Decabromodiphenyl Ether (BDE-209) and Degradation Products in the Eggs of Herring Gulls (*Larus argentatus*) From the Laurentian Great Lakes of North America

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Introduction. As environmental contaminants, polybrominated diphenyl ethers (PBDEs) are at present the most extensively studied class of additive brominated flame retardants (BFRs) that have been shown to bioaccumulate in tissues of 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). In the case for eggs of colonial herring gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America, mainly tetra- and penta-BDE congeners were shown to be increasing exponentially between 1981 and 2000 (Norstrom et al. 2002). There is increasing regulation and phasing out of production for the commercial usage of Penta- and Octa-BDE technical formulations by members of the BFR industry (Tullo 2003; European Government). However, as these PBDE mixtures are removed from commercial markets, a consequential production increase may result for other non-regulated BFRs, such as tetrabromobisphenol A (TBBPA), hexabromocyclododecanes (HBCDs) and the DeBDE formulation. Decabomodiphenyl ether (BDE-209) is the major congener in the DeBDE commercial mixture (>97%) and is a heavily used PBDE formulation worldwide at greater than 56 000 metric tons in 2003 (BSEF).

The use of BDE-209 is highly controversial as it persists and subsequently bioaccumulates in the tissues of aquatic feeding wildlife at low to non-detectable levels. However, there are reports showing that BDE-209 can metabolically (e.g. fish) or photocatalytically degrade to lower brominated congeners (Bezares-Cruz et al. 2004; Gerecke et al. 2005; Stapleton et al. 2006). Less brominated PBDEs (e.g. BDE-47, -99 and -100) are more bioaccumulative and potentially exhibit greater toxicological properties relative to BDE-209.

In the Laurentian Great Lakes basin the herring gull is a facultative piscivore. Gulls are exposed to persistent organic pollutants (POPs) via their aquatic environment and food web, making them an ideal species for POP biomonitoring. Through the annual collection of eggs from fifteen colonies across the Great Lakes, the Canadian Wildlife Service (CWS) uses the herring gull to monitor spatial and temporal trends of legacy POPs (e.g. PCBs, DDE). In this study, we report the presence of BDE-209, along with numerous hepta-, octa- and nona-BDE congeners in the eggs of herring gulls. Several of these are potentially sequential debromination products of BDE-209, some of which may be contributing to levels of BDE congeners derived from the currently banned Penta- and Octa-BDE commercial mixtures. In addition to this, we also provide a post-2000 update (relative to Norstrom et al. 2002) on the current status of the environmental levels of the most prominent and bioaccumulative BDEs (namely Penta-derived), in the eggs from herring gulls in the Laurentian Great Lakes.

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.

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 1981 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 of neutral, organohalogen compounds for which procedures have been previously described (Norstrom et al. 2002). Quantification of all BDE 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 $^{81}Br^-$.

Results and Discussion. BDE-209 was only detected in the egg pools at four of the six herring gull colonies from the latest year included in this assessment. Of these four, BDE-209 was quantifiable at two of these four colonies. Concentrations were determined to be 0.14 and 0.21 ng/g ww at Channel Shelter Island and Niagara River, respectively. However, as a part of this evaluation for BDE-209, we also assessed for, and positively identified, a total of twenty-one hepta- to nona-BDE congeners, where several could be associated with the degradation (debromination) of BDE-209. Of these twenty-one congeners, BDE-183 was, in nearly all situations, the most dominant of the hepta- to deca-BDE congeners. A series of eight other hepta-BDE congeners were identified, although at much lower levels. In addition to this, ten of the twelve possible octa-BDE congeners were positively identified and quantified at all six colonies. The most prominent octa-BDE was BDE-197 at every site and year included this study. Similarly, BDE-206 was the most dominant and extensively detected of the three nona-BDEs. Spatially, the six colonies did not show much variation with respect to hepta- to nona-BDE congener patterns in 2004. The mean percent ± SE (N=6) to the total hepta-, octa- and nona-BDEs are as follows: hepta-BDEs, 62.3 ± 0.7%; octa-BDEs, 27.1 ± 0.3%; nona-BDEs, 10.6 ± 0.9%.

The major portion of BFR contaminant levels are comprised of Penta-BDE mixture-derived congeners, namely BDE-47, -99 and -100, which had been reported recently to be increasing exponentially over the

period of 1981 to 2000 (Norstrom et al. 2002). It appears that concentrations of PBDEs at the six colonies included in this investigation may be decreasing post-2000 (Figure 2). Concentrations at these six colonies ranged from 186 to 498 ng/g ww in 2004 for $\sum_3$BDEs (BDE-47, -100, -99) and 269 to 621 for $\sum_7$BDEs (BDE-28, -47, -100, -99, -154, -153 and -183).

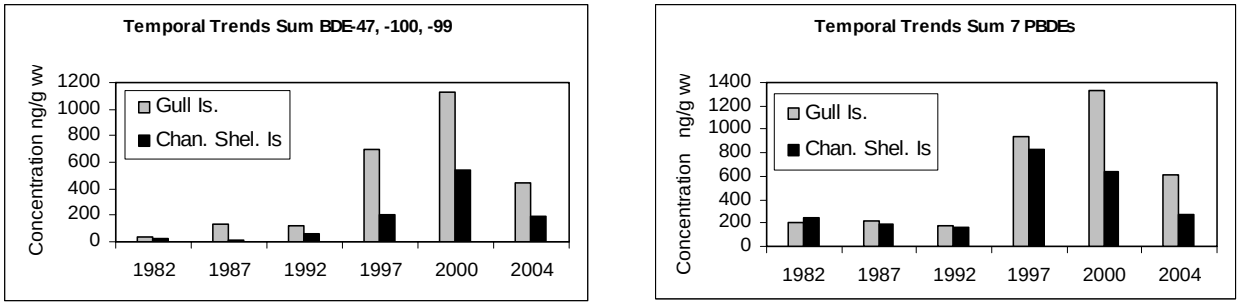

Figure 2. Temporal trends of PBDEs in herring gull egg pools from two representative colonies from the North American Great Lakes: a) levels of $\sum_3$BDEs (BDE-47, -100, -99) and b) $\sum_7$BDEs (BDE-28, -47, -100, -99, -154, -153 and -183). Levels reported from 2000 are referenced from (Norstrom et al. 2002).

In light of the apparent decrease in $\sum_3$BDEs and $\sum_7$BDEs (Figure 2), a similar decline in the levels of BDE-209 degradation products does not appear to follow these trends at all six sites. The colonies that shows this similar decreasing trends in contaminant levels are at Channel Shelter Island (Figure 3c), Toronto Harbour (Figure 3f), followed by the Agawa Rock colony (Figure 3a). The other three colonies (Figure 3b, d, e), however, appear to show a steady incline in the levels of hepta- to nona-BDE contamination, which may be representative of industrial production of the DeBDE commercial formulation.

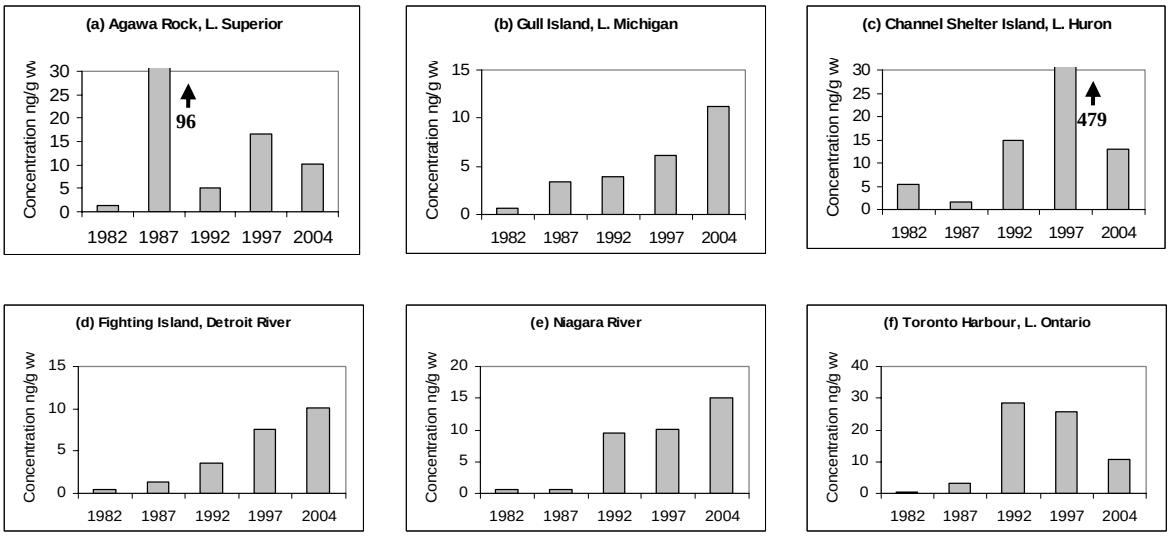

Figure 3. Temporal trends of known BDE-209 degradation products ($\sum_{\text{hepta-nona}}$BDE) in herring gull egg pools from at six colonies from the North American Great Lakes

Conclusions. In summary, it is evident BDE-209 is bioavailable and bioaccumulates in the herring gull from North American Great Lakes and is subsequently transferred *in ovo* to the egg. Additionally, a series of several hepta- to nona-BDEs are also present and are clearly bioaccumulative in this top predator avian species. The temporal trends presented here provide further proof that known degradation products BDE209 are becoming more prevalent in Great Lakes biota.

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