromination. As presented in Chapter 4, the degradation/debromination of BDE-209 to lower brominated PBDEs is clearly possible and results in greater bioaccumulation potential with increasing debromination. Several recent reports have indicated that BDE-209 is unstable in the environment. These studies have shown that BDE-209 can metabolically degrade in biota (e.g. fish, rats and birds) (Huwe and Smith, 2007; Stapleton et al., 2004d; Van den Steen et al., 2007b) or undergo abiotic photocatalytic degradation (Ahn et al., 2006; Bezares-Cruz et al., 2004; Soderström et al., 2004) to lower brominated congeners. A study by Stapleton et al. (2004) investigated the *in vivo* debromination of BDE-99 and BDE-183 in common carp (*Cyprinus carpio*); the results indicated significant formation of BDE-47 (tetra-brominated) from BDE-99 (penta-brominated) (Stapleton et al., 2004b). Given the elevated concentrations of tetra- and penta-BDEs in herring gull egg pools (namely BDE-47, -100 and -99), there exists a likelihood PBDEs may also debrominate to yield PBDEs for which authentic reference standards are not presently unavailable. The preliminary screening for PBEB in existing herring gull egg pool extracts also exemplifies the importance of thorough confirmation of FR identification in the environment.

### 3.2.2. Hexabromobenzene

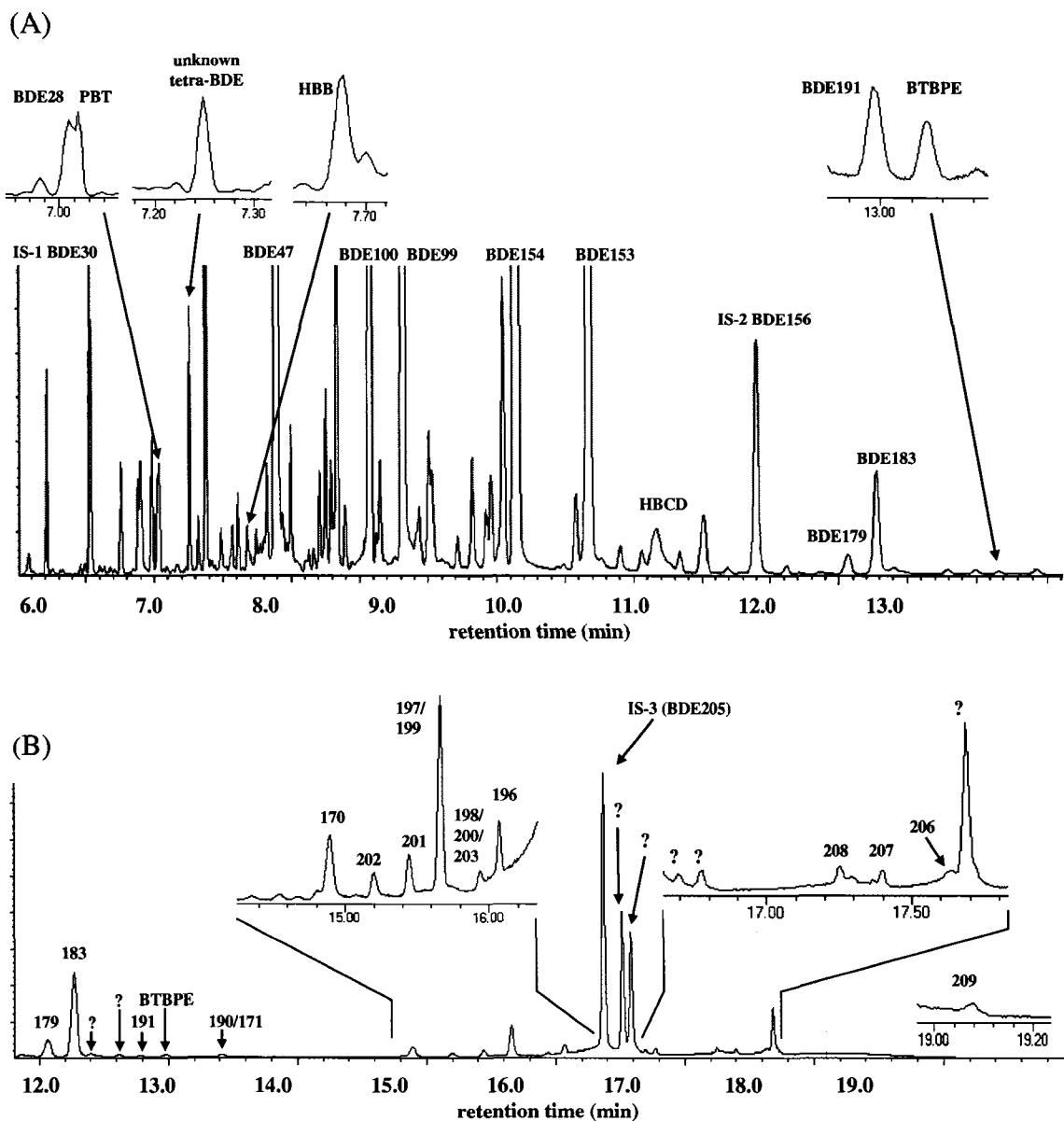
HBB eluted just prior to BDE-47 (Figure 3.2), and was structurally confirmed by GC/HRMS-EI. Among colonies, HBB concentrations in egg pools ranged from 0.24 to 0.53 ng/g ww and were generally the highest relative to other non-PBDE FRs (Table 3.1). Contaminant levels of HBB were <0.2% of the  $\sum_3$ PBDE concentrations.

Historically, HBB has been used as an additive FR in such applications as paper and plastic electronic goods (Watanabe et al., 1986b). Current production figures are not available but HBB is classified as a low production volume FR (1000 to 5000 t) and falls under the European Existing Chemicals Inventory. Information pertaining to the manufacture of HBB is scarce, although Dayang Chemicals (Hangzhou City, China) and Nippon Chemicals (Chiba, Japan) are known to produce this compound. Other sources of HBB in the environment result from thermal degradation of BDE-209 (Thoma and Hutzinger, 1987). The formation of tetra- to hexabromobenzenes were observed during the pyrolysis of DecaBDE formulations; where the C-O bond is cleaved and a bromine radical is transferred, forming the more thermally favourable bromobenzene. In the vicinity of the Great Lakes, a large historical source of this compound was Velsicol Chemical Corporation (now part of Chemtura), St. Louis, MI, which was shut down in the 1980s due to high levels of chemical contaminants in the surrounding region (USEPA, 2006). Widespread presence of HBB in Great Lakes herring gulls may be the result of atmospheric transport combined with cumulative exposure over a long period of time. The subject of bioaccumulation of HBB is controversial and has been suggested that HBB has a low bioaccumulation potential in aquatic food webs due to its large

molecular size, resulting in inefficient membrane permeation (Muller-Herold et al., 2005). However, there are numerous compounds with similar degrees of bromination that are present in herring gull eggs at much more elevated levels (i.e. BDE-153). The reasons for low levels of HBB may be related to low exposure and bioavailability. Nonetheless, HBB has been detected in air (Japanese Government, 2001), sediment (Japanese Government, 2001; Watanabe et al., 1986b), and human adipose tissue in Japan (Yamaguchi et al., 1988b).

### **3.2.3 Pentabromotoluene**

PBT eluted closely with BDE-28 (Figure 3.2), but was quantifiable in the egg pools from all six herring gull colonies using GC/HRMS-EI, although concentrations were the lowest among the non-PBDE FRs that were determined (0.004 to 0.02 ng/g ww) (Table 3.1). PBT was on the order of <0.05% of the  $\sum_3$ PBDE concentration (BDE-47, -99, and -100) (Figure 3.1). PBT has, and currently is, being used as a flame retardant in textiles,



**Figure 3.2.** Representative GC/MS-ECNI mass chromatogram (scale 20 × magnification, scales of insets are 100 × magnification) showing the elution order of (A), newly identified current-use brominated flame retardants and tri- to hepta-BDEs; (B), hepta- to deca-BDEs in the egg pool from Channel-Shelter Island herring gull colony (2004).

**Table 3.1.** Concentrations (ng/g ww) of dominant PBDEs and newly identified, current-use FRs in Herring Gull Egg pools (n = 10-13 individuals) for colonies from the Laurentian Great Lakes (Figure 3.1).

	Herring gull Colony in the Great Lakes					
	Agawa Rocks	Gull Island	Channel Shelter Is.	Fighting Island	Niagara River	Toronto Harbour
<b>HBB</b>	0.44	0.53	0.32	0.41	0.24	0.46
<b>PBT</b>	0.012	0.022	0.017	0.011	0.004	0.013
<b>BTBPE</b>	0.06	0.16	0.04	0.26	0.70	0.04
<b><math>\alpha</math>-HBCD</b>	12	20	n.a.	2.1	4.7	4.6
<b><math>\gamma</math>-HBCD</b>	0.22	0.67	n.a.	n.d.	n.q.	n.q.
<b><math>\Sigma</math>DP</b>	1.7	1.5	2.2	4.2	4.5	2.5
<b><math>\Sigma_{\text{hepta}}</math>-BDE</b>	7.1	7.6	4.9	6.8	11	6.8
<b><math>\Sigma_{\text{octa}}</math>-BDE</b>	3.0	3.3	2.6	2.1	3.6	3.8
<b><math>\Sigma_{\text{nona}}</math>-BDE</b>	0.27	0.12	0.30	0.11	0.52	0.10
<b>BDE-209</b>	n.d.	n.q.	0.14	n.q.	0.21	n.q.
<b><math>\Sigma_7</math>-PBDE</b>	621 (498)	607 (447)	269 (186)	353 (260)	281 (210)	375 (259)
<b><math>\Sigma_{40}</math>PBDE</b>	664	636	281	366	296	392
<b>% lipid</b>	9.4	6.0	7.6	8.0	9.5	10.5

Comprised levels of  $\Sigma_7$ PBDEs (BDE-28, -47, -100, -99, -154, -153 and -183) for representative herring gull colonies in the Great Lakes in 2004, major congeners as reported for BDE levels in 2000 (Norstrom et al, 2002).  $\Sigma_{\text{hepta}}$ -BDE: sum of BDE-171, -180, -181, -183, -184, -190, -191;  $\Sigma_{\text{octa}}$ BDE (BDE-196, -197, -201, -202, -203);  $\Sigma_{\text{nona}}$ BDE (BDE-207 and -208) and  $\Sigma$ DP is reported as total *syn*- and *anti*-DP isomers.  $\Sigma_{40}$ PBDE represents the total number of PBDEs (Chapter 2). Data in parenthesis are the summation of most abundant PBDE congeners as associated with the PentaBDE derived mixture  $\Sigma_{40}$ PBDE (BDE-47, -99 and -100) in egg pools from selected Great Lakes Herring Gull colonies. n.d. = not detected, n.q. = not quantifiable and n.a. = not available

polyester resins, and paint emulsions (Mattsson et al., 1975). Production volume information for PBT is not publicly available; however, it is used and distributed in the United States under the trade name FR-105 (US Patent, 2006) by Ameribrom (Fort Lee, NJ, U.S.A.), a subsidiary of the Dead Sea Bromine Group (ICL Industrial Products, Tel Aviv, Israel) and Chemtura (St. Louis, MI, U.S.A.). These findings are further supported by the recent detection of PBT in a similar, top predatory avian species, the glaucous gull from the Norwegian Arctic (Verreault et al., 2007).

Other sources of PBT in the environment may result from the thermal decomposition of flame retarded high impact polystyrene (HIPS). A study investigating the pyrolysis of currently-used FR DBDPE revealed that PBT and other brominated toluenes were the major byproduct (Jakab et al., 2003). Whether degradation to PBT is feasible in the environment is not known. It has been shown that PBT is a major thermal degradation product of DBDPE (Jakab et al., 2003). Interestingly enough, PBT has recently been detected in air (Hoh et al., 2005), river sediment (Schwarzbauer et al., 2001), and blubber from beluga whales (Gouteux et al., 2006). There are very few reports of this FR in environmental samples, however PBT also has been detected in sediment (Hyotylainen and Kartonen, 2002), as well as at a Swedish wastewater treatment plant (Mattsson et al., 1975).

### **3.2.4 1,2-Bis(2,4,6-tribromophenoxy)ethane**

BTBPE was also detected in the herring gull egg homogenates (Figure 3.2), and the identity was confirmed by GC/HRMS-EI via the characteristic and abundant *m/z* ratio

corresponding to the fragment  $[M-C_6H_2Br_3O]^+$ . Several GC peaks eluted prior to BTBPE and were of much greater intensity (up to 30 $\times$ ). These peaks were not present in the authentic reference standard and present in samples from all six colonies (Figure 3.1, Table 3.1). These unknown peaks may be homologous structures or degradation products of BTBPE containing this fragment. During the initial assessments of the egg homogenate pools, BTBPE coeluted with BDE-191 (15 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m DB5). With further GC optimization using a DB5-HT GC column (15 m  $\times$  0.25 mm  $\times$  0.10  $\mu$ m), we were able to chromatographically resolve BTBPE from BDE-191 (Figure 3.2). BTBPE was present in egg homogenates from all six colonies (Table 3.1), which demonstrated that this FR is widely distributed throughout the Great Lakes. BTBPE concentrations were highest at the Niagara River, Detroit River, and Fighting Island, Detroit River colonies, which may be the result of higher exposure than other Great Lakes colonies.

However, similar to HBB, and PBT, BTBPE concentrations were <0.1% of the  $\sum_3$ PBDE concentrations (BDE-47, -99, -100). BTBPE has been detected in herring gull eggs from North America, as well as glaucous gull eggs from the very remote and distant Norwegian Arctic (Verreault et al., 2007). Other studies of BTBPE have been previously reported in tree bark and atmospheric samples from various sites in North America (Hoh and Hites, 2005; Zhu and Hites, 2006). BTBPE has also been detected in ambient air and sediment samples from various sites in the United States (Hoh et al., 2005). The levels in dated layers of sediment cores collected in Lake Michigan showed rapid increases (doubling time of ~2 years) until 1985, after which concentrations leveled off (Hoh et al.,

2005), which was consistent with a decrease in production volume during the same time frame (IUR, 2002b). Another sediment study from Lake Ontario indicated levels of BTBPE were half of BDE-209 but increased analogously with this high production volume FR. In addition to this, BTBPE has also been found in indoor air at an electronics recycling plant (Sjödin et al., 2001). Very recent studies have reported BTBPE in fish from Lake Winnipeg (Canada) (Law et al, 2006), as well as in eggs from Northern Fulmars (*Fulmarus glacialis*) from the Faroe Islands (Karlsson et al., 2006).

### 3.2.5 Hexabromocyclododecane

Unlike the current-use, non-PBDE FRs discussed previously, HBCD isomers are classified as a high volume production FR and are known to be a global contaminant (Covaci et al., 2006). Similar to PBDEs, HBCD isomers are additive FRs and exhibit similar pathways of entering the environment. Few studies have examined contaminant levels of HBCDs in avian species. Reports of HBCDs in the eggs of top predator avian species are rare and include peregrine falcon (*Falco peregrinus*) from Sweden (Lindberg et al., 2004) and guillemot (*Uria aalge*) from areas around the Baltic Sea (Sellstrom et al., 2003b).

In the present herring gull egg pools,  $\alpha$ - and  $\gamma$ -HBCD were quantifiable whereas the  $\beta$ -HBCD isomer was not detected (<0.01 ng/g ww) (Table 3.1). This is consistent with reports for other wildlife samples where  $\alpha$ -HBCD was the most pronounced isomer, which is highly contrasting to the technical product where  $\gamma$ -HBCD is the dominant isomer (Covaci et al., 2006). This difference in isomer profiles between gulls and the

technical mixture is thought to be the result of bioisomerization that frequently occurs in biota (Covaci et al., 2006). The sum of the  $\alpha$ - and  $\gamma$ -HBCD concentrations ranged from 0 to 4.5% of the  $\sum_3$ PBDE concentrations (Table 3.1). The two highest concentrations of  $\alpha$ -HBCD in the gull eggs were found at the two most western Great Lakes sites, Agawa Rocks and Gull Island colonies (20 and 12 ng/g ww, respectively). Elevated concentrations of  $\alpha$ - and  $\gamma$ -HBCD isomers at Gull Island may be reflective of the proximity of urban sources located on Lake Michigan, namely, Chicago. High levels in eggs from the Agawa Rocks colony may not be reflective of regional environmental exposure. Gulls in the northern Great Lakes may undertake post-breeding movements with the onset of winter (Hebert, 1998). Increasing ice cover may limit their access to aquatic prey; therefore, southern Lake Michigan is a likely destination for Agawa Rocks birds because it never freezes over completely. Any spatial trend interpretation for the HBCD isomer data, and equally for all FRs in the present study, must be considered with caution as they are based on data from single pools for each colony. The spatial distribution of FR contaminants may also be affected by fluctuations in diet composition as has been reported for herring gulls using stable nitrogen isotopes and fatty acids as ecological tracers (Hebert and Weseloh, 2006a).

### 3.2.6 Dechlorane Plus

The flame retardant DP was recently reported to be present in air, sediment, and fish from the Great Lakes (Hoh et al., 2006; Qiu et al., 2007). Both DP isomers appear, therefore, to bioaccumulate in the aquatic food web of the Great Lakes, and as a consequence the diet is a likely exposure route for herring gulls and to their eggs (Table 3.1). The highest

$\Sigma$ DP concentration (4.5 ng/g ww) was found at the Niagara River colony. This is consistent with the results of Hoh et al. (2006), where the single highest  $\Sigma$ DP air concentration was found at Sturgeon Point, Lake Erie. Coincidentally, Sturgeon Point is about 50 km south of the manufacturing plant of DP, located in Niagara Falls, NY. The most western colony in this study is Agawa Rock, Lake Superior, where a slightly higher level of  $\Sigma$ DP was measured with respect to Gull Island. A preliminary spatial trend for  $\Sigma$ DP appears to show an east to west decrease in concentration, with the exception of Toronto Harbor, Lake Ontario. This follows the spatial distribution of DP in the air particulate phase reported by Hoh et al. (2006), where higher DP concentrations were observed at the eastern Great Lakes sites compared to western sites.

The ratio of *syn*-DP and *anti*-DP was also calculated at the six herring gull colonies. The *anti*-DP fraction, as a function of the total DP area count, observed in the reference standard (0.74 to 0.77) was similar to that of commercial DP (0.75 to 0.80) (Hoh et al, 2006). At 60% of the colonies, the *anti*-DP fraction in the egg pools ranged from 0.72 to 0.77. This agrees with the *anti*-DP fraction in the greater portion of atmospheric samples (Hoh et al, 2006), also suggesting that the main source is from the commercial DP. Interestingly, the two colonies furthest from the manufacturing plant, in Niagara Falls, NY, contained *anti*-DP fractions identical to that of the commercial mixture, which is the opposite to that found in the atmospheric DP study (Hoh et al, 2006). In addition to this, the remaining 40% of the colonies that had low *anti*-DP fractions, Toronto Harbour and Detroit River (0.55 and 0.67 respectively), were those in closest proximity to the manufacturing plant, where levels were the highest of all six herring gull colonies. These

differences may be related to annual fluctuations in input of DP into the Great Lakes ecosystem, as well as a degree of transformation over long distances. The only other reported study of DP in biota demonstrated an *anti*-DP ratio of  $0.60 \pm 0.5$  for Lake Erie walleye (*Sander vitreum*), where it was suggested that the bioavailability or biodegradation (metabolism) of the two isomers may be different (Hoh et al, 2006).

### 3.2.7. 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane

In the process of monitoring for currently-used FRs in herring gull eggs, a pair of chromatographic responses were observed eluting early in the temperature program. The retention time of these unknown bromine-containing compounds corresponded to that of the 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (TBECH) technical mixture, previously obtained as a reference material. Structure confirmation was not possible under the GC/HRMS-EI conditions applied for other FRs previously discussed, and hence the analysis was performed using an alternate system and different parameters at Wellington Laboratories (Guelph, ON, Canada). It was revealed that TBECH was present in both the herring gull eggs, as well as in the DCCO SRM; however TBECH was also detected in the method blank and contributed to a portion of the response from each egg sample. These findings suggested that the response in eggs was likely carryover from the extraction and workup procedure. Interestingly enough, when analysed by GC/MS-NCI, there was no signal in or around the retention region corresponding to TBECH in the method blank. In addition, the bromine response for the unknown peaks tentatively identified as TBECH, is considerably abundant in the egg samples. A possible explanation for this discrepancy in analysis may lie in that the detection of

TBECH in the blank (as well as the egg samples) is coming from the method of analysis, i.e. from the GC/HRMS-EI instrumentation. Since this is a currently-used FR, the possibility exists that TBECH may be available in materials composing the GC/HRMS-EI method of analysis. The present screening for TBECH remains a conundrum, however further investigation into the identification of this currently-used FR is necessary.

### **3.2.8. Polybrominated Diphenyl Ethers**

Also completed in this study was a comprehensive identification and quantification of numerous PBDE congeners ranging from tri- to nona-BDE and BDE-209. In a previous 1981-2000 assessment of PBDEs in Great Lakes herring gull eggs (Norstrom et al., 2002), BDE-209 was not detected, and with the exception of BDE-183, congeners determined were of the tetra- to hexa-brominated variety, and the dominant PBDE congeners (in terms of concentration) were those derived from the PentaBDE mixtures, i.e., BDE-47, -99, and -100 (Table 3.1). Herring gull colonies located at Agawa Rocks and Gull Island show the two highest levels for total- $\sum$ PBDEs and  $\sum_7$ PBDEs in eggs collected in 2004 (Table 3.1). These sites are among the fifteen colonies reported to have the highest levels of  $\sum_7$ PBDE for eggs that were collected in 2000, which were shown to have increased exponentially over the period of 1981-2000 (Norstrom et al., 2002). However, comparing the 2000 levels in Norstrom et al. (2002), to the 2004 levels for the same six sites in the present study, the trend appears to be that  $\sum_7$ PBDE concentrations have decreased considerably. This apparent decline may be consistent with the corresponding regulation/phasing-out of PentaBDE and OctaBDE commercial mixtures.

BDE-209 was detected (<0.1 ng/g ww MLOQ) at four and quantifiable at two of the six herring gull colonies where eggs had been collected (Table 3.1). Quantifiable concentrations were determined to be 0.14 and 0.21 ng/g ww at Channel-Shelter Island and the Niagara River, respectively. However, up to a total of 17 hepta- to nona-BDE congeners (Table 3.1, Figure 3.2) were detected in the present 2004 egg pools. Five octa-BDE congeners eluted as single peaks with baseline separation. BDE-198, -200, and -203 coeluted (Figure 3.2)(Appendix 1 and Appendix 2), while BDE-199 was unaccounted for but may have coeluted with BDE-197 (Wellington Laboratories, Guelph, ON, Canada; personal communication). Two bromine-containing compounds eluted in the region of octa-BDEs (Figure 3.2) and were speculated to be BDE-194 and 195, however, it was later confirmed that the identities are unknown. In general, BDE-197/199 was the most dominant octa-BDEs in the gull eggs. Of the baseline-separated nona-BDEs in the gull eggs, BDE-207 was the most dominant and extensively detected. BDE-206 was present below the MLOQ in some samples and coeluted with a much larger unknown bromine-containing compound (Figure 3.2). It could be hypothesized that this unknown peak, and several other unidentified late eluters, are currently-used FRs for which no reference standard is available, i.e. brominated trimethyl phenyl indanes (Figure 1.3). The  $\Sigma_{\text{hepta-}}$  BDE,  $\Sigma_{\text{octa-}}$  BDE, and  $\Sigma_{\text{nona-}}$  BDE concentrations ranged from 1.4 to 5.2%, 0.8 to 1.7 %, and 0.03 to 0.25 %, respectively, relative to the dominant, BDE-47, -99, and -100 concentrations ( $\Sigma_3\text{PBDE}$ ) (Table 3.1). Furthermore, sum of all hepta- to nona-BDE concentrations relative to the total- $\Sigma_{40}\text{PBDE}$  concentrations ranged from 1.6 to 5.1% (Table 3.1). This demonstrates that relative to PBDEs, in general, hepta- to nona-BDE

congeners are quantitatively more important relative to the non-PBDE BFRs in herring gull eggs.

Several octa- and nona-BDE congeners have been demonstrated to be sequentially formed through debromination of BDE-209 by means of metabolic pathways in fish, birds, and laboratory rats (Huwe and Smith, 2007; Soderström et al., 2004; Stapleton et al., 2004c; Van den Steen et al., 2007b). For example, in a first stage degradation, the meta-debromination of BDE-209 results in BDE-207 formation (Van den Steen et al., 2007b). Also reported were relatively high muscle and liver concentrations of BDE-197 (product originating via di-*meta*-debromination of BDE-209) (Appendix 1 and Appendix 2) in passerine birds, although BDE-208 and particularly BDE-207, which are *para*- and *meta*-debromination products, respectively, of BDE-209, were the most abundant congeners. These findings suggest that multiple degradation products of BDE-209 are likely formed in Great Lakes herring gulls, but also may have bioaccumulated (at least in part) via the herring gull food web, and that these highly brominated congeners are maternally deposited during egg formation.

### **3.3. Conclusions**

These findings have confirmed that several, newly identified PBDE congeners are present in herring gull egg pools. In addition, non-PBDE FRs that are currently in commercial and industrial use are present in herring gull egg pools spanning sites across the Great lakes, and transferred *in ovo* to their eggs. Levels and trends of the previously discussed FRs are to be further investigated in Chapter 4 (PBDEs) and Chapter 5 (non-PBDEs).

Also detected, but could not confirm the identity of, numerous other persistent bromine-containing substances in the eggs of herring gulls (Figure 3.2). The identity of these unknown, bromine-containing compounds could possibly be anthropogenic in origin, abiotic degradation products accumulated in the gulls, and/or metabolic debromination products of anthropogenic FRs for which authentic reference standards are not presently available.

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## CHAPTER 4

### **Emergence and Temporal Trends of Decabromodiphenyl Ether Flame Retardant and Lower Brominated Congeners in Herring Gull Eggs From the Laurentian Great Lakes**

#### **4.1 Introduction**

Several formulations of polybrominated diphenyl ethers (PBDEs) have been used as fire-retarding additives to industrial and household materials for nearly three decades (Chapter 1). Of the three PBDE technical mixtures, Penta- and OctaBDE were widely used until recently, but strict regulations have been imposed on commercial usage and in 2004 were withdrawn for commercial use in Europe (Chapter 1). These PBDE products are also currently facing legislative regulation and restriction in North America. For example, in Canada, PentaBDE and OctaBDE mixtures were voluntarily phased out in 2006 and are no longer available commercially. The increasing regulation and phasing out of PentaBDE and OctaBDE mixtures has been in response to their persistence and bioaccumulation in the environment, and the known and potential toxicity of some individual congeners such as BDE-47 and BDE-99 (Kuriyama et al., 2007b; Muirhead et al., 2006). In contrast, presently there are no restrictions worldwide on the DecaBDE commercial mixtures, which largely dominate the demand and use of PBDEs as an additive flame retardant in the global market.

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The continued use of BDE-209 is highly controversial as it has been shown to persist and bioaccumulate in the tissues of aquatic feeding wildlife at low to non-detectable levels. In contrast to congeners present in the PentaBDE and OctaBDE technical mixtures, it is assumed that BDE-209 is not easily absorbed through the gut. Its bioavailability is assumed to be low because of its high molecular weight (959 amu) and hydrophobicity ( $\log K_{ow} = 10$ ) (IPCS, 1994). Based on these characteristics, DecaBDE does not appear to meet traditional criteria used to identify persistent, bioaccumulative and inherently toxic (PB&T) substances (Muir and Howard, 2006), as presented in Chapter 1. There is also considerable controversy regarding the environmental stability and degradation of BDE-209. For example, captive/dietary exposure studies with fish and birds showed that BDE-209 degraded to lower brominated congeners (Stapleton et al., 2004a; Stapleton et al., 2006b; Van den Steen et al., 2007a). In Chapter 3, quantifiable levels were found of BDE-209, as well as hepta- to nona-BDEs, several of which could only be sourced from the debromination of BDE-209, in eggs collected in 2004 from herring gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America. BDE-209 and nona- and octa-BDE congeners have also been reported in eggs of sea and top predatory birds from northern Norway, Svalbard, Greenland and Sweden (Herzk et al., 2005; Knudsen et al., 2006b; Lindberg et al., 2004; Verreault et al., 2007; Vorkamp et al., 2005).

There is increasing experimental evidence that PBDE exposure is detrimental to wildlife health. For example, whole organism studies with fish and birds exposed to individual congeners (e.g., BDE-47, -99 and -209) and PentaBDE mixtures, found impacts on sex and thyroid hormones as well as effects on the modulation of liver enzyme activity,

thyroid hormone immunotoxicity and neurological development (Birnbaum and Staskal, 2004; Darnerud et al., 2001a; Kierkegaard et al., 2006). Furthermore, there are several recent reports showing that BDE-209 is unstable in the environment. BDE-209 has been shown to metabolically degrade in biota (e.g. fish, rats and birds) (Huwe and Smith, 2007; Stapleton et al., 2004a; Stapleton et al., 2006b; Van den Steen et al., 2007a) or undergo abiotic photocatalytic degradation (Ahn et al., 2006; Bezares-Cruz et al., 2004; Soderström et al., 2004) to lower brominated congeners. A postulation that continues to be controversial is that BDE-209 degradation leads to sequentially less brominated PBDE congeners, and ultimately to highly bioaccumulative and potentially more toxic congeners such as BDE-47, -99 and -100 (Kuriyama et al., 2007b; Muirhead et al., 2006).

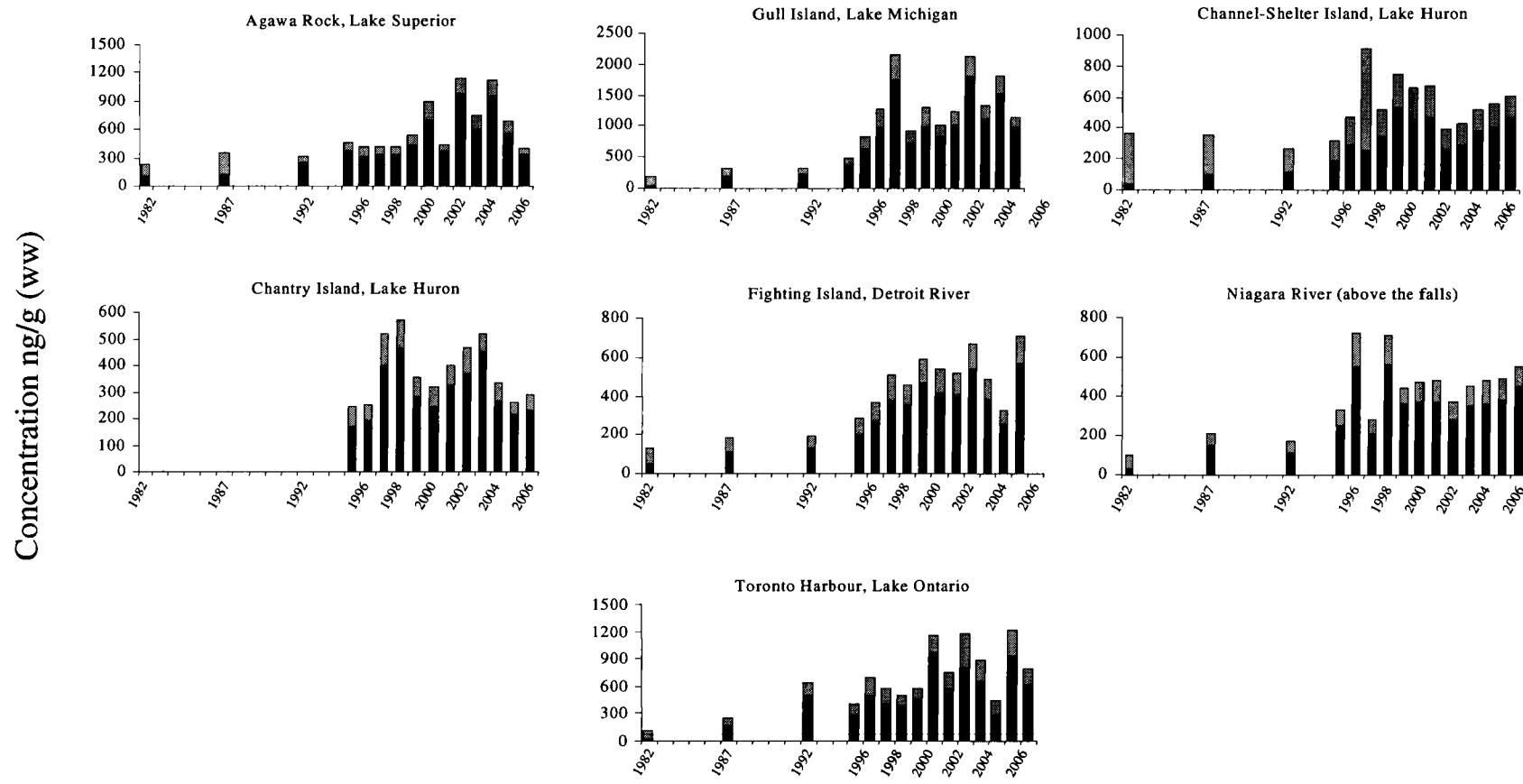
Norstrom *et al.* (2002) recently showed that PBDEs, mainly PentaBDE-derived congeners (BDE-47, -99, and -100), increased exponentially in herring gull egg pools over the period 1981 to 2000 (Norstrom et al., 2002); however, in Chapter 3, it was observed that relative to 2000, PBDE levels appear not to have increased as of 2004 (Chapter 3). The objective of the present study was to investigate the temporal trends of all possible PBDE congeners, including BDE-209 that could be quantified in herring gull egg pools from colony sites across the Great Lakes (Chapter 3).

## 4.2 Results and Discussion

### 4.2.1 Temporal and Spatial Trends – Established PBDEs

Of the 43 PBDE congeners monitored, 39 congeners were identified and thus determined in the present study. For all sampling sites, six congeners constituted  $94 \pm 2\%$  of the  $\sum\text{PBDE}$  concentrations measured in the 2006 herring gull egg pools (Table 1), and were those derived from the PentaBDE (BDE-47, -99 and -100) and OctaBDE (BDE-153, -154 and-183) commercial mixtures. BDE-47, 99, and -100 constituted,  $24 \pm 5\%$ ,  $36 \pm 6\%$  and  $14 \pm 2\%$ , respectively, of the  $\sum\text{PBDEs}$  and BDE-153, BDE-154/BB-153 and BDE-183 constituted  $9 \pm 2\%$ ,  $7 \pm 2\%$ ,  $1.1 \pm 0.4\%$  respectively.

For the most recent year studied (2006), concentrations of  $\sum\text{PBDEs}$  in herring gull egg pools from all seven Great Lakes sites (Figure 1.4) ranged from 321 to 1191 ng/g ww (Table 4.1). The highest concentration for  $\sum\text{PBDEs}$  was found at the remote Gull Island colony located in northern Lake Michigan.  $\sum\text{PBDE}$  concentrations at the remaining remote colonies (Chantry Island and Agawa Rocks) ranged from 323 to 419 ng/g ww (Table 4.1).  $\sum\text{PBDE}$  concentrations in egg pools collected at colonies close to centers of industrialization/urbanization (Channel/Shelter Island, Saginaw Bay; Fighting Island, Detroit River; Niagara River; and Toronto Harbour, Lake Ontario) ranged from 591 to 862 ng/g ww (Table 4.1). The greater concentrations at these colonies compared to Chantry Island and Agawa Rocks likely reflected sources associated with industrial/urban activities. Higher concentrations at Gull Island may have reflected post-breeding movements of these birds exposing them to high PBDE concentrations on their wintering grounds in southern Lake Michigan (see below).



**Figure 4.1.** Temporal trends between 1982 and 2006 for major PBDEs (grouped separately: BDE-47, -99, -100 and BDE-153, -154/BB153, -183) in herring gull egg pools collected from seven herring gull colonies on the Laurentian Great Lakes. Major PBDEs grouped separately: black bars,  $\Sigma$ BDE-47, -99, and -100 and grey bars,  $\Sigma$ BDE-153, -154/BB153, and -183.

**Table 4.1.** Concentrations of PBDE flame retardants in herring gull eggs (pools of  $n = 10$  to 13 individuals) collected in 2006 from seven colonies in the Laurentian Great Lakes (see Figure 1.4).

	Agawa Rocks, L. Superior	Gull Is., L. Michigan	Channel-Shelter Is., L. Huron	Chantry Is., L. Huron	Fighting Is., Detroit R.*	Niagara River	Toronto Harbour, L. Ontario
$\Sigma_{\text{tri}}\text{BDE}$	1.5 (0.40)	2.9 (0.20)	4.1 (0.62)	1.8 (0.60)	1.2 (0.20)	2.1 (0.40)	7.1 (0.80)
$\Sigma_{\text{tetra}}\text{BDE}$	128 (30)	274 (23)	122 (19)	91 (28)	127 (17)	143 (24)	228 (26)
$\Sigma_{\text{penta}}\text{BDE}$	211 (50)	708 (59)	369 (56)	147 (46)	447 (59)	322 (54)	391 (45)
$\Sigma_{\text{hexa}}\text{BDE}$	60 (14)	168 (14)	137 (21)	51 (16)	145 (19)	92 (16)	174 (20)
$\Sigma_{\text{hepta}}\text{BDE}$	6.4 (1.5)	8.0 (0.70)	9.2 (1.4)	6.9 (2.1)	14 (1.8)	10 (1.7)	17 (2.0)
$\Sigma_{\text{octa}}\text{BDE}$	4.0 (1.0)	5.6 (0.47)	5.6 (0.85)	5.4 (1.7)	13 (1.7)	8.6 (1.5)	19 (2.2)
$\Sigma_{\text{nona}}\text{BDE}$	1.9 (0.5)	4.0 (0.34)	3.7 (0.56)	3.4 (1.1)	2.3 (0.31)	3.2 (0.54)	8.5 (1.0)
BDE209	6.1 (1.5)	20 (1.7)	10 (1.5)	14 (4.5)	4.5 (0.60)	9.4 (1.6)	18 (2.1)
$\Sigma_3\text{PBDE}$	334 (80)	973 (82)	474 (72)	233 (72)	563 (75)	454 (77)	607 (70)
$\Sigma_7\text{PBDE}$	396 (95)	1140 (96)	610 (92)	288 (89)	714 (95)	550 (93)	791 (92)
$\Sigma\text{PBDE}$	418	1191	660	321	754	591	862
$\Sigma_{\text{Br8}}/\Sigma_{\text{Br8-10}}$	$0.44 \pm 0.18$	$0.55 \pm 0.14$	$0.52 \pm 0.17$	$0.46 \pm 0.16$	$0.52 \pm 0.17$	$0.56 \pm 0.15$	$0.57 \pm 0.18$
$\Sigma_{\text{Br9}}/\Sigma_{\text{Br8-10}}$	$0.20 \pm 0.06$	$0.26 \pm 0.05$	$0.24 \pm 0.05$	$0.20 \pm 0.02$	$0.14 \pm 0.05$	$0.14 \pm 0.03$	$0.15 \pm 0.08$
% lipid	7.9	10.7	7.7	8.7	8.8	8.6	9.4

Sum concentrations of the seven major congeners ( $\Sigma_7\text{PBDE}$ ) BDE-28, -47, -100, -99, -154/BB-153, -154 and, -183) and  $\Sigma_3\text{PBDE}$  (BDE-47, -99, and -100) summation of most abundant PBDE congeners as associated with the PentaBDE-derived mixture, based on those reported in Norstrom *et al.*(2002). Data in parentheses are the percent contribution of indicated PBDE homologue groups as a percentage of the total  $\Sigma\text{PBDEs}$ . tri-BDE (BDE17, 25, 28); tetra-BDE (BDE49, -54, -47, -66, -71, -75, -77); penta-BDE (BDE85, -99, -100, -116, -119); hexa-BDE (BDE-138, -139, -140, -155, -153, -154/BB-153); hepta-BDE (BDE-170, -171, -179, -180, -181, -183, -184, -190, -191; octa-BDE (BDE-196, -197, -201, -202, -203); nona-BDE (BDE-207 and -208).  $\Sigma_{\text{Br8}}/\Sigma_{\text{Br8-10}} =$  ratio total octa-BDEs with respect to sum octa-BDEs, nona-BDEs and BDE209 over the period 1995 to 2006,  $\pm$  standard deviation (similarly for  $\Sigma_{\text{Br9}}/\Sigma_{\text{Br8-10}}$ ). \* Data for Fighting Island are from eggs collected in 2005.

Temporal trends of the concentrations of major PBDEs (namely those congeners associated with the PentaBDE and OctaBDE commercial mixtures) have changed dramatically compared to those reported in 2000 (Norstrom et al., 2002); although tetra-through hepta-BDE congeners continue to be of high environmental relevance in 2006 (Figure 4.1, Table 4.1). Essentially, the exponential increases reported for PentaBDE derived PBDEs over the 1981 to 2000 period have ceased. Doubling times of major PBDEs over the period of 1981 to 2000 were previously reported to be 2.6 and 3.1 years (Norstrom et al., 2002) for Gull Island (Lake Michigan) and Channel-Shelter Island (Lake Huron), respectively. Re-analysis of selected samples (1982, 1987, 1992 and 1995-2000) analysed by Norstrom *et al.*(2002), reproduced sum concentrations of BDE-47, -99, -100 and BDE-153, -154/BB-153 and -183 (Figure 4.1), and thus we were able to calculate comparable doubling times for PBDE concentrations over the period of 1982-2000. However, for  $\Sigma$ PBDE concentrations of BDE-47, -99, and -100, and BDE-153, -154, and -183 over the period of 2000-2006, levels are not increasing, but rather appeared to be stabilizing or perhaps are decreasing gradually (Figure 4.1).  $\Sigma_3$ PBDE concentration (BDE-47, -99, -100) doubling times over the 1982-2006 period were 4.9 ( $r_s = 0.80$ ,  $p = 0.0004$ ) and 7.4 ( $r_s = 0.76$ ,  $p = 0.002$ ) years for Gull Island (Lake Michigan) and Channel-Shelter Island (Lake Huron), respectively, and were comparable with doubling times of 6.4 to 8.7 years for the other sites (Table 4.2). This is substantially longer than the doubling times of 2.6 and 3.1 years for two of the same sites, Channel Shelter Island and Gull Island, respectively reported over the 1981 to 2000 period by Norstrom *et al.*(2002).

**Table 4.2.** Calculated doubling times for PBDEs measured at representative herring gull colonies over the period of 1982 to 2006 (n = 15 time points) and regression results, Spearman rank coefficient ( $r_s$ ) and significance ( $p$ ). Statistical tests were deemed significant at  $p < 0.05$ .

		Agawa Rocks, L. Superior	Gull Is., L. Michigan	Channel-Shelter Is., L. Huron	Fighting Is., Detroit R. *	Niagara River	Toronto Harbour L. Ontario
$\Sigma_3$ -BDE	$r_s$	0.71	0.80	0.76	0.78	0.78	0.66
	$p$	0.004	0.0004	0.002	0.002	0.002	0.007
$\Sigma_{\text{octa}}$ -BDE	$T_d$	8.7	4.9	7.4	7.3	7.9	6.4
	$r_s$	0.43	0.63	0.28	0.64	0.73	0.66
$\Sigma_{\text{nona}}$ -BDE	$P$	0.1	0.02	0.3	0.02	0.003	0.008
	$T_d$	11	5.7	6.9	3.0	3.2	3.0
BDE-209	$r_s$	0.66	0.78	0.59	0.58	0.70	0.95
	$p$	0.008	0.0006	0.02	0.03	0.004	0.00001
	$T_d$	3.9	2.6	5.3	3.5	2.6	2.4
	$r_s$	0.63	0.77	0.69	0.57	0.55	0.63
	$p$	0.02	0.0008	0.01	0.03	0.05	0.002
	$T_d$	2.8	2.5	3.0	2.5	2.6	2.1

$\Sigma_3$ -BDEs,  $\Sigma_{\text{octa}}$ -BDEs and  $\Sigma_{\text{nona}}$ -BDEs are the same as previously delegated in Table 4.1.

$T_d$  = Doubling time for the period of 1982 to 2006, excluding Fighting Island, Detroit River (1982-2005).

\* Data available for 1982 to 2005 for Fighting Island, Detroit River;

The declining importance of the BDE-47, -99 and -100 in Great Lakes herring gull eggs is likely in response to increased regulation and phasing-out of PentaBDE and OctaBDE derived PBDEs. The only North American manufacturer of PBDEs ceased production of the PentaBDE and OctaBDE commercial mixtures in December 2004, these two commercial mixtures had limited and declining use in recent years (BSEF, 2006). Decreasing ecosystem inputs of PentaBDE and OctaBDE derived PBDEs from human use is being manifested as a rapid response and decline in the loading and accumulation in Great Lakes food webs. Temporal trends for PBDEs in suspended sediments collected from the Niagara River over 1980 to 2002 showed levels of BDE-47 and -99 were generally decreasing from around 1996 to 2002, despite increasing temporal trends over the period of 1980 to mid 1990s (Marvin et al., 2007). The general decline in the production and use of PentaBDE and OctaBDE formulations worldwide is consistent with PBDE temporal trend declines reported elsewhere. For example, in common guillemot (*Uria aalge*) eggs from the Baltic Sea (Sellstrom et al., 2003a), levels between 1969 and 2001 peaked during the mid-1980s and then rapidly decreased during the 1990s. Exhaustive literature assessments reveal that there is a lack of temporal trend data in wildlife and human tissues for PBDEs post 2000, thus further comparisons are not possible.

Although temporal trends of PBDE concentrations have changed considerably since 2000, the relative differences among sites of major PBDEs have not changed much between 2000 and 2006 (Figure 4.1). In 2006, PBDE levels ranked in decreasing order were Gull Island > Toronto Harbour > Detroit River > Channel-Shelter Island > Niagara

River > Agawa Rocks > Chantry Island. In 2000, PBDE levels ranked in decreasing order were Gull Island > Toronto Harbour > Agawa Rocks > Channel-Shelter Island > Detroit River > Niagara River > Chantry Island. These similarities likely reflect the apparent basin-wide stabilization or decrease in major PBDEs levels over the period 2000 to 2006 (Figure 4.1). The difference in rank order for PBDE levels at the Agawa Rock colony in 2006 may have reflected inter-year differences in post-breeding movements for northern Great Lakes herring gulls as influenced by winter severity (see below) (Hebert, 1998).

The congener patterns in 2000 eggs (mean  $\pm$  standard deviation, N = 6) for tri-BDEs, 0.5  $\pm$  0.2%, hexa-BDE, 17  $\pm$  3% and hepta-BDEs, 1.6  $\pm$  0.5% of  $\Sigma$ PBDEs were similar to those reported in Norstrom *et al.* (2002), where tri-BDEs, 0.6  $\pm$  0.1%, hexa-BDE, 15  $\pm$  1% and hepta-BDEs, 1.8  $\pm$  0.6% of  $\Sigma$ PBDEs. However, the congener patterns in 2006 egg pools had changed considerably relative to 2000. In this study, tetra-BDEs and penta-BDEs comprised 25  $\pm$  4% and 52  $\pm$  6%, respectively, of  $\Sigma$ PBDEs in 2006. Previously, tetra-BDEs and penta-BDEs constituted 43  $\pm$  1% and 39  $\pm$  1%, respectively, of  $\Sigma$ PBDE levels (Norstrom et al., 2002). This difference between the tetra- and penta-BDEs could likely be a result of the dominating presence and dramatic increase and post-2000 occurrence of BDE-209 and higher brominated PBDEs presented current study.

#### **4.2.2 Temporal and Spatial Trends: Emerging PBDEs**

In addition to the six major PBDEs (BDE-47, -99, -100, -153, -154/BB-153, and -183), the majority of the thirty-five congeners that were determined was largely composed of numerous and newly identified congeners with a greater degree of bromination (e.g.

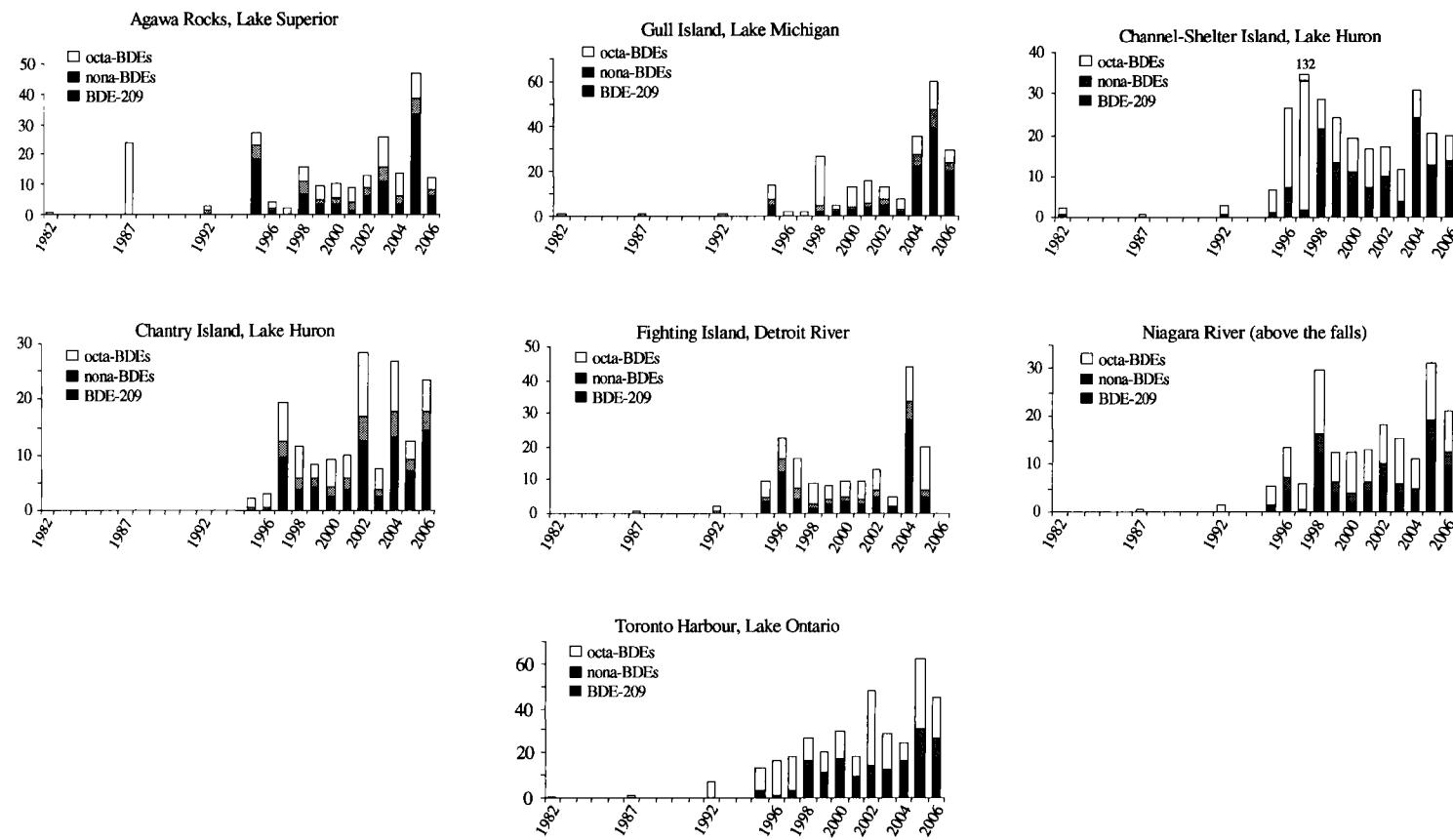
hepta- to nona-BDEs, and BDE-209) (Chapter 3). In 2006, BDE-209 concentrations in Great Lakes herring gull egg pools ranged from 4.5 to 20 ng/g ww and contributed 0.6 to 4.3% of  $\sum$ PBDE concentrations (Table 4.1). The highest concentration of BDE-209 measured in 2006 was 20 ng/g ww from Gull Island, Lake Michigan and was comparable to the second highest level measured from Toronto Harbour, Lake Ontario, a highly industrialized/urbanized region. Gulls from the northern Great Lakes are known to undertake post-breeding movements (Hebert, 1998) and may partially explain the elevated levels at Gull Island and Agawa Rocks. These birds could have over-wintered at southerly urban centers such as Milwaukee and Chicago. A similar situation may explain the elevated levels of BDE-209 from the Chantry Island colony, as gulls from this location are prone to winter in more south-easterly locations such as eastern Lake Erie and Toronto Harbour, Lake Ontario (Hebert, 1998).

In addition to BDE-209, sixteen novel hepta- (BDE-170, -179, -180, -181, -184, -191 and -190/-171), octa- (BDE-196, -197, -201, -202, and -203) and nona- (BDE-206, -207 and -208) BDEs were present in egg pools from all colonies collected in 2006 (Chapter 3, Tables 4.1). With no exceptions, in 2006 individual octa- and nona-BDE concentrations were surpassed by BDE-209. Octa- and nona-BDE and BDE-209 congener patterns did not vary noticeably among sites; BDE-207 was the most prominent of the nona-homologue group and the general order of concentration was BDE-207 >-208 >>-206. It has been shown that lower brominated congeners can form photocatalytically or enzymatically (dietary feeding studies with fish and birds) via sequential debromination of BDE-209 (Ahn et al., 2006; Bezares-Cruz et al., 2004; Huwe and Smith, 2007;

Soderström et al., 2004; Stapleton et al., 2006b; Van den Steen et al., 2007a). Specifically, in a feeding study with European starlings (*Sturnus vulgaris*), van den Steen et al. (2007a) showed that BDE-207 and BDE-208 were the most pronounced congeners in muscle and liver tissue as a result of exposure to BDE-209. This indicated that *meta*- and *para*-debromination of BDE-209 resulted in the formation of BDE-207 and BDE-208, respectively. In herring gull eggs, the same nona-BDE pattern was observed. Furthermore, the octa-BDE congener profiles of BDE-197 >> -201 > -196 >-203 ≈ -202 were also comparable to the European starling feeding study, BDE-197 > -196 > -203 ≈ -205 (BDE-205 was not detected in the present herring gull eggs). The dominance of BDE-197 may be explained by *meta*-debromination of BDE-207. These results suggest that herring gulls possess the capacity to *meta*-debrominate BDE-209 and BDE-207. Products of debromination are then transferred *in ovo* to their eggs. The most important hepta-BDEs in herring gull eggs were BDE-183 >> BDE-179 > BDE-170; the remaining hepta-BDE congeners appeared sporadically and at low to non-detectable levels.

Regardless of their source, the present findings of hepta- to deca-BDE congeners in the eggs of Great Lakes herring gulls are important since there are exceedingly few reports in the scientific literature of highly brominated PBDE congeners in tissues of wildlife or humans. With respect to wild birds and specifically bird eggs, octa- and/or nona-BDEs have been reported in higher trophic level avian species (Knudsen et al., 2006b; Verreault et al., 2007). In seabird eggs from northern Norway and Svalbard; Knudsen et al., reported BDE-209 (n = 11 eggs) and nona-BDEs (n = 26 eggs), although the relative contribution of these congeners was highly variable and present at much lower levels

Concentration ng/g (w/w)



**Figure 4.2.** Temporal trends between 1982 and 2006 for concentrations of BDE-209,  $\sum_{\text{octa}}\text{BDEs}$  (BDE-196, -197, -201, -202, -203);  $\sum_{\text{nona}}\text{BDEs}$  (BDE-207 and -208) in herring gull eggs from seven representative Great Lakes herring gull colonies. Black bars represent BDE-209, grey bars represent  $\sum_{\text{octa}}\text{BDEs}$ , and white bars represent  $\sum_{\text{nona}}\text{BDEs}$ .

than in eggs of Great Lakes herring gulls. In the Norwegian seabird eggs, BDE-209 concentrations were higher than for the three nona-BDEs, which in decreasing order were: BDE-207>-208, whereas octa-BDEs were not detected, in eggs collected between 1983 and 2003 (Knudsen et al., 2006b). In addition, octa-BDEs were recently discovered in eggs (yolk, n = 9 and plasma n = 1) of glaucous gulls (*Larus hyperboreus*) from the Norwegian Arctic (Verreault et al., 2007).

There are an increasing number of reports pertaining to PBDE temporal trends in the environment; however, there is a paucity of trend data for BDE-209 in wildlife as its occurrence has mainly been reported at low to non-detectable levels. In one recent study, BDE-209 was detected in peregrine falcon (*Falco peregrinus*) eggs from Greenland, where levels ranged from 0.29 to 17 ng/g ww and an increasing trend was observed over the period of 1986 to 2003 (Vorkamp et al., 2005). Temporal trends of the octa- and nona-BDE and BDE-209 concentrations in Great Lakes herring gull eggs contrasted with those of the major, PentaBDE and OctaBDE derived congeners. Over the period of 1982 to 2006 concentrations of  $\Sigma_{\text{octa}}\text{BDE}$ ,  $\Sigma_{\text{nona}}\text{BDE}$  and BDE-209 generally increased in eggs from all seven sites (Table 4.1, Figure 4.2). Contaminant levels of BDE-209 were first detected and quantifiable in 1982 but were quantifiable basin-wide in the mid-1990s (Figure 4.2). These recent BDE-209 findings likely reflect the growing environmental inputs resulting from the global demand and use of this high production volume chemical, which have been reported to be 56,100, 65,600 and 56,400 metric tons in 2001, 2002 and 2003, respectively (BSEF, 2006). Given that more recent volume estimates are not publicly available, it is likely that the current demand for the DecaBDE commercial

mixture is greater than reported in 2003. The temporal increases were generally the most dramatic over the years 2004 to 2006, and tended to be most recently elevated at the Gull Island, Toronto Harbour and Channel-Shelter Island sites. Relative to more remote sites such as Agawa Rocks and Chantry Island, recent and more highly elevated BDE-209 levels in eggs from Toronto Harbour and other southern, urban colonies may reflect regional and high PBDE exposure and accumulation as these gulls reside year-round in ice-free portions of the lower Great Lakes. For each Great Lakes site over the period of 1982 to 2006, temporal trends in BDE-209 concentrations appear to have several phase changes. With a few exceptions, in 1982 and 1996, BDE-209 was often low or <MLOQ, after which elevated levels occurred and were maintained from 1997 to early 2000, and what appears to be for some sites (e.g., Gull Island) increases over the 2004 to 2006 period .

Doubling times for BDE-209 over the entire period of 1982 to 2006 were considerably lower compared to those of the major PBDEs over this time frame. Among the most rapid doubling times for BDE-209 were 2.5 ( $r_s = 0.77$ ,  $p < 0.0008$ ) and 2.1 ( $r_s = 0.63$ ,  $p < 0.002$ ) years for Gull Island and Toronto Harbour, respectively (Figure 4.2). Doubling times for BDE-209 at the six sites ranged from 2.1 to 3.0 years, with Spearman rank coefficients  $r = 0.55$  to 0.77 (Table 4.2). It is interesting to note that the present BDE-209 doubling times are comparable to those previously reported for PentaBDE derived PBDE congeners (namely BDE-47, -99, and -100) in gull egg pools from the same colonies over the period of 1981 to 2000 (Norstrom et al., 2002).

In terms of doubling time or rate of growth, the order rank is  $\Sigma_{\text{octa}}\text{BDEs} < \Sigma_{\text{nona}}\text{BDE} < \text{BDE-209}$ , where the doubling times for  $\Sigma_{\text{nona}}\text{BDE}$  (site average of  $3.4 \pm 1.1$  years) were more comparable to those of BDE-209 ( $2.6 \pm 0.3$  years); see Table 4.2 for doubling times at individual colonies. Furthermore, the ratios for  $\Sigma_{\text{octa}}\text{BDE}$  and  $\Sigma_{\text{nona}}\text{BDE}$  with respect to total  $\Sigma_{\text{Br8-10}}\text{BDE}$  concentrations over the period that BDE-209 was quantifiable basin wide for all sites and all years were  $0.52 \pm 0.05$  and  $0.17 \pm 0.02$ , respectively (Table 4.1). This high co-variance between  $\Sigma_{\text{octa}}\text{BDE}$  and  $\Sigma_{\text{nona}}\text{BDE}$  and BDE-209 concentrations suggests that the octa- and nona-BDEs are derived from the sequential debromination of BDE-209. Debromination may be occurring via enzyme-mediated processes in the gull with the resulting PBDEs transferred to eggs, but the degradation may also be occurring further down the food web and perhaps abiotically as well. Stapleton *et al.* (2004) reported that diet-exposed juvenile common carp (*Cyprinus carpio*) could rapidly debrominate BDE-99, -183 or -209 to lower brominated metabolites (Stapleton *et al.*, 2004b; Stapleton *et al.*, 2004a).

The temporal trends in concentrations of established PBDEs are either stabilizing or perhaps appear to be decreasing as of 2000 (Section 4.2.1). In 2006, levels of BDE-209 in herring gull egg pools were 1.8 to 6.2 % of the summation of the most abundant PBDE congeners associated with the PentaBDE commercial mixtures (i.e. BDE-47, -99, and -100). Assuming that these PentaBDE-derived congeners remain constant at the present levels, and BDE-209 continues to persist and increase at the existing rates, it will only take between 11 to 17 years for BDE-209 to reach levels of major PBDEs and become the most abundant organobromine contaminant in Great Lakes herring gull eggs.

#### 4.3. Conclusions

Several conclusions can be made from the present study. Despite phase-outs of PentaBDE and OctaBDE formulation use in North America, there are likely still significant loadings of PBDEs into the Great Lakes ecosystem as evidenced by the absence of precipitous declines in the eggs of herring gulls. Continued environmental surveillance of PBDEs is justified by the emergence of BDE-209 and higher brominated PBDE congeners that clearly must be derived from the degradation of BDE-209. Debromination of BDE-209 in the DecaBDE formulation may continue to act as a source of lesser-brominated congeners to wildlife, other biota, and people. It is evident that BDE-209 is widely bioavailable and accumulates in herring gulls and is subsequently transferred to their eggs. Moreover, the significance of the bioaccumulation of BDE-209 has been under-estimated since BDE-209 and octa- and nona-BDEs have rapidly increased post-1995, especially in 2005 and 2006. A number of factors likely explain observed regional differences in patterns of PBDE accumulation in herring gull eggs. These include differences in: 1) regional loadings of PBDEs as influenced by urban and industrial activities, 2) differences in gull diet composition, and 3) colony-specific differences in the importance of post-breeding movements that could regulate PBDE exposure (Hebert et al 1998, Hebert et al., 2006b; Hebert and Weseloh, 2006b). The remarkable changes in the levels and PBDE congener composition in Great Lakes herring gull eggs emphasize the need to re-visit the criteria under which chemicals are deemed persistent and bioaccumulative, as well as reassessing the need to restrict the production and commercial usage of the DecaBDE formulations. Having said this, it is also

important to monitor the environment for alternative FRs as other, non-regulated compounds leave (Chapter 5).

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## CHAPTER 5

### Temporal and Spatial Trends of Current-Use Flame Retardants in the Eggs of Herring Gulls (*Larus argentatus*) from the Laurentian Great Lakes

#### 5.1. Introduction

Once an FR chemical has established a significant environmental presence and demonstrates properties of a classic POP (i.e. persistence, bioaccumulation and toxicity), certain legislative pressures are applied accordingly to implement appropriate production and usage regulations. For example, brominated biphenyls (PBB) were used as additive FRs in the early 1970s, but their production was banned in the United States in 1976 because of an industrial accident resulting in widespread contamination of PBBs in the state of Michigan, USA. This accident caused many human and animal health problems and quickly led to the ban of PBB flame retardants (WHO, 1994). This accident may have triggered the transition into heavy usage of PBDEs. In direct comparison to this scenario, and given the circumstances of present bans and regulations for some PBDE technical mixtures (Chapter 4), it is possible that non-PBDE FRs (Chapter 3) will become the next ‘major players’ as far as PBDE alternatives inside global markets.

There is an increasing number of scientific studies revealing the presence of non-regulated, non-PBDE FRs in the environment (Chapter 1, Table 1.6). In recent years, two non-PBDE FRs that have been receiving considerable attention are 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE). In

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Gauthier, L.T., Hebert, Letcher, R.J. 2007. In preparation.

addition, Chemtura has announced that they will replace the OctaBDE technical mixture with BTBPE (trade name FF-680) (Chemtura, 2004; Renner, 2004), which will likely result in increased production and usage of BTBPE. And similarly, DBDPE is marketed as a replacement and alternative to the presently used high production volume DecaBDE commercial mixture (trade name Saytex 8010, by Albemarle Corporation). After recent regulatory initiatives to reduce the use of the DecaBDE mixture, it is likely that the use of DBDPE will also increase. In addition, there are no reports on temporal trends of hexabromobenzene (HBB) in the environment, although there are a few identifications in the past (Japanese Government, 2001; Watanabe et al., 1986b; Yamaguchi et al., 1988).

Although both BTBPE and DBDPE have been detected in the environment from various locations around the world, there is exceedingly little temporal trend data available for these compounds. Hoh et al. (2005) reported doubling times of ~2 years for BTBPE in sediment samples from Lake Michigan, beginning around 1973, which was consistent with when BTBPE was introduced to the market (approximately 25 to 30 years ago) (Zweidinger et al., 1977). A very recent study by the same researchers measured BTBPE in a sediment core from Lake Ontario (Qiu et al., 2007). Levels were comparable to the Lake Michigan sediment core (Hoh et al., 2005); however surficial sediment concentrations were half that of BDE-209. Other studies have detected BTBPE in the environment and humans (Hoh and Hites, 2005; Karlsson et al., 2007; Law et al., 2006; Pettersson-Julander et al., 2004; Sjödin et al., 2001; Zhu and Hites, 2006). BTBPE has also been detected in eggs of Northern Fulmars (*Fulmarus glacialis*) from the Faroe Islands (Karlsson et al., 2006). Similar to BTBPE, DBDPE has been detected in the

environment, although presently there are no temporal trend data available for this currently-used FR. DBDPE has been detected in a few biotic samples, fish species from Lake Winnipeg (Canada) (Law et al., 2006) and tree bark from Arkansas, U.S. (Zhu and Hites, 2006), however environmental detection has generally been in abiotic samples, such as sewage sludge (Eljarrat et al., 2005; Kierkegaard et al., 2004; Konstantinov et al., 2006) and household dust (Julander et al., 2005b; Karlsson et al., 2007; Pettersson-Julander et al., 2004).

Dechlorane Plus (DP) is a chlorinated FR that consists of two isomers, *syn*-DP and *anti*-DP (Figure 1.1M/N) and was introduced as a substitute for Dechlorane (also called Mirex,  $C_{10}Cl_{12}$ ) by Hooker Chemical (now a part of OxyChem) in the mid-1960s. DP is still being used (Green, 1995; Weil and Levchik, 2004). Despite the commercial longevity of DP's production and usage, this currently-used FR has only recently been detected in the environment (Hoh et al., 2006). Hoh et al. (2006) were the first to report on DP isomers in air, fish, and sediment from the Great Lakes. This suggested that DP isomers were widely distributed and could bioaccumulate in Great Lakes biota and surrounding regions, which was further confirmed by their detection in Lake Winnipeg and Lake Ontario food webs (Tomy et al., 2007b).

A powerful tool in wildlife residue monitoring is the systematic, periodical sampling of tissues from the same location. Regardless of the precise levels of contamination, changes in contaminant levels can be accurately measured and correlated with remedial measures (Mineau et al., 1984). As an extension to Chapter 3, the present study

objectives are to investigate temporal and spatial trends of HBB, BTBPE, DBDPE, and DP in the eggs of herring gulls from the Laurentian Great Lakes. The seven colonies were chosen according to reasons described in Chapter 2. The period 1982 to 2006 was selected for the present study to represent two potentially important timeslots in the emergence of non-PBDE alternative FRs in Great Lakes herring gull eggs. The first period, 1982-1995, signifies minimal environmental contamination of FRs in the Great Lakes, as previously reported for PBDEs (Norstrom et al., 2002). The second, 1996-2006, signifies a period where non-PBDE FRs were potentially emerging as environmental contaminants in response to increasingly stringent fire safety standards and recent regulation/phasing-out of the PentaBDE and OctaBDE technical mixtures in North America, Europe and other parts of the world.

## **5.2. Results and Discussion**

### **5.2.1. Hexabromobenzene**

HBB (Figure 1.3H) was quantifiable in herring gull egg pools basin-wide in the Great Lakes for all years under study (Figure 5.1). Environmental levels of HBB ranged from 0.10 to 3.92 ng/g ww for the seven colonies over 1982 to 2006 and showed much variability among sites and years. In the most recent year of this study (2006), concentrations in eggs pools were present at levels below 1.0 ng/g and the highest level was measured at the Toronto Harbour colony (0.66 ng/g ww). Comparable levels among colonies could suggest a common origin of exposure to HBB, such as atmospheric transport and ingestion via particle-bound HBB, although, sediment and physical contact

or ingestion via the herring gull diet may also be a contributing factor. Clearly, there are a wide range of possibilities for HBB exposure, which are discussed further below.

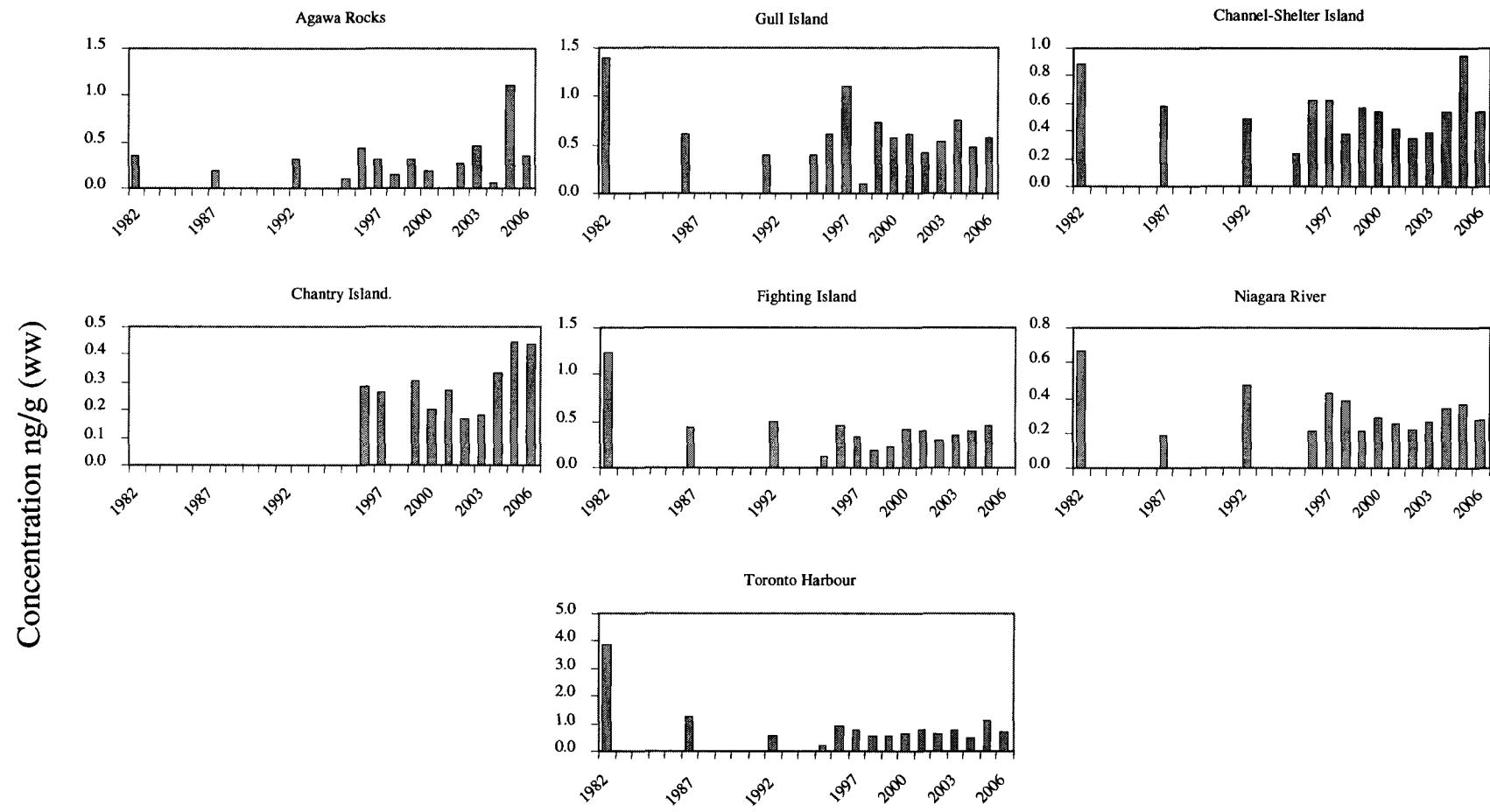
The low levels of HBB detected over time imply wide-spread distribution of this FR across the Great Lakes basin. HBB levels were greatest in 1982 at five of the six colonies monitored for this time point (Figure 5.1). Levels of HBB are consistently low in comparison to PBDEs (<0.2%) in the Great Lakes, and lack any obvious temporal changes over the period of 1982 to 2006. A reason for low levels of HBB in herring gull eggs could be the result of the low bioaccumulation potential in aquatic food webs due to large molecular size, resulting in inefficient membrane permeation (Muller-Herold et al., 2005; Zitko and Hutzinger, 1976). There are numerous compounds with similar degrees of bromination that are present in herring gull eggs at much more elevated levels (i.e. BDE-153). The reasons for low levels of HBB may be related to low exposure and bioavailability/biotransformation, where HBB is taken up by the mother herring gull but is converted to metabolites (i.e. OH-brominated benzenes).

Current production volumes for HBB are not publicly available. However, HBB is classified under the European Existing Chemicals Inventory as a low production volume FR (1000-5000 metric tonnes) and according to Zang et al. (2002) the manufacture of HBB has increased every year. Historically, this additive FR has been used in the process of paper applications and plastic electronic goods (Watanabe et al., 1986a). Although information on the production of HBB is limited, Dayang Chemicals

(Hangzhou City, China) and Nippoh Chemicals (Chiba, Japan) both currently produce this compound.

Whether or not HBB is produced or applied to products that ultimately contribute to the widespread presence of HBB in Great Lakes herring gull eggs is not known. There are many sources of HBB to the environment. For example, it is known that thermal degradation of the high production volume FR, DecaBDE (Chapter 4), can yield HBB as a main product of pyrolysis (Thoma and Hutzinger, 1987). In addition, HBB may also enter the environment as a result of the high temperature breakdown of components comprising the OctaBDE technical mixture (Buser, 1986). The formation of tetra- to hexabromobenzenes were observed during the pyrolysis of DecaBDE formulations; where the C-O bond is cleaved and a bromine radical is transferred, forming the more thermally favourable bromobenzene. OctaBDE and DecaBDE technical mixtures were used extensively throughout the 1980s and 1990s (Chapter 4), which may partially explain the wide distribution and uniformly low levels of HBB occurrence in Great Lakes herring gull eggs.

HBB can be present in the environment in the vicinity of the Great Lakes through historical application and direct use of this compound. Velsicol Chemical Corporation (now part of Chemtura) located in St. Louis, MI, was shut down in the 1980s due to high levels of chemical contaminants in the surrounding region (USEPA, 2006). This chemical plant operated from 1936 through 1978 and manufactured and distributed animal feed



**Figure 5.1.** Temporal trends for the occurrence of hexabromobenzene (HBB) in herring gulls from seven colonies in the Laurentian Great Lakes.

and a variety of inorganic chemicals including HBB (USEPA, 2005) and thus, past usage and heavy environmental loading of HBB in past years may be reflective of levels observed in the present retrospective study. The possible production and use of HBB as a FR may also be released through various waste water streams (Watanabe et al., 1985) as well as through atmospheric transport (Hoh et al., 2005). HBB has also been detected in sediment (Japanese Government, 2001), and human adipose tissue in Japan (Yamaguchi et al., 1988).

If released into the atmosphere, HBB would likely exist solely in the particulate phase in the ambient atmosphere, based on an estimated vapour pressure of  $1.6 \times 10^{-8}$  mm Hg (at 25°C). Hoh et al. (2005) reported HBB in particulate air collected in and around the Great Lakes, which suggests that this may be a possible route of exposure to herring gulls from the same location. On the other hand, particulate-phase HBB may be removed from the air and deposited to the soil or sediment in the Great Lakes. HBB has been detected in soil and sediments from Japan (Japanese Government, 2003; Watanabe et al., 1986b). Under such circumstances, HBB could readily become available for dietary uptake by aquatic species, as well as exposure to aquatic-feeding species such as herring gulls. Conflicting data are available on the bioaccumulation of HBB in fish and aquatic organisms. In short- and long-term studies (5 and 96 days), HBB was found to be non-accumulative in fish (Zitko and Hutzinger, 1976). HBB was listed as a chemical compound confirmed to be non-accumulative in screening studies. Nonetheless and contrary to this, HBB has been detected in the present herring gull eggs, as well as in the environment and in humans from different locations around the world (Table 1.6). The

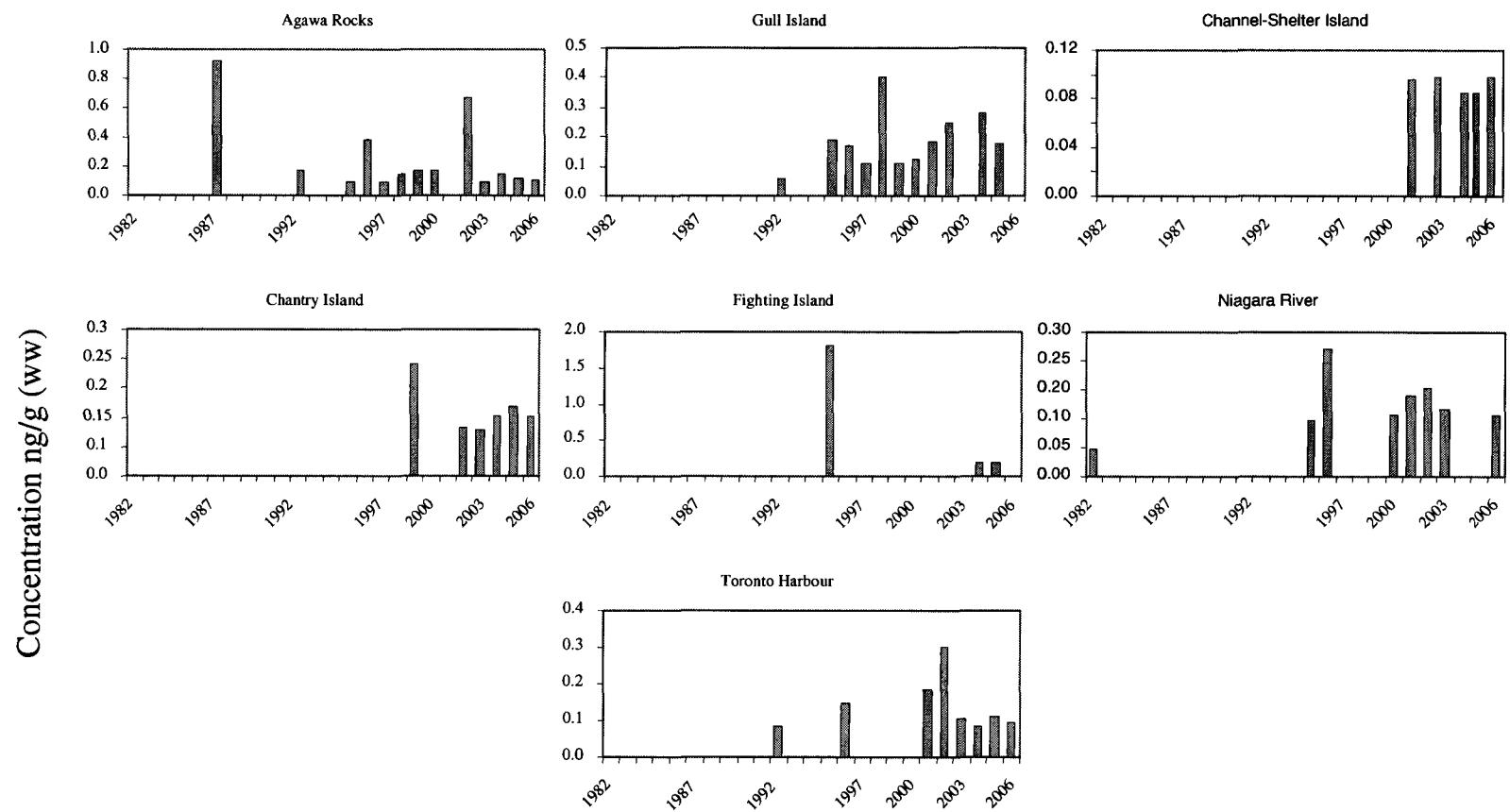
temporal results presented here suggest that sources and inputs to the Great Lakes ecosystem have been low between 1982 and 2006; as well, HBB may have been produced prior to 1982, as early as the mid-1970s (EPA, 2003).

### **5.2.2. 1,2-Bis(2,4,6-tribromophenoxy)ethane**

The temporal trends for BTBPE indicate that this currently-used FR is present at all seven herring gull colonies where eggs were collected between 1982 and 2006 (Figure 5.2, Chapter 3). Concentrations ranged 0.06 to 1.82 ng/g ww and showed much variability among sites and years. Approximately 90% of the samples collected contained BTBPE above the limit of detection; however, approximately 60% of the sampling sites and years were quantifiable. The single highest value was found at the Fighting Island colony in 1996. Levels at other sites and years were all below 0.5 ng/g ww, with two exceptions at the Agawa Rock colony. Over time, slight fluctuations among sites and years were observed, although similar to HBB, BTBPE was low in comparison to PBDEs (Chapter 4). This suggests that similar exposure pathways may be responsible for the long-term exposure observed for BTBPE in the present herring gull egg pools. In comparison to dramatic increases in PBDE contaminant levels in herring gull egg pools (Chapter 4), levels of BTBPE (and HBB) may simply be a coincidence and the result of lower level of production and use. BTBPE, like HBB, is hexa-brominated and thus it would be expected that the substitution would influence the accumulation in biota across the Great Lakes. BTBPE is produced in much higher amounts than HBB, but environmental levels are similarly low in the present study.

Temporal trends in BTBPE levels were not evident in herring gull egg pools. Among the seven colonies, BTBPE was present most frequently at the Agawa Rocks and Gull Island colonies (Figure 5.2). At these two westerly sites, levels were generally higher than colonies located in the south-eastern Great Lakes basin. Here, BTBPE levels began appearing around the late 1990s, after which BTBPE was above the limit of quantitation for each year assessed. The occurrence of BTBPE at Chantry Island, Niagara River and Toronto Harbour was quantifiable on an annual basis starting around 2002 (Figure 5.2). For both Channel-Shelter Island and Fighting Island colonies, BTBPE was detected more sporadically.

The production and use of BTBPE as an additive flame retardant for many thermoplastic and thermoset systems may result in its release into the environment through various waste streams. If released into air, an estimated vapour pressure of  $7.5 \times 10^{-7}$  mm Hg indicates BTBPE will exist solely in the particulate phase in the ambient atmosphere. BTBPE has been reported in household dust (Karlsson et al., 2007) and dust collected at an electronics recycling facility in Sweden (Julander et al., 2005a; Pettersson-Julander et al., 2004). Particulate-phase BTBPE will be removed from the atmosphere by wet and dry deposition. The low levels of BTBPE in herring gull eggs between 1982 and 2006 may, in part, have reflected low exposure through air and soil/sediments in the past. However, presently there are an increasing number of reports describing BTBPE in the environment (Table 1.6). In recent years, this current-use FR has been detected in ambient air and sediment samples from various sites across the United States (Hoh et al., 2005; Qiu et al., 2007). In the Hoh et al. (2005) study, dated layers of sediment showed



**Figure 5.2.** Temporal trends for the occurrence of 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) in herring gulls from seven colonies in the Laurentian Great Lakes.

rapid increases (doubling time of ~2 years) until 1985, after which concentrations leveled off (Hoh et al., 2005). As well, a very recent report of BTBPE in a sediment core collected from Lake Ontario, revealed this current-use FR to be present at levels half of BDE-209 and more than twice that of tri- to hepta-BDEs (Qiu et al., 2007). BTBPE findings in sediment do not compare with the present temporal study however occurrences of BTBPE in herring gull eggs are generally more frequent in the later years of this retrospective study (Figure 5.2).

Great Lakes Chemical produced BTBPE in the United States ranging from 4,500 to 22,500 metric tonnes each year from 1986 to 1994. BTBPE concentrations in sediment suggested that its production could be comparable to that of PBDEs in recent years; in fact, in North America, 450 to 4,500 metric tonnes of BTBPE were produced in 1998 (IUR, 2002), as compared to 33,000 metric tonnes of the PentaBDE, OctaBDE, and DecaBDE products produced in 2001 (BSEF, 2006). Since BTBPE is now being used to replace the discontinued OctaBDE product (Renner, 2004), it is likely that BTBPE presence in the environment (e.g. herring gulls) and in humans will also increase in the near future. As presented in Chapter 4, exponential increases of BDE-209 were observed in annually collected herring gull eggs between 1982 and 2006. FR accumulation in bird's eggs is likely responsive to changes in environmental exposure, e.g. post-2000 transformation of PentaBDE derived congeners as a result of recent regulation/phase-out (Chapter 4) and similarly PBDEs in guillemot (*Uria algea*) eggs from the Baltic Sea (Sellstrom et al., 2006). Given the relative amounts of BTBPE produced as a replacement to the OctaBDE commercial mixture, compared to PentaBDE in the past, as well as the

rising frequency of its detection in the environment, it could be postulated that BTBPE will potentially bioaccumulate to increasingly higher environmental levels.

The low levels of BTBPE contamination over time may also be related to the diet of herring gulls integrated throughout the year. Dietary uptake of BTBPE in juvenile rainbow trout (*Oncorhynchus mykiss*) was recently investigated (Tomy et al., 2007a). The authors suggested that BTBPE has a high potential for biomagnification in aquatic food webs, although retention of BTBPE over the period of elimination was minimal. This is consistent with the present findings as BTBPE measured in fish collected from Lake Winnipeg (Canada) and Lake Ontario, were generally an order of magnitude lower than levels reported in the present temporal and spatial assessment. In addition, there may be an increased biotransformation of BTBPE in birds relative to fish, as gulls occupy a higher trophic position and may possess a greater capability to metabolize this FR. A BTBPE dosing study using rats examined its pharmacokinetic behavior (Hakk et al., 2004; Nomeir et al., 1993). The authors report that the oral ingestion of BTBPE in rats led to poor gastrointestinal absorption, high biotransformation and as a consequence, low residual concentrations in tissues. Since herring gulls are environmentally exposed to BTBPE, a possibility exists that it is cleared quickly by the gull's metabolism and residue levels in eggs only reflect the diet shortly before yolk deposition.

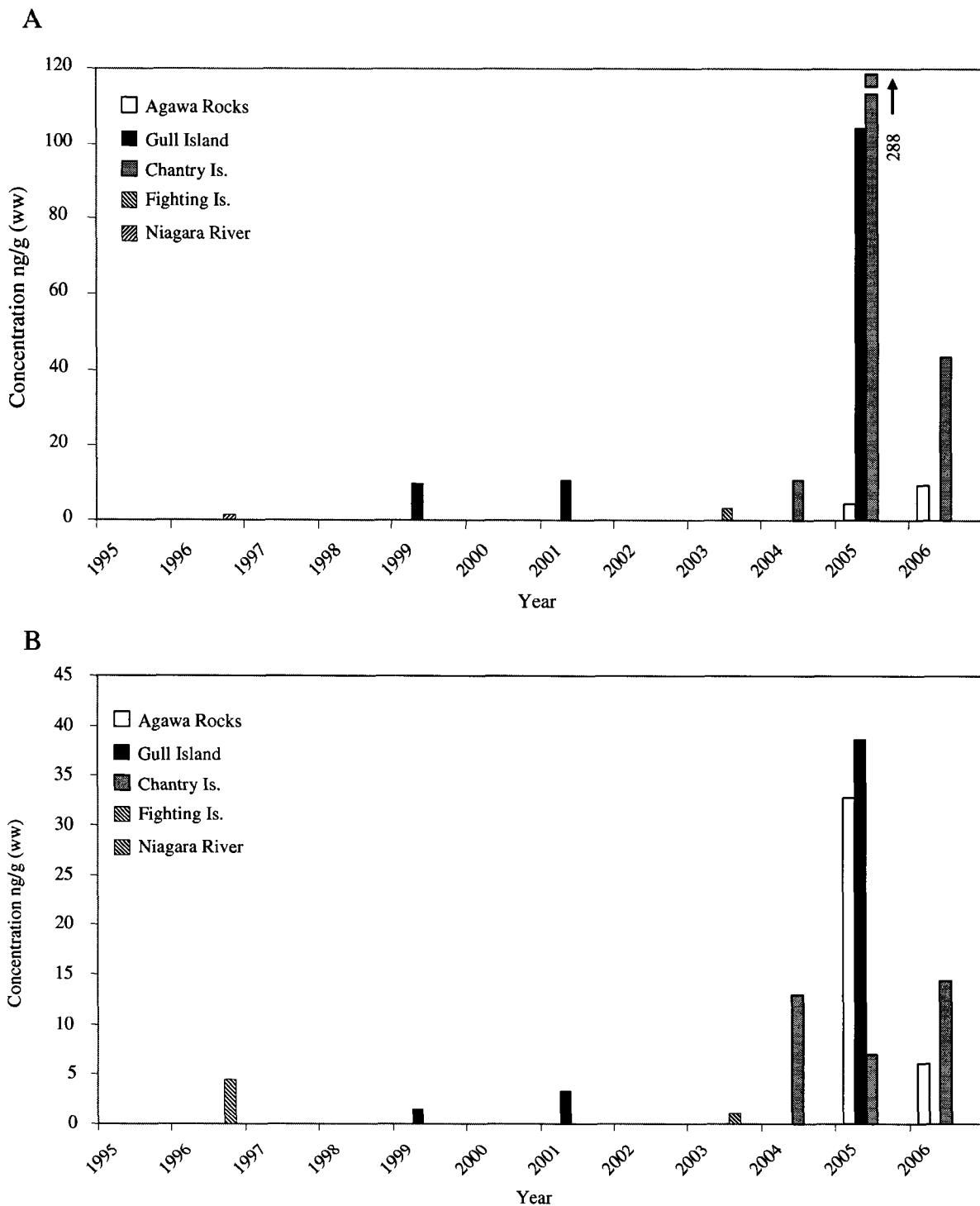
### **5.2.3. Decabromodiphenyl ethane**

Decabromodiphenyl ethane or, 1,2-bis(pentabromodiphenyl) ethane (DBDPE) (Figure 1.1D), was introduced to the FR market in the mid-1980s (EPA, 2001) but became

commercially important as an alternative to the DecaBDE formulation in the early 1990s (Arias, 2001). DBDPE is marketed under the trade names SAYTEX® 8010 (Albemarle Corporation) and Firemaster® 2100 (Chemtura Corporation, West Lafayette, IN) and has the same applications as the DecaBDE commercial product, i.e. as an additive to different polymeric materials such as high-impact polystyrene and textiles. There are currently no figures on the global consumption of DBDPE, but with increasing concern about PBDEs in the environment (Chapter 3 and Chapter 4), the use of DBDPE is predicted to increase in the future. Based on the structural resemblance of DBDPE to BDE-209, its physical-chemical properties are assumed to be similar, i.e. low volatility and low water solubility. Toxicity data for DBDPE is scarce; however oral toxicity in rats is low, possibly due to poor absorption efficiency of the compound (Hardy et al., 2002).

In the initial screening for current-use flame retardants in herring gull eggs collected in 2004 (Chapter 3), DBDPE was consistently below the limit of detection at all six of the six Great lakes colonies. Nonetheless, DBDPE was included in this temporal assessment from 1982 to 2006, under the hypothesis that DBDPE is a FR that accumulates in Great Lakes herring gulls, is transferred to their eggs, and is only present in eggs sampled in recent years.

Spanning the temporal period under study, DBDPE was quantifiable in eggs from five of the seven herring gull colonies (Figure 5.3A). The levels of quantification ranged from 1.3 to 288 ng/g ww and were dispersed sporadically among sites and years. DBDPE was not detected in eggs collected prior to 1996 and without a doubt, the presence of DBDPE



**Figure 5.3.** Temporal trends for the occurrence of (A), decabromodiphenyl ethane (DBDPE) and corresponding (B) BDE-209 in herring gull eggs collected from five colonies in the Laurentian Great Lakes.

is a very recent phenomenon and corresponds to trends observed for BDE-209 (Chapter 4). Generally, contaminant levels were highest and more disperse in eggs collected in the later years of this study. In 2005, DBDPE was measured at three of the seven sites ranging from 4.3 to 288 ng/g ww, although in 2006 levels were considerably lower than in 2005, measuring 10 and 44 ng/g ww. In contrast to this, prior to 2005, DBDPE was detected at less than 10 ng/g ww and occurred at only five, non-consecutive time points dating back to 1996.

How do DBDPE concentrations compare to those of other FRs in herring gull eggs? Given that BDE-209 was previously identified in herring gull eggs (Chapter 3 and Chapter 4) and given that BDE-209 has such structural and physio-chemical similarities to DBDPE, a comparison of the two FRs would be pertinent. For simplicity, concentrations of BDE-209 are shown in concert with the colonies and years where DBDPE was found (Figure 5.4B), even though BDE-209 was determined in the eggs of herring gulls at virtually every colony and year subsequent to the mid 1990s (Chapter 4). The occurrence of BDE-209 and DBDPE were similar to each other over time at the five sampling sites, although concentrations of DBDPE were similar or considerably higher than BDE-209 in most instances. A highly notable observation is that the occurrence of DBDPE is clearly in the mid 2000s, which is similar to that previously reported for BDE-209 in herring gull eggs from the Great Lakes (Chapter 4).

As noted earlier, DBDPE was under the detection limit in eggs of herring gulls collected from six colonies in 2004 (Chapter 3). A seventh colony, Chantry Island, was later added

for the temporal trends assessment of current-use FRs. Chantry Island was chosen among the nine remaining CWS GLHGMP sites because of its unique dietary habits with respect to the other colonies on the Great Lakes. At Chantry Island, ice often remains inshore in later spring than elsewhere on the lower Great Lakes, so aquatic foods may not be available when gulls reoccupy territories in the spring (Ewins et al., 1994). Herring gulls at Chantry Island tend to incorporate more mammalian prey in their diets than at other colonies (Ewins et al., 1994; Fox et al., 1990; Hebert et al., 1999) making them more reliant on terrestrial-based foods.

Since DBDPE is highly hydrophobic and has an affinity for binding to particulate matter, a terrestrial-based diet may reflect the regional environmental loading of these FRs better than gulls that maintain an aquatic-based diet. Having said this, in the re-analysis for temporal trends, DBDPE was measured in 2004 at Chantry Island and at this same site, the highest level of DBDPE was also measured (288 ng/g ww in 2005). DBDPE surpassed the levels of BDE-209 between 1982 and 2006; the highest BDE-209 level being 39 ng/g ww at Gull Island (Figure 5.3B and Chapter 4). Recently, elevated levels of DBDPE were confirmed in house dust samples, where, in one sample, levels of DPDPE present exceeded the BDE-209 concentrations (Karlsson et al., 2007).

BDE-209 is not expected to bioaccumulate in the tissues of wildlife and similarly, DBDPE is even less likely to be present in the tissues of wildlife and humans due to its physical-chemical characteristics. The behavior of DBDPE is in many ways similar to that of BDE-209, both being large, superhydrophobic and thermolabile compounds.

BDE-209 is widely bioavailable and is present on a global context. In the scientific literature, the reports on DBDPE in the environment are few, although there appears to be an increasing number of occurrences. The presence of DBDPE has also been confirmed in air and dust samples from a Swedish electronic recycling facility (Julander et al., 2005b; Pettersson-Julander et al., 2004). Additionally, DBDPE was detected along with PBDEs in tree bark collected in Arkansas, U.S. Their occurrence was traced to emissions from two major BFR manufacturing plants in southern Arkansas. Data regarding bioavailability/absorption of DBDPE is scarce. Recently, DBDPE was included in a study investigating the bioaccumulation of a number of BFRs in a food web from Lake Winnipeg, Canada (Law et al., 2006). Although DBDPE was not detected in zooplankton, mussels or whitefish, it was present in some of the other fish species, such as walleye (*Sander vitreus*) and burbot (*Lota lota*).

DBDPE (and BDE-209 to some extent) debrominate to lower brominated congeners during sample preparation/analysis, where two nona-BDPEs were previously identified in one of the technical products (Kierkegaard et al., 2004). Furthermore, there are several recent reports showing that BDE-209 is unstable in the environment. BDE-209 has been shown to metabolically degrade in biota (e.g. fish, rats and birds)(Huwe and Smith, 2007; Stapleton et al., 2004; Van den Steen et al., 2007), or undergo abiotic photocatalytic degradation (Ahn et al., 2006; Bezares-Cruz et al., 2004; Soderström et al., 2004) to lower brominated congeners. Whether DBDPE is susceptible to degradation is not known. However, preliminary results exposing DBDPE to a daylight fluorescent lamp showed that DBDPE is degraded, producing two nona-brominated diphenyl ethane

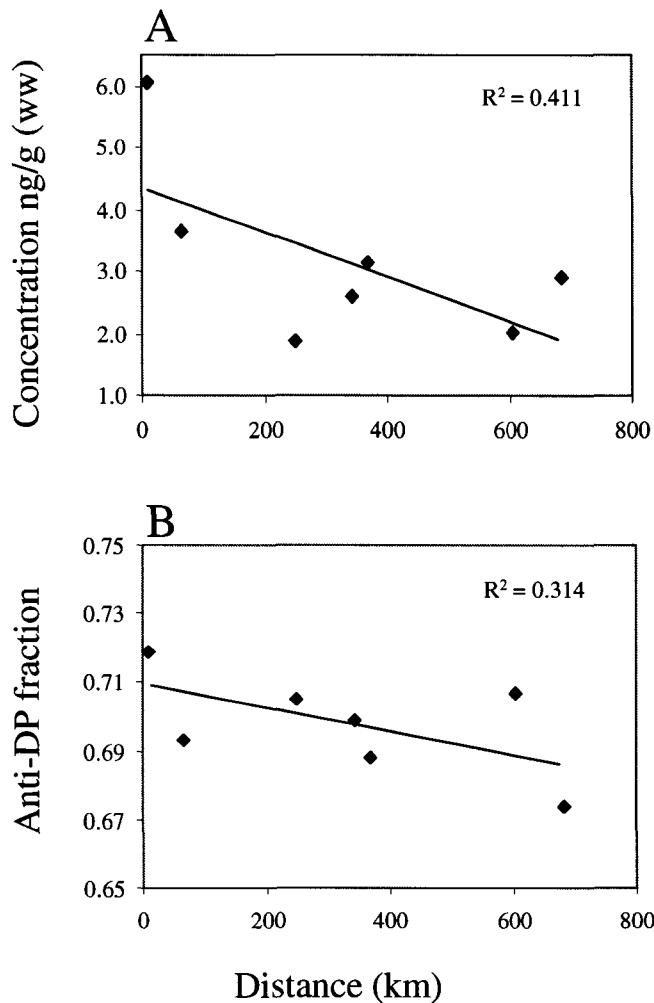
congeners as well as a number of peaks tentatively identified as octa-brominated diphenyl ethane products (Kierkegaard, 2007). Global production volumes for DBDPE are not public, however, with recent legislative pressure by governments and environmental agencies to find non-PBDE alternatives, it could be hypothesized that DBDPE will or already has become a high production volume FR.

### **Dechlorane Plus**

Major applications of DP are industrial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material. Currently, there is no scientific literature on the environmental fate and toxicity of DP and very few reports of DP as an environmental contaminant.

In the present study, for the most recent year studied (2006), concentrations of  $\Sigma$ DP in herring gull eggs pools from all Great Lakes sites ranged from 2.4 to 5.2 ng/g ww and constituted  $0.62 \pm 0.36\%$  of the  $\sum_{41}$ PBDE measured in the 2006 herring gull egg pools, as reported in Chapter 4 (Table 4.1). The highest concentration for  $\Sigma$ DP in this year was found at the Niagara River colony. This effect result of emission of DP from its manufacturing plant, which is located in Niagara Falls, NY. Although temporal trends are to be discussed later, the average concentrations of  $\Sigma$ DP from 1982 to 2006 ( $n = 12$  to 15 years) indicated decreasing contamination levels with respect to increasing distance from the DP manufacturing plant in Niagara Falls, NY (Figure 5.4) and is further supported by DP contaminant levels reported in particulate air from the Great Lakes (Hoh et al., 2006) where highest levels were found at Sturgeon Point (eastern Lake Erie), just 50 km from

Niagara Falls. This is comparable to the second highest concentration measured from Agawa Rocks, located in eastern Lake Superior. The location is relatively isolated in comparison with the other six colonies, which suggest that DP isomers are capable of long-range transport (Hoh et al., 2006). Gulls from the northern Great Lakes are also known to undertake post-breeding movements upon the onset of winter (Hebert, 1998).

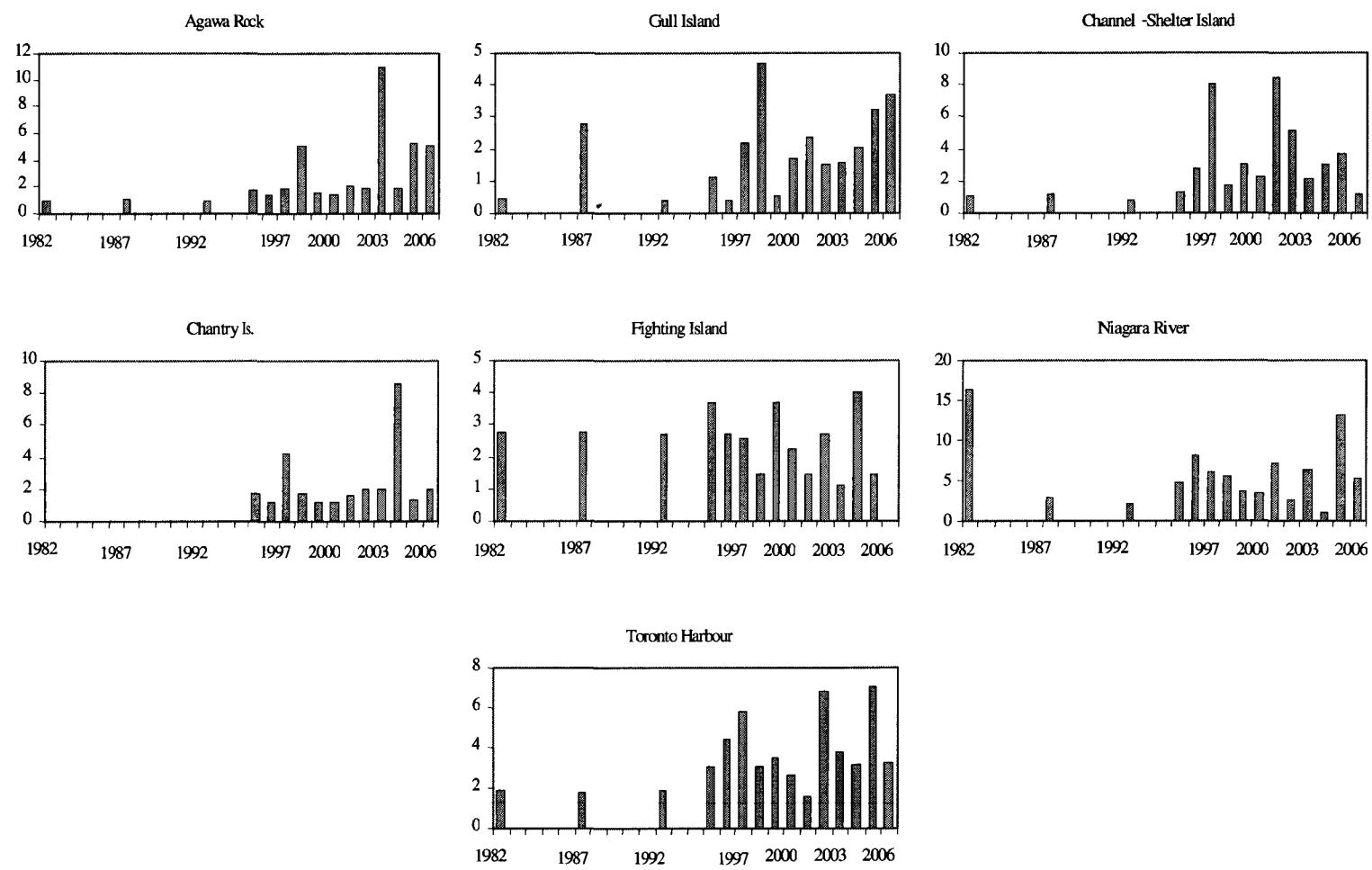


**Figure 5.4.** Concentration of  $\Sigma$ DP (A) and (B) *anti*-DP fraction in herring gull egg pools with respect to distance of colony from manufacturing plant in Niagara Falls, NY.

Elevated levels at Agawa Rocks (5.0 ng/g) may also be reflective of these birds over-wintering in southerly urban areas such as Milwaukee and Chicago. This could also partially explain the third highest levels measured in 2006 at the Gull Island (3.7 ng/g ww) colony located in northern Lake Michigan. The remaining colonies contain lower  $\Sigma$ DP concentrations and range from 2.0 to 3.3 ng/g ww in 2006.

Given the spatial distribution of the seven colonies included in the present study, it was possible to assess for the relationship between the proximity of gull breeding colonies, to the DP point source (Niagara Falls, NY) and DP levels in gull eggs. A linearly decreasing trend of DP levels with distance from the NY site was observed (Figure 5.4A). This widespread, long-term detection of DP isomers likely reflects growing environmental input resulting from the global demand and use of this high production volume flame retardant.

The occurrence of DP is ubiquitous in the environment surrounding the Great Lakes; concentrations of  $\Sigma$ DP, as a function annual herring gull egg collection, are shown in Figure 5.5. The single highest DP concentration (18 ng/g ww) was measured in eggs collected from the Niagara Falls colony in 1982, which was 6 to 16 time higher than the other five collection sites. Hoh et al. (2006) reported peak concentrations of DP in sediment around late 1970 to early 1980s in Lake Michigan and Lake Erie. Following this peak concentration, decreased levels are observed at the Niagara River colony until mid-1990s (Figure 5.5). Between 1996 and 1998, elevated concentrations of DP in herring gulls eggs collected from the Niagara River were observed and as potentially as a



**Figure 5.5.** Temporal trends for the occurrence of summation Dechlorane Plus isomers ( $\Sigma$  anti- and syn-DP) in herring gulls from seven colonies in the Laurentian Great Lakes .

consequence, resulted in elevated levels across the Great Lakes. This is consistent with Qiu et al. (2007), who determined the surficial sediment flux of DP in Lake Ontario. With this data, the authors were able to estimate the historical highest input rate of DP into the sediment of Lake Ontario was in the mid 1990s. Although contaminant levels fluctuated considerably over 1982 to 2006, post-2000 levels ( $3.8 \pm 2.8$  ng/g ww) appeared to be higher than pre-2000 ( $2.8 \pm 2.6$  ng/g ww) time points. Dominated contaminant levels of  $\Sigma$ DP at the Niagara River colony were observed for 66% of the herring gull sampling locations under study.

Considerable variations in  $\Sigma$ DP concentrations were observed at all seven sites over the period 1982 to 2006, thus qualitative trends can only be considered (Figure 5.5). The overall temporal trend for four of the seven sites indicates higher levels of contamination beginning in the mid 1990's, particularly at Gull Island, Channel-Shelter Island, Niagara River and Toronto Harbour. These four colonies have considerably different geographical locations relative to dense urban populations as well as location distance from the DP manufacturing facility. The Channel-Shelter Island colony is situated close to a region of high industrial activity and human population, as well, contributions to contamination may come from namely Detroit, MI and the surrounding area. As stated earlier, the Gull Island colony is likely to accumulate contaminants during post-breeding migration to southern Lake Michigan during the onset of winter (Hebert, 1998), thus being exposed to highly polluted regions such as Chicago and Milwaukee. Inherently gulls would be exposed to high levels of DP at the Toronto Harbour colony and may

reflect increasing amounts of DP released into the environment by neighbouring Niagara Falls. Contaminant levels of  $\Sigma$ DP at the remaining three herring gull colonies indicate some degree of fluctuation between 1982 and 2006; any temporal trends at these sites were not obvious.

Herring gull colonies in closest proximity to Niagara River also show elevated levels in comparison more remote sampling sites. For example, where the maximum level of DP was measured (i.e. Niagara River), sites containing the second highest DP concentration were in closest proximity. This was the situation for 12 of the 15 time points monitored, which provides further evidence that diffuse DP is observed in herring gull eggs with increasing distance from the production facility. A further confirmation can be found in recent sediment studies in Lake Erie and Lake Ontario (Hoh et al., 2006; Qiu et al., 2007). The authors found decreasing levels of DP in superficial sediment collected from east to west Lake Erie. As well, exceedingly high levels were observed from Lake Ontario, suggesting most of DP expelled from the manufacturing facility in Niagara Falls and deposited via the watershed to Lake Ontario.

Both isomers were detected in all samples between 1982 and 2006; the *anti*-DP fraction being consistently greater than that of the *syn*-DP isomer. The *anti*-DP fraction (defined as the concentration of the *anti* isomer divided by the sum of the concentrations of the *syn* and *anti* isomers) was observed in the commercial product to be 0.74 to 0.77 and is in agreement with that reported by Hoh et al. (2006) (0.75 to 0.80) and Qiu et al. (2007), but varies slightly from that reported by Tomy et al. (2007), which was reported as 0.65

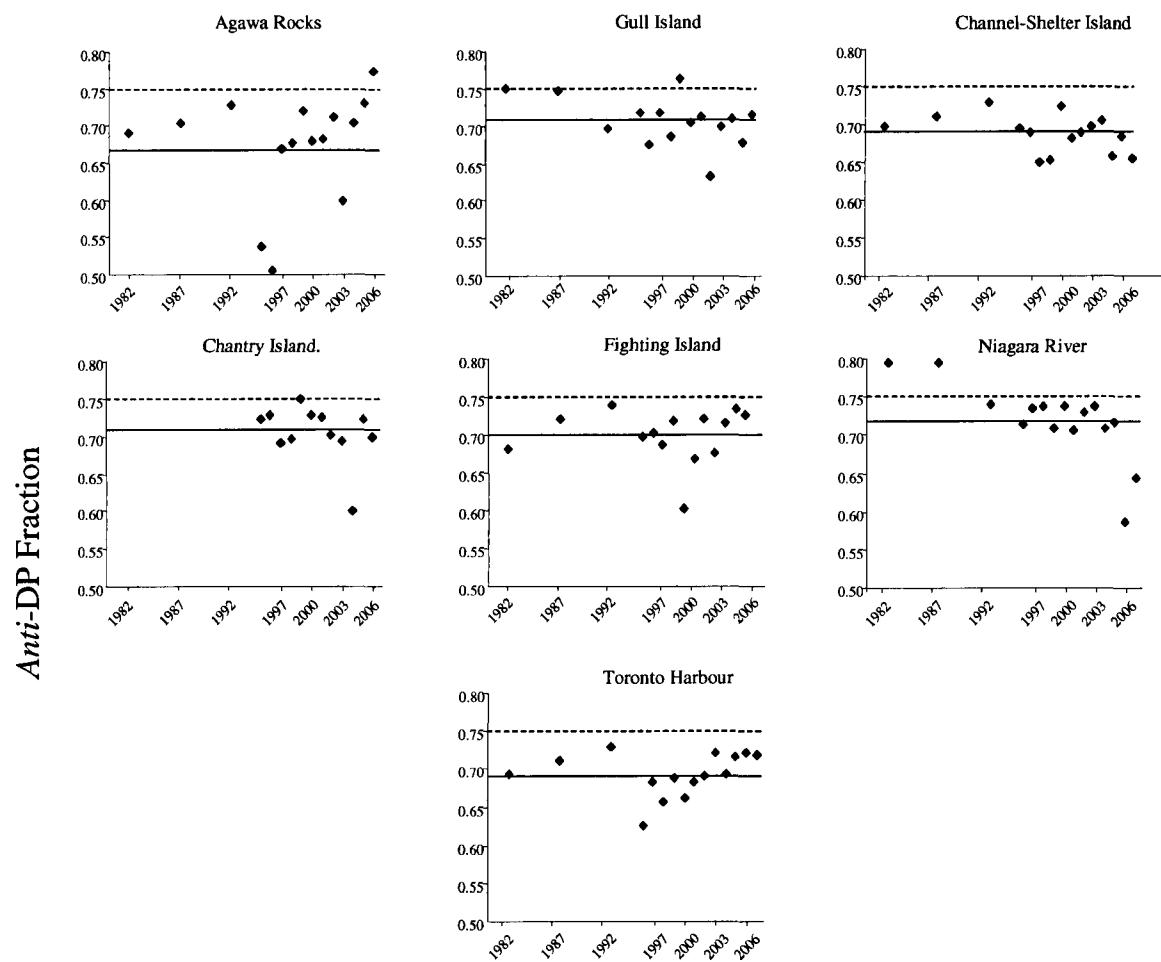
(Tomy et al., 2007b). There was some variation among *anti*-DP fraction in herring gull eggs measured over the period of 1982 to 2006 and ranged from 0.53 to 0.80 with a mean of  $0.74 \pm 0.04$ . Seeing as though there was considerable fluctuation in *anti*-DP ratios among sites and years, a comparison was made relating the average *anti*-DP fractions for each site ( $n = 12$  to 15 years) and the distance of the herring gull colony from the DP production plant (Figure 5.5B). The overall trend suggests that a higher *anti*-DP fraction is observed for the eggs collected closer to the DP production plant and lower *anti*-DP fractions are observed at greater distances from the production plant. Since DP is susceptible to atmospheric transport and is widely distributed in sediments and fish in the Great Lakes basin (Hoh et al., 2006; Qiu et al., 2007), this flame retardant could be facing transformation in the environment during or prior to uptake by herring gulls. Hoh et al. (2006) reported low *anti*-DP fractions (<0.50) in air samples collected from remote sites, which are far from DP's production source in Niagara Falls. It was suggested that long-range atmospheric transport may change the *anti*-DP fraction as a result of differences in the physical or chemical properties of the two isomers. Closer to the proximity of the main source of DP, gulls contained higher *anti*-DP fractions; which is in greater agreement with that of the technical mixture.

The fractional abundance of the *anti*-DP isomer did not appear to follow any collective trend over time, although fluctuations of this fraction were observed (Figure 5.6) over time. In a sediment core taken from Lake Ontario, the temporal trend in *anti*-DP indicated that the sediment value was 0.76, a value close to that of the technical product (Qiu et al., 2007). This value of *anti*-DP increased in the deeper layers, and around 1980,

it was  $>0.90$ . The levels of DP present in mother herring gulls are reflective of levels measured in the eggs at that period in time. Having said this, and assuming the relative composition of *anti*-DP in the technical mixture is maintained over time, it could be hypothesized that the accumulation of *anti*-DP in herring gulls should follow closely with that of the technical mixture from year to year. Clearly this is not the present situation (Figure 5.6).

There are a complexity of factors that govern the accumulation of environmental contaminants in herring gulls (and subsequently transferred to their eggs) and are likely partially explain the regional and temporal differences in the isomeric DP composition in the present study as it is assessed over time (Figure 5.6). These include differences in: 1) regional loadings of DP as influenced by urban and industrial activities 2) differences in gull diet composition and 3) colony-specific differences in the importance of post-breeding movements that could regulate DP exposure (Hebert, 1998; Hebert et al., 2006; Hebert and Weseloh, 2006). In addition, it has been suggested that the *anti*-isomer is more environmentally persistent than the *syn*-isomer in sediment and food webs (Qiu et al., 2007; Tomy et al., 2007b), thus, the presence of DP in herring gull eggs may be reflective of long-term exposure to both technical and degraded DP isomers.

Another reported study of DP in biota (Hoh et al. 2006) demonstrated an *anti*-DP ratio of  $0.60 \pm 0.5$  for Lake Erie walleye. It was suggested that the bioavailability or biodegradation (metabolism) of the two isomers may be different. This can be supported by the longer retention of DP in fish (low *anti*-DP fraction), as opposed to that of herring



**Figure 5.6.** Temporal trends of the fraction of the *anti*-isomer relative to the total concentration of the two DP isomers. The dotted line at *anti*-fraction = 0.75 indicates the isomeric composition of the commercial DP technical product and the solid line represents the average *anti*-fraction at each site spanning 1982 to 2006.

gull egg (high *anti*-DP fraction), where contaminants are very reflective of present commercial DP. However, the metabolism of fish greatly differs from that of the herring gulls and the transformation of DP may also be completely dissimilar. While DP isomer levels reported in the present herring gull egg pools from the Laurentian Great Lakes are small relative to PBDEs (Chapter 3 and Chapter 4), their inclusion in environmental monitoring programs should be considered.

### **5.3. Conclusions**

The non-PBDE FRs discussed in this chapter (and Chapter 3) have been detected in sediment from the Great Lakes (Hoh et al., 2005; Hoh et al., 2006; Qiu et al., 2007). As a result, the only temporal trend studies presently available in the literature for non-PBDE FRs, have been in abiotic samples. The present study has provided information pertaining to levels of several FR chemicals in biota from the Laurentian Great Lakes. Contaminant levels in eggs are reflective of regional pollution in surrounding environments. Clearly, there are several currently-used FR chemicals that accumulate in herring gulls and are transferred to their eggs; some of which are changing rapidly throughout time and others are present at low levels. Having said this, and given the rapidly changing FR industrial market with respect to PBDE alternatives and replacements (Chapter 3 and Chapter 4), it is essential to continue monitoring new and existing anthropogenic chemicals in the environment.

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## **CHAPTER 6**

### **Conclusions and Future Directions**

#### **6.1 Conclusions**

The present study investigated the occurrence and temporal trends of several classes of FR chemicals accumulating in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes. A number of newly identified polybrominated diphenyl ether (PBDE) congeners, not known to be present in commercial technical mixtures, were identified in the current study (Chapter 3). Specifically, BDE-209 and several debromination products were present basin-wide. In instances where selected PBDE congeners had previously been reported present in herring gull eggs collected from the Great Lakes in 2000, contaminant levels show dramatic changes in temporal trends post-2000 (Chapter 4). In addition, a number of other, FRs were identified for the first time in herring gull eggs from the Great Lakes (Chapter 3 and Chapter 5). The highlight of the present study was to identify and characterize a wide range of PBDE and non-PBDE flame retardants and evaluate their existence as current potential environmental contaminants and how they occur through time.

The composition of brominated and chlorinated FRs varied greatly among years and sites. In comparing the total contaminant burden, for the majority of sites and years, PBDEs dominated the total bromine containing compounds detected in herring gull eggs. This is likely reflective of the high level of usage and widespread distribution of the three technical mixtures. The bioaccumulation potential of the PentaBDE and OctaBDE

derived congeners (approximately 90%) were much greater than those with higher degrees of bromination (approximately 5%). HBB and BTBPE were generally <0.1 % of  $\Sigma$ PBDEs. The levels may reflect a low bioavailability and exposure of these compounds through the herring gull's diet or possibly that HBB and BTBPE are not readily retained in the tissues of gulls and thus minimal transfer to the eggs is occurring. DP isomers were generally 1 % of  $\Sigma$ PBDEs, which indicates that this chlorinated FR is bioavailable to a greater extent. In contrast to the previous, DBDPE was measured at exceedingly high levels and surpassed  $\Sigma$ PBDEs for a later year included in this study, although DBDPE was measured on an infrequent basis.

The conclusions that have stemmed from the present findings are numerous. Despite regulations/phase-outs of PentaBDE and OctaBDE formulation use in North America, there are likely still significant loadings of PBDEs into the Great Lakes ecosystem as evidenced by the absence of precipitous declines in the eggs of herring gulls. Continued environmental surveillance of PBDEs is justified by the emergence of BDE-209 and higher brominated PBDE congeners that clearly must be derived from the degradation of BDE-209. Debromination of BDE-209 in the DecaBDE formulation may continue to act as a source of lesser-brominated congeners to wildlife, other biota, and people. It is evident that BDE-209 is widely bioavailable and accumulates in herring gulls and is subsequently transferred to their eggs. Moreover, the significance of the bioaccumulation of BDE-209 has been under-estimated since BDE-209 and octa- and nona-BDEs have rapidly increased post-1995, especially in 2005 and 2006 (Chapter 4). A number of factors likely explain observed regional differences in patterns of PBDE accumulation in

herring gull eggs. These include differences in: 1) regional loadings of PBDEs as influenced by urban and industrial activities 2) differences in gull diet composition and 3) colony-specific differences in the importance of post-breeding movements that could regulate PBDE exposure. The remarkable changes in the levels and PBDE congener composition in Great Lakes herring gull eggs emphasize the need to re-visit the criteria under which chemicals are deemed persistent and bioaccumulative, as well as reassessing the need to restrict the production and commercial usage of the DecaBDE formulations.

With respect to non-PBDE FRs included in the present study, variable levels and temporal trend data were observed. Some non-PBDE flame retardants were present at low levels and sporadic occurrences (BTBPE), while some others point toward very recent phenomena (DBDPE); comparison to the latter two FRs, HBB displayed a pattern suggesting long term exposure and bioaccumulation at low levels (HBB). DP is the only currently produced chlorinated FR in the world and is widely bioavailable in the Great Lakes. Levels of DP in herring gull eggs are comparable to some PBDEs with higher degrees of bromination, although occurrence is with more consistent over time (Chapter 5).

In recent FR production phase-outs and regulations of PentaBDE and OctaBDE commercial mixtures, there exists and the inconceivable deficiency of FR production volume information and application status for these currently-used FRs. Further monitoring for non-PBDE FRs should be considered, as production and usage patterns for FRs are shifting as a result of recent regulations of PBDEs and recent thrust for non-

PBDE alternatives. However, assessments of the chemical fate and bioaccumulation/biotransformation process, which may impact environmental levels, would lead to improve the understanding of monitoring observations.

The following could not be stressed more: Regardless of the source or origin, it is prudent to monitor the environment for the presence of unexpected flame retardants that may enter the marketplace as other, regulated compounds leave.

## **6.2 Future Directions**

There exists a huge knowledge gap with respect to information on non-PBDE FRs in the environment. Literature on available toxicity, effects and exposure data are virtually non-existent for the majority of FR compounds investigated in the present study. In addition, production volumes and applications of current-use non-PBDE BFRs are not publicly available. Availability of authentic reference standards is limited; the FR industry has not been cooperative in supplying governments, universities or environmental agencies with technical mixtures to aid environmental monitoring efforts.

Although the present assessment of currently-used FRs was completed using herring gull egg pools, a comparative assessment using individual egg homogenates would be beneficial to provide data regarding sample variation within and among colonies on the Great Lakes. With this information, extensive statistical analyses could be applied in order to observe less obvious inter-year and inter-colony differences.

Accumulation of some current-use FRs may possibly be sensitive to dietary change. Using individuals (or pools), temporal trends could be contrasted with those of stable isotopes and fatty acid profiles reflective of food web composition.

As presented earlier, numerous unidentified bromine-containing compounds were present and yet to be identified in herring gull egg pools. A hypothesis is that these compounds stem from environmental degradation or debromination/metabolic transformation of currently-used FRs, i.e. brominated trimethylphenyl indanes or such others (PBDEs, DBDPE even FRs not currently known to be produced). Other projects extending from the present findings may reveal the identity of these unknown bromine-containing compounds. For instance *in vivo* or *in vitro* studies involving current-use FRs would assist in identifying potential metabolic by-products.

With the recent mass regulatory push on the FR industry for the use of alternatives, the present may possibly be a cusp for the environmental availability of non-PBDE flame retardants and thus, monitoring exercises such as this are necessary.

## APPENDICES

**Appendix 1 –IUPAC names for individual PBDE congeners present in herring gull egg pool from the Laurentian Great Lakes.**

### TRIBROMODIPHENYL ETHERS

17	2,2',4-Tribromodiphenyl ether
25	2,3',4-Tribromodiphenyl ether
28	2,4,4'-Tribromodiphenyl ether
30	2,4,6-Tribromodiphenyl ether *

### TETRABROMODIPHENYL ETHERS

47	2,2',4,4'-Tetrabromodiphenyl ether
49	2,2',4,5'-Tetrabromodiphenyl ether
54	2,2',6,6'-Tetrabromodiphenyl ether
66	2,3',4,4'-Tetrabromodiphenyl ether
71	2,3',4',6-Tetrabromodiphenyl ether
75	2,4,4',6-Tetrabromodiphenyl ether
77	3,3',4,4'-Tetrabromodiphenyl ether

### PENTABROMODIPHENYL ETHERS

85	2,2',3,4,4'-Pentabromodiphenyl ether
99	2,2',4,4',5-Pentabromodiphenyl ether
100	2,2',4,4',6-Pentabromodiphenyl ether
116	2,3,4,5,6-Pentabromodiphenyl ether
119	2,3',4,4',6-Pentabromodiphenyl ether

### HEXABROMODIPHENYL ETHERS

138	2,2',3,4,4',5-Hexabromodiphenyl ether
139	2,2',3,4,4',6-Hexabromodiphenyl ether
140	2,2',3,4,4',6'-Hexabromodiphenyl ether
153	2,2',4,4',5,5'-Hexabromodiphenyl ether
154	2,2',4,4',5,6'-Hexabromodiphenyl ether
155	2,2',4,4',6,6'-Hexabromodiphenyl ether
156	2,3,3',4,4',5-Hexabromodiphenyl ether *

\* Internal standard for quantification (see Chapter 2)

### HEPTABROMODIPHENYL ETHERS

170	2,2',3,3',4,4',5-Heptabromodiphenyl ether
171	2,2',3,3',4,4',6-Heptabromodiphenyl ether
179	2,2',3,3',5,6,6'-Heptabromodiphenyl ether
180	2,2',3,4,4',5,5'-Heptabromodiphenyl ether
181	2,2',3,4,4',5,6-Heptabromodiphenyl ether
183	2,2',3,4,4',5',6-Heptabromodiphenyl ether
184	2,2',3,4,4',6,6'-Heptabromodiphenyl ether
190	2,3,3',4,4',5,6-Heptabromodiphenyl ether
191	2,3,3',4,4',5',6-Heptabromodiphenyl ether

### OCTABROMODIPHENYL ETHERS

194	2,2',3,3',4,4',5,5'-Octabromodiphenyl ether
195	2,2',3,3',4,4',5,6-Octabromodiphenyl ether
196	2,2',3,3',4,4',5,6'-Octabromodiphenyl ether
197	2,2',3,3',4,4',6,6'-Octabromodiphenyl ether
201	2,2',3,3',4,5,6,6'-Octabromodiphenyl ether
202	2,2',3,3',5,5',6,6'-Octabromodiphenyl ether
203	2,2',3,4,4',5,5',6-Octabromodiphenyl ether*
205	2,3,3',4,4',5,5',6-Octabromodiphenyl ether*

### NONABROMODIPHENYL ETHERS

206	2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether
207	2,2',3,3',4,4',5,6,6'-Nonabromodiphenyl ether
208	2,2',3,3',4,5,5',6,6'-Nonabromodiphenyl ether

### DECABROMODIPHENYL ETHER

209	2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether
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**Appendix 2 - Chemical structures of individual PBDE congeners included in the present investigation of FRs in herring gull egg pools collected from the Laurentian Great Lakes. See Table A1 for IUPAC congener names associated with individual structures. Hydrogen atoms are omitted for clarity.**

