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Spatio-temporal trends and monitoring design of perfluoroalkyl acids in the eggs of gull (*Larid*) species from across Canada and parts of the United States

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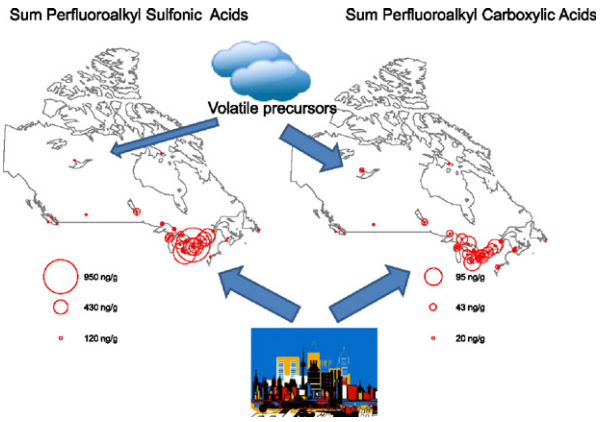
HIGHLIGHTS

- PFAAs determined in gull eggs in Canada and parts of USA in 2009–2014
- Concentrations of PFOS and other PFSAs were highest in urban/industrial areas.
- Concentrations of PFCAs surprisingly elevated in remote locations.
- Atmospheric transport of precursor chemicals may be influencing trends of PFCAs.
- Power analysis showed importance of long-term data collection.

GRAPHICAL ABSTRACT



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ABSTRACT

A large spatial dataset of perfluoroalkyl acid (PFAA) concentrations in eggs of herring gulls (*Larus argentatus* or congeneric species) collected from late April to early June between 2009 and 2014 from 28 colonies across Canada and parts of the Unites States was used to evaluate location-specific patterns in chemical concentrations and to generate hypotheses on the major sources affecting PFAA distributions. The highly bioaccumulative perfluorooctane sulfonic acid (PFOS) as well as other perfluoroalkyl sulfonic acids (PFSAs) showed the greatest concentrations in eggs from the lower Great Lakes of southern Ontario as well as from the St. Lawrence River. Despite the 2000 to 2002 phase-out of PFOS and related C_8 chemistry by the major manufacturer at the time, ongoing losses from consumer products during use and disposal in urban/industrial locations continue to

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be major sources to the environment and are influencing the spatial trends of PFOS in Canada. In comparison to PFOS, perfluoroalkyl carboxylic acids (PFCAs) were not as concentrated in eggs in close proximity to urbanized/industrialized centers, but had surprisingly elevated levels in relatively remote regions such as Great Slave Lake, NT and East Bay in Hudson Bay, NU. The present results support the hypothesis that atmospheric transport and degradation of precursor chemicals, such as the fluorotelomer alcohols 8:2 FTOH and 10:2 FTOH, are influencing the spatial trends of PFCAs in Canada. A power analysis conducted on a representative urbanized/industrialized colony in the Toronto Harbour, ON, and a relatively remote colony in Lake Superior, emphasized the importance of consistent and long-term data collection in order to detect the anticipated changes in PFAA concentrations in Canadian gull eggs.

1. Introduction

Since the 1950s, perfluoroalkyl acids (PFAAs) and their precursors have been used for numerous industrial and commercial applications as polymers and surfactants due to their chemical and thermal stability and because they contain both hydrophobic and lipophobic properties (Buck et al., 2011; Paul et al., 2009; Prevedouros et al., 2006). Although their emissions are associated with anthropogenic activities, PFAAs have been detected throughout the environment, even in abiotic and biotic samples from seemingly remote areas such as the Arctic (Braune and Letcher, 2013; Butt et al., 2010; Houde et al., 2011) and the North Pacific (Miller et al., 2015). Longer chain perfluoroalkyl sulfonic acids (PFSAs), especially perfluorooctane sulfonic acid (PFOS), and perfluoroalkyl carboxylic acids (PFCAs), especially perfluorooctanoic acid (PFOA), have been the most widely reported PFAAs in environmental media (Buck et al., 2011).

Between 2000 and 2002, the primary global manufacturer of perfluorooctane sulfonyl fluoride (PFOSF, used to make PFOS and its precursors) voluntarily phased-out PFOSF and PFOS production as a result of potential environmental impacts and toxicological effects (including hepatotoxicity, tumor induction, developmental toxicity, immunotoxicity, neurotoxicity and endocrine disruption) (3 M Company, 2012; Lau, 2015). In Canada, regulations published in 2008 prohibit the manufacture, use, sale, and import of PFOS, its salts, and its precursors with some exemptions (Government of Canada, 2008, 2015). Efforts to reduce the emissions of PFCAs started in 2006 where eight major manufacturers entered into a voluntary agreement with the United States Environmental Protection Agency (USEPA) to reduce emissions of PFOA, related higher homologue chemicals (i.e., with nine carbons and greater), and their known precursors in products by 95% by 2010, and to work towards their elimination by 2015. Reports from 2013 and 2014 show that the eight manufacturers were on track to phase out these chemicals by the end of 2015 (http://www.epa.gov/assessing-and-managing-chemicals-under-tsca/20102015-pfoa-stewardship-program). A similar agreement was reached in Canada between Environment and Climate Change Canada/Health Canada and five major manufacturers (http://ec.gc.ca/epe-epa/default.asp?lang=En&n=81AE80CE-1) to reduce residual PFOA, long-chain PFCAs (with a carbon chain length of nine or more), and precursors in products. In addition, proposed regulations in Canada would prohibit PFOA and longer chain PFCAs and products containing them, unless present in manufactured items (Government of Canada, 2015). In 2009, PFOS and related compounds were included in Annex B of the Stockholm Convention on Persistent Organic Pollutants (http://chm.pops.int/Convention/POPsReviewCommittee/Reviewedchemicals/tabid/781/Default.aspx), which restricts manufacturing and use to specific applications (Buck et al., 2011; Lindstrom et al., 2011). In addition, regulatory and voluntary actions exist for these chemicals in countries throughout the world (Buck et al., 2011; Lindstrom et al., 2011; Vierke et al., 2012). However, the production of PFOS, long-chain PFCAs, and their precursors continues in continental Asia (e.g., China and India) (Wang et al., 2014; Xie et al., 2013; Zhang et al., 2012), and use exemptions exist in several countries (Carloni, 2009; Environment Canada, 2009).

The data generated from monitoring programs are critical for determining the status of PFAAs in the environment and their response to recent voluntary and regulatory actions (Gebbink et al., 2011a; Gebbink et al., 2011b; Letcher et al., 2015). One such monitoring program is the Great Lakes Herring Gull (*Larus argentatus*) Monitoring Program (GLHGMP) where the collection of eggs from sites across the Great Lakes has been on-going since 1974 for the monitoring of legacy persistent pollutants (Hebert et al., 1999). More recently, in retrospective egg collections (1990–2010) and in eggs collected in recent years (2012 — 2013), PFAAs have been monitored as part of the GLHGMP (Gebbink et al., 2011b; Letcher et al., 2015). In 2008, a more comprehensive national monitoring program was initiated as part of Canada's Chemicals Management Plan (CMP) (Gebbink et al., 2011a), by drawing upon the GLHGMP as well as other avian collections that were already occurring across Canada e.g., (Braune and Letcher, 2013; Burgess et al., 2013; Champoux et al., 2006; Elliott and Elliott, 2013). In 2011, Gebbink et al. (2011a) evaluated the spatial trends of PFSAs and PFCAs in eggs of herring gull or congeneric species collected from 15 colonies located along an east to west transect across Canada. They detected relatively elevated concentrations of both PFSAs and PFCAs in eggs from urbanized areas of the Great Lakes and the St. Lawrence River.

In this era of fiscal restraint, it is important to design monitoring programs that best utilize available resources (Gilbertson et al., 1987; Hebert and Weseloh, 2003; Nicholson et al., 1997). The herring gull egg program design is particularly complex given that eggs are typically analyzed for PFAAs in pools as a means to reduce costs while providing information more representative of the population compared to the same number of individual samples (Bignert et al., 2014; Bignert et al., 1993). Power analysis, i.e., evaluating the probability of detecting a given trend if it is actually occurring, has been shown useful in optimizing program design (Gerard et al., 1998; Gewurtz et al., 2012; Gilbertson et al., 1987; Nicholson et al., 1997). One of the most difficult aspects of a power analysis is estimating the variance associated with each component of the study design (e.g., within pools and within and between years) (Nicholson et al., 1997). This information is best obtained through a pilot study or by assessing a program following a preliminary period of time (Steidl et al., 1997).

The first objective of this study was to expand the work of Gebbink et al. (2011a) on eggs collected in 2008 to evaluate the spatial trends of PFAAs in 28 herring gull (or congeneric species) colonies across Canada (including two additional locations north of the 60th parallel) and parts of the United States using eggs collected between 2009 and 2014. This large spatial PFAA dataset was used to evaluate location-specific patterns in chemical concentrations in order to generate hypotheses on the major sources that could be affecting PFAA distribution across Canada. The second objective was to use variance components estimated from this as well as previous studies (Gebbink et al., 2011a; Gebbink et al., 2011b) in a power analysis to optimize the herring gull (and congeneric species) egg monitoring program design for detecting responses of PFAAs to voluntary/regulatory actions.