Temporal Trends of Current-Use Brominated Flame Retardants and Dechlorane Plus in the Eggs of Colonial Herring Gulls (*Larus argentatus*) From the Laurentian Great Lakes of North America

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Introduction. Polybrominated diphenyl ethers (PBDEs) are currently the most widely studied class of additive brominated flame retardants (BFRs) that have been shown to bioaccumulate in wildlife and humans (Hites 2004). There are an increasing number of reports on PBDEs in top predator avian species (Norstrom et al. 2002; Verreault et al. 2005; McKinney et al. 2006). Specifically, the North American Great Lakes herring gulls (*Larus argentatus*), which have shown tetra- and penta-BDE congeners to be increasing exponentially between 1981 and 2000 (Norstrom et al. 2002).

There are approximately 75 different bromine-based compounds in production and commercially used as additives to polymeric products (Birnbaum and Staskal 2004). Recently, there have been reports of non-BDE BFRs to be environmental contaminants. For the first time, pentabromoethylbenzene (PBEB) and 1,2-bis(2,4,6-triphenoxy)ethane (BTBPE) were found in the Great Lakes (Hoh and Hites 2005). As well, another flame retardant compound, the *syn*- and *anti*-stereoisomers of the highly chlorinated flame retardant Dechlorane Plus (DP), was detected and identified in Lake Erie and Lake Michigan (Hoh and Hites 2006). There is exceedingly little to no toxicological or biological effects data available for wildlife or humans for non-PBDE BFRs.

Herring gulls from the North American Great Lakes have been shown to bioaccumulate persistent organic pollutants (POPs), including PBDEs. The annual collection of herring gull eggs, from selected colonies, allows the Canadian Wildlife Service to biomonitor POP exposure and trends. We examined and screened for ten current-use, non-PBDE flame retardants (with reference standards commercially available) in herring gull egg pools (n=10-13 individual eggs) from six colonial sites spanning all five Great Lakes. We also present a temporal assessment of five year intervals for 1982 to 2004 and a detailed, year-by-year assessment for 1995 to 2006 for the identified current-use, non-PBDE BFRs.

Materials and Methods. The locations of the sampling colonies in the Laurentian Great Lakes are shown in Figure 1. All samples were collected, as part of the CWS Herring Gull Monitoring Program, between 1982 and 2006. Eggs (n=10 to 13 per site) were subsequently pooled on an equal wet weight basis in preparation of pooled homogenates for each site. A standard procedure was followed, and slightly modified, for the extraction for neutral, organohalogen compounds for which procedures have been previously described (Norstrom et al. 2002). Quantification of all PBDE congeners by gas chromatography-mass spectrometry, operating in the electron capture negative ionization mode (GC-NCI-MS), selected ion monitoring (SIM) for isotopic bromine anions $^{79}Br^-$ and $^{81}Br^-$. Structure confirmation of

current-use, non-BDE BFRs was determined by gas chromatography-high resolution mass spectrometry (GC-HRMS). Isomer-specific analysis of HBCD was achieved via liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS).

Figure 1. Sites of herring gull colonies in the Laurentian Great Lakes: (1) Agawa Rock, Lake Superior; (2) Gull Island, Lake Michigan; (3) Channel-Shelter Island, Lake Huron; (4) Fighting Island, Detroit River; (5) Niagara River, above the falls; (6)Toronto Harbour, Lake Ontario.

Results and Discussion. This assessment screened for several current-use, non-PBDE flame retardants, for which six were detected and quantified at herring gull colonies from the Great Lakes (Table 1). The α-HBCD concentrations in 2004 varied from 2.12 to 20.20 ng/g (wet weight), with the highest levels found in the Agawa Rock and Gull Island colonies. Other "new" BFR levels ranged from 0.004-1.43 ng/g (wet weight) and were much lower than those of the major BDE congeners comprising of technical PentaBDE formulations (namely BDE-47, -99, -100), where Σ_3PBDE ranged from 186 to 498 ng/g (wet weight) for the same pools. *Syn*- and *anti*-DP isomers were also quantifiable in eggs from all sites, where Σ-DP ranged from 1.53 to 4.50 ng/g (wet weight), the highest levels being in the Niagara River colony.

Table 1. Concentrations of dominant (Penta-derived) PBDEs and newly identified, current-use BFRs in Herring Gull Eggs (pools n = 10-13) from colonial sites in the Laurentian Great Lakes (Figure 1).

	Agawa Rock	Gull Island	Channel Shelter Is.	Fighting Island	Niagara River	Toronto Harbour
∑-PBDE†	621 (498)	607 (447)	269 (186)	353 (260)	281 (210)	375 (259)
PBEB	0.07	0.03	1.43	0.16	0.03	0.04
HBB	0.44	0.53	0.32	0.41	0.24	0.46
PBT	0.012	0.022	0.017	0.011	0.004	0.013
BTBPE	0.06	0.16	0.04	0.26	0.70	0..04
α-HBCD	12.20	20.24	-	2.12	4.71	4.61

γ-HBCD	0.221	0.671	-	n.d	n.q.	n.q.
Σ-DP	1.75	1.53	2.20	4.17	4.50	2.53
% lipid	9.40	6.01	7.57	7.95	9.51	10.46

† Levels of $\sum_7$BDEs (BDE-28, -47, -100, -99, -154, -153 and -183) for the six representative herring gull colonies in the Great Lakes in 2004, major congeners as reported for BDE levels in 2000 (Norstrom et al. 2002). Data in parenthesis are the summation of most abundant congeners as associated with the Penta-derived formulation $\sum_3$BDE (BDE-47, -99 and -100) in egg pools from selected Great Lakes Herring Gull colonies. n.d. = not detected and n.q. = not quantifiable. Data is preliminary for isomer specific HBCD, not available for Channel Shelter Island.

The second focus of this study was to investigate the temporal distribution of these non-PBDE flame retardants for five years, spanning 1982-2004 (Figure 2). For four of the six flame retardants, the temporal distribution is shown in Figure 2. Three of the four, were detected at all six colonies for every year included in the timeframe. The general trend for PBEB and HBB indicates a slight decrease in appearance at every site. This is evident, except for PBEB at the Channel Shelter Island and Niagara River colonies, where, in the past decade, levels appear to increase. Similarly, the presence of BTBPE appears to be increase in frequency over this time period and was detected at all colonies in 2004. The highest levels of Σ-DP are reported at the Niagara River colony in 1982, although the five other colonies appear to show a slight increase until 1997, then decrease in 2004.

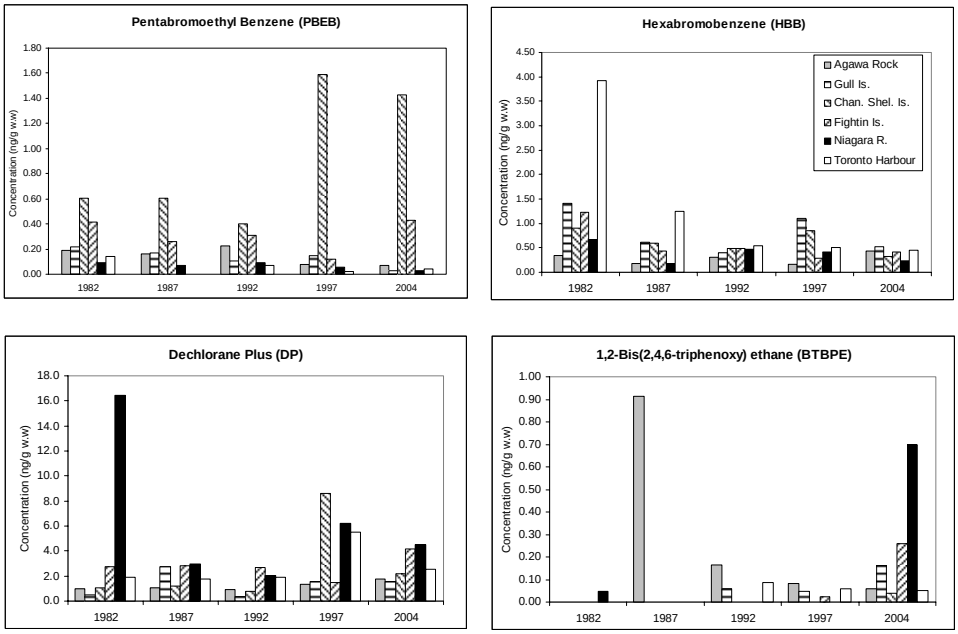

Figure 2. Temporal trends, spanning 1982-2004 (five year intervals), for current-use, non-BDE BFRs at six colonies in the North American Great Lakes.

Conclusions. These findings demonstrate for the first time, that a number of new, current-use flame retardants are contaminating the Great Lakes herring gull eggs. In addition, the temporal trends presented here, illustrate long-term presence for a number of non-BDE BFRs, while others are of emerging environmental concern in the North American Great Lakes. We are currently assessing the six identified non-BDE BFRs for temporal trends, on an individual year-by-year basis, for the period of 1995 to 2006.

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