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Spatial and temporal comparisons of legacy and emerging flame retardants in herring gull eggs from colonies spanning the Laurentian Great Lakes of Canada and United States

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ABSTRACT

In the Laurentian Great Lakes basin of North America, an increasing number of chemicals of emerging concern (CECs) are being investigated, including legacy and replacement flame retardants (FRs). In the present study, 14 polybrominated diphenyl ethers (PBDEs), 23 non-PBDEs halogenated FRs (NPHFRs) and 16 organophosphate ester FRs (OPE-FRs) were analyzed in 100 individual eggs collected in 2012 and 2013 and in 15 egg pools of herring gulls collected in 2012 from 20 colonies across the entire Laurentian Great Lakes basin. For CEC-FRs in eggs from all colonies, 14 PBDEs, 12 NPHFRs and 9 OPE-FRs were quantifiable in at least one of the 115 analyzed samples. The mean sum PBDE (Σ_{14}PBDE) concentrations ranged from 244 to 657 ng/g wet weight (ww), and on average were 1–2 orders of magnitude greater than the Σ_{12}NPHFR concentrations (13.8–35.6 ng/g ww), and 2–3 orders of magnitude greater than Σ_9OPE-FR concentrations (0.31–2.14 ng/g ww). Mean Σ_{14}PBDE and sum of *syn*- and *anti*-Dechlorane Plus isomer (Σ_2DDC-CO) concentrations in eggs from colonies within Laurentian Great Lakes Areas of Concern (AOCs) were in most cases greater than in eggs from nearby colonies outside of AOCs. Comparing CEC-FR concentrations in eggs collected in 2012–2013 to those previously measured in eggs collected approximately 7 years earlier (2006 and 2008) showed that Σ_7PBDE (BDE-28, -47, -100, -99, -154, – 153 and -183) mean concentrations in eggs from 6 colonies were approximately 30% less than they were in eggs from the same colonies from the earlier time period, whereas 3 current-use FR (BDE-209, HBCDD and Σ_2DDC-CO) concentrations were significantly greater ($p < 0.05$) than previously measured. Between 2006 and 2013 there were significant changes in individual PBDE patterns for BDE-71, -138, -153, -203, -206 and -207. Among all of the examined CEC-FRs, concentrations of Σ_4PBDE (BDE-47, -99, -100 and -153) and HBCDD in gull eggs from all colonies were greater than or comparable to their lowest observed effect concentrations (LOECs) based on in ovo egg injection studies. Overall, the current profiles of a broad suite of FRs in Laurentian Great Lakes herring gull eggs highlights the need to better understand e.g., exposure-effect implications and metabolism of FRs, i.e. OPE-FRs, and emphasizes the importance of continued monitoring of CEC-FRs whose concentrations appear to be increasing, including BDE-209, HBCDD and DDC-COs.

1. Introduction

Over the last several decades, flame retardants (FRs) have been widely used and added to various manufactured materials such as plastics, foams, textiles, furniture and many others materials to delay the ignition of flame and to prevent the spread of fire (Covaci et al., 2011; Sjodin et al., 2003; van der Veen and de Boer, 2012). FR

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consumption in the global market in 2013 was more than two million tons, and are forecasted to generate revenues of US$7.15 billion in 2021 (Ceresana Research, 2015).

FR chemicals can be separated into two different broad classes of organic and inorganic FRs. Organic flame retardants (OFRs), including organohalogen and organophosphate FRs, are of environmental concern based on their substantial market share (e.g., more than 45% of total volume in 2011; Townsend Solutions Estimate 2015), environmental persistence and bioaccumulation, and their increasing detection frequencies in biota (Covaci et al., 2011; van der Veen and de Boer, 2012). For example, avian eggs analyzed retrospectively from archived samples collected up to 2010 from ecosystems such as the basin of the Laurentian Great Lakes of North America have been shown to contain measurable concentrations of numerous OFRs (Chen et al., 2012a, 2012b, 2012c, 2012d; Gauthier et al., 2007; Greaves and Letcher, 2014; Letcher et al., 2009; Su et al., 2014b).

The herring gull (*Larus argentatus*) is a colonially-nesting, facultative piscivore that breeds throughout the Laurentian Great Lakes basin of North America. These gulls are an ideal avian species for the spatial and temporal monitoring of persistent organic pollutants (POPs) in the Laurentian Great Lakes. Over the last four decades, eggs from up to 15 breeding colonies have been monitored annually for legacy POPs and mercury as part of the Environment Canada's Laurentian Great Lakes Herring Gull Monitoring Program (GLHGMP) (Gewurtz et al., 2011; Hebert et al., 1999). Over the last 5 years and retrospectively over the last 3 decades up to as recently as 2010, eggs and mainly egg pools from several GLHGMP colonies have been monitored annually for an increasing number of chemicals of emerging concern (CECs) that are OFRs. These include polybrominated diphenyl ethers (PBDEs) and a wide range of non-PBDE FR replacements such as numerous brominated FRs and organophosphate triester FRs (OPE-FRs) (Chen et al., 2012a, 2012b, 2012c, 2012d; Gauthier et al., 2007; Su et al., 2014a, 2014b, 2014c, 2014d). However, only 4 of the monitored GLHGMP colonies are in the United States (U.S.) while the rest are located in Canada. Since 2002, the Michigan Department of Environmental Quality and collaborators have collected eggs from 5 to 10 Michigan gull colonies to expand the geographic coverage for contaminants of focus for the GLHGMP under the Clean Michigan Initiative-Clean Water Fund (CMI-CWF) monitoring strategy (MDEQ, 1997).

The Laurentian Great Lakes of North America contain over 20% of the world's freshwater supply. The Canada–U.S. International Joint Commission (IJC) renewed the U.S.–Canada Great Lakes Water Quality Agreement (GLWQA) on September, 2012 (Great Lakes Water Quality Agreement, 2012). The prime objective of the GLWQA is to restore and protect the chemical, physical and biological integrity and to address the changing impacts on the quality of waters of the Laurentian Great Lakes. This updated version of the GLWQA calls for more binational coordination and monitoring in pursuit of the reduction and elimination of contaminant threats and specifically calls for the identification and monitoring of CECs (GLWQA, 2012).

The present study objectives are (1) to conduct a recent and more extensive assessment of CEC-FRs in herring gull eggs from 20 colonies (15 colonies under GLHGMP and 5 under CMI-CWF) within both Canada and U.S. waters of the Laurentian Great Lakes through binational coordination and integration with the GLHGMP, (2) to compare CEC-FR concentrations in colonies in Laurentian Great Lakes Areas of Concern (AOCs) with nearby non-AOC colonies, (3) to evaluate any changes in CEC-FR concentrations in herring gull eggs from the GLHGMP colonies over the time period from 2006 to 2013, and (4) to address whether CEC-FR concentrations in more current herring gull eggs (2012–2013) may be posing possible exposure-effect risks.

2. Experimental section

2.1. Chemical standards

A full list of the 53 target CEC-FRs (14 PBDEs, 23 other flame retardants (NPHFRs) and 16 OPE-FRs), along with their full chemical names is provided in Table S1. These chemicals and the analytical internal standards used were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada), Sigma-Aldrich (St. Louis, MO, USA), AK Scientific (Union City, CA, USA), TCI America (Portland, OR, USA), GL Chemtech (Oakville, ON, Canada), Cambridge Isotope Laboratories (Tewksbury, MA, USA), or from Dr. Vladimir Belov (Max Planck Institute for Biophysical Chemistry; Germany). Exceptions were 2,2-bis(chloromethyl-propyl-1,3-diyl) tetrakis (2-chloroethyl) bis (phosphate) (V6) and octabromo-1,3,3-trimethyl-1-phenylindane (OBTMI), which were generously donated by Dr. Heather Stapleton (Duke University, USA) and Dr. Åke Bergman (Stockholm University, Sweden), respectively.

2.2. Sample collection

The 20 colony sampling locations are broadly distributed across the Laurentian Great Lakes (Figs. 1 and 2). In 2012 and 2013, 13 herring gull eggs were collected in late April to early May from each of the 5 U.S. CMI-CWF colonies: Little Charity Island in Saginaw Bay in Lake Huron; Five Mile Island (St. Mary's River) in the Upper St. Mary's River; Bellow Island in Lake Michigan; Monroe, Michigan, at the mouth of the River Raisin at Lake Erie; and Gull Island in Lake Superior. These colonies include those in 3 U.S. Areas of Concern (AOCs; Saginaw Bay, River Raisin, St. Mary's River), 1 control colony (Gull Island) near Isle Royale in Lake Superior and one colony (Bellow Island located in the West Bay of Grand Traverse Bay in Lake Michigan) that may be heavily

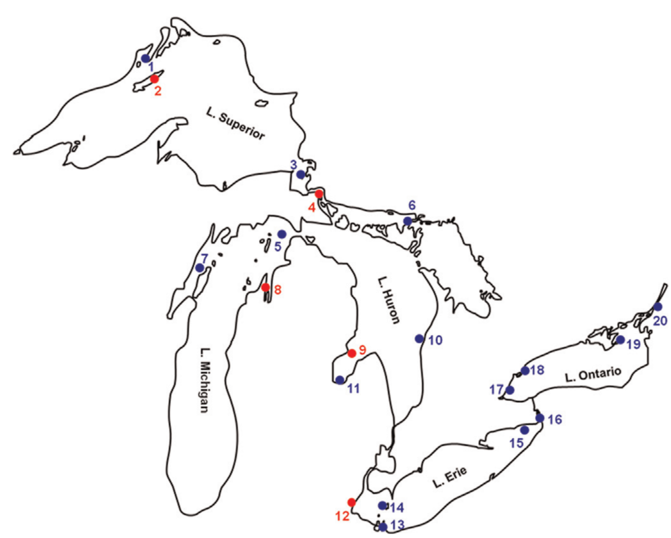

Fig. 1. Sampling locations of herring gull eggs in the North American Laurentian Great Lakes. Fifteen colonies sampled by the Environment Canada/Canadian Wildlife Service (CWS) as part of the Great Lakes Herring Gull Monitoring Program (GLHGMP) are marked with blue dots (collected in 2012), whereas five U.S. CMI-CWF colonies are marked with red dots: 1 Granite Island, Lake Superior; 2: Gull Island, Lake Superior; 3 Agawa Rock, Lake Superior; 4 Five Mile Island, Upper St. Mary's River; 5 Gull Island, Lake Michigan; 6 Double Island, Lake Huron; 7 Big Sister Island, Lake Michigan; 8 Bellow island, Lake Michigan; 9 Little Charity Island, Lake Huron; 10 Chantry Island, Lake Huron; 11 Channel-Shelter Island, Lake Huron; 12 Monroe, Lake Erie; 13 Mouse Island, Lake Erie; 14 Middle Island, Lake Erie; 15 Port Colborne, Lake Eire; 16 Weseloh Rocks, Niagara Falls, above the falls; 17 Hamilton Harbor, Lake Ontario; 18 Toronto Harbor, Lake Ontario; 19 Snake Island, Lake Ontario; 20: Strachan Island, St. Lawrence River. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)