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Perfluoroalkyl acids in the Canadian environment: Multi-media assessment of current status and trends

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ABSTRACT

In Canada, perfluoroalkyl acids (PFAAs) have been the focus of several monitoring programs and research and surveillance studies. Here, we integrate recent data and perform a multi-media assessment to examine the current status and ongoing trends of PFAAs in Canada. Concentrations of perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), and other long-chain perfluorocarboxylates (PFCAs) in air, water, sediment, fish, and birds across Canada are generally related to urbanization, with elevated concentrations observed around cities, especially in southern Ontario. PFOS levels in water, fish tissue, and bird eggs were below their respective Draft Federal Environmental Quality Guidelines, suggesting there is low potential for adverse effects to the environment/organisms examined. However, PFOS in fish and bird eggs tended to exceed guidelines for the protection of mammalian and avian consumers, suggesting a potential risk to their wildlife predators, although wildlife population health assessments are needed to determine whether negative impacts are actually occurring. Long-term temporal trends of PFOS in suspended sediment, sediment cores, Lake Trout (*Salvelinus namaycush*), and Herring Gull (*Larus argentatus*) eggs collected from Lake Ontario increased consistently from the start of data collection until the 1990s. However, after this time, the trends varied by media, with concentrations stabilizing in Lake Trout and Herring Gull eggs, and decreasing and increasing in suspended sediment and the sediment cores, respectively. For PFCAs, concentrations in suspended sediment, sediment cores, and Herring Gulls generally increased from the start of data collection until present and concentrations in Lake Trout increased until the late 1990s and subsequently stabilized. A multi-media comparison of PFAA profiles provided evidence that unexpected patterns in biota of some of the lakes were due to unique source patterns rather than internal lake processes. High concentrations of PFAAs in the leachate and air of landfill sites, in the wastewater influent/effluent, biosolids, and air at wastewater treatment plants, and in indoor air and dust highlight the waste sector and current-use products (used primarily indoors) as ongoing sources of PFAAs to the Canadian environment. The results of this study demonstrate the utility of integrating data from different media. Simultaneous evaluation of spatial and temporal trends in multiple media allows inferences that would be impossible with data on only one medium. As such, more co-ordination among monitoring sites for different media is suggested for future sampling, especially at the northern sites. We emphasize the importance of continued monitoring of multiple-media for determining future responses of environmental PFAA concentrations to voluntary and regulatory actions.

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1. Introduction

Perfluoroalkyl acids (PFAAs) are recognized as chemicals of environmental concern due to their ubiquitous presence in the environment both near and far from emission sources (Buck et al., 2011; Butt et al., 2010; Giesy and Kannan, 2001). PFAAs are highly persistent (Vecitis et al., 2010) and some are bioaccumulative (Conder et al., 2008; Houde et al., 2011). The toxicological profiles of individual PFAAs vary considerably and those for perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the best developed (Beach et al., 2006; Lau et al., 2007; Letcher et al., 2010; Lindstrom et al., 2011b). PFAAs belong to a larger group that includes both perfluoroalkyl and polyfluoroalkyl substances (Buck et al., 2011). Since the late 1940s, perfluoroalkyl and polyfluoroalkyl substances, and surfactants and polymers made with the aid of these substances, have had numerous industrial and commercial applications. For example, they are used as stain and soil repellents for textiles, surfactants in fluoropolymer manufacture, in food-contact paper, in aqueous film forming foam for fighting fuel fires, and in personal care products such as cosmetics (Buck et al., 2011; De Silva et al., 2012). The most commonly monitored and regulated PFAAs are "long-chain" perfluoroalkyl sulfonates (PFSAs), which contain six or more carbon atoms (i.e., with six or more perfluorinated carbons) and perfluorocarboxylates (PFCAs), which contain eight or more carbon atoms (i.e., with seven or more perfluorinated carbons) (Buck et al., 2011). Of the "long-chain" PFSAs and PFCAs, PFOS and PFOA have received the greatest attention.

The first known action taken to reduce the emission of PFSAs occurred between 2000 and 2002. Upon discovery that PFOS was widely distributed in the environment, the primary global manufacturer of perfluorooctane sulfonyl fluoride (PFOSF, used to make PFOS and its precursors), voluntarily phased-out PFOSF and PFOS production (3M Company, 2012). 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). In 2006, eight major manufacturers entered into a voluntary agreement with the United States Environmental Protection Agency (USEPA) to reduce emissions of PFOA, long-chain PFCAs, and their known precursors in products by 95% by 2010 and to work toward their elimination by 2015 (http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html). A similar agreement was reached in Canada between Environment Canada/Health Canada and four major manufacturers (http://ec.gc.ca/epe-epa/default.asp?lang=En&n=81AE80CE-1) to reduce residual PFOA, long-chain PFCAs, and precursors in products. 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., 2011b). In addition, regulatory and voluntary actions exist for these chemicals in countries throughout the world (Buck et al., 2011; Lindstrom et al., 2011b; Vierke et al., 2012). However, PFOSF-based production continues in China (Xie et al., 2013; Zhang et al., 2012), and use exemptions exist in several countries (Carloni, 2009; Environment Canada, 2009).

Monitoring and surveillance activities are essential for tracking environmental and health risks of contaminants of concern and for identifying knowledge gaps to be filled by research. Both Environment Canada (under the Chemicals Management Plan, CMP) and the Ontario Ministry of the Environment (OMOE) monitor PFAAs in a variety of environmental media, such as air, freshwater, sediment (surficial, suspended, and cores), fish, and birds across Canada and Ontario, respectively. Potential sources are also evaluated under certain monitoring and surveillance programs. For example, PFAAs have been monitored in indoor air, dust, and clothes dryer lint in order to examine the importance of commercial products in the indoor environment as a source of PFAAs to humans and wildlife. Recognizing that PFAAs are found in products that are ultimately disposed of in waste and wastewater systems, monitoring at landfills and wastewater treatment systems is also conducted.

Integrated multimedia sampling can provide important information that would be difficult to determine through an evaluation of each media separately as mechanisms affecting the transport and fate of PFAAs differ for each media. Abiotic media such as air, sediment, water, wastewater, and landfill leachate can provide details on loadings and sources of PFAAs to the environment whereas biota can generate information on the extent that PFAAs are available to be taken up and accumulated in animals.

The goal of this study is an integrated multi-media assessment of PFAAs using recent and long-term trend data generated by Environment Canada and the OMOE in order to examine and better understand the status and sources of PFAAs across Canada. The results for each media have also been or will be published independently in separate papers e.g., (Ahrens et al., 2011c; De Silva et al., 2010, 2011; Gebbink et al., 2011b; Genualdi et al., 2010; Myers et al., 2012; Shoeib et al., 2011). Here we combine these data to provide an integrated account of PFAAs in Canada.

2. Methods

2.1. Sample collection

2.1.1. Sample collection for spatial and temporal trends

Air (passive and high volume samplers), water, sediment, fish (focus on top predators), and eggs of European Starlings (*Stumus vulgaris*) and Gulls (focus on Herring Gull (*Larus argentatus*) or congeneric species) were collected at locations across Canada between 2006 and 2011 (Table S-1). The sampling locations were selected to be representative of drainage basins across Canada and to include locations of long-term monitoring and research sites so that baseline and ancillary information would be available as much as possible. Some sites were specifically chosen because of their relation to prospective contamination sources, while others were selected as reference areas representative of ambient loadings. For temporal trends assessment, air, sediment, suspended sediment, fish, Herring Gull eggs, and water were evaluated (Table S-2). Sample collection methods for spatial and temporal trends have been described previously (Ahrens et al., 2011a, 2011c; Conestoga Rovers and Associates, 2011; De Silva et al., 2011; Furdui et al., 2008b; Gebbink et al., 2011b; Genualdi et al., 2010; Gewurtz et al., 2012; Helm et al., 2011; Myers et al., 2012) and are briefly summarized in the Appendix.

2.1.2. Sample collection for monitoring of the indoor environment

Between 2007 and 2008, the homes of 152 women were evaluated as part of the Vancouver-based Chemicals, Health and Pregnancy Study (CHirP) (De Silva et al., 2012; Shoeib et al., 2011). Dust was collected from all 152 homes, indoor and outdoor air were collected using SIP disk air samplers from a subset of 59 and six homes, respectively, and lint from dryer machines were collected from 63 homes.

2.1.3. Sample collection for wastewater and landfill leachate monitoring

Wastewater was sampled from 20 wastewater treatment plants (WWTPs) (Guerra et al., In Prep.) and landfill leachate were collected from ten Canadian municipal solid waste landfill sites between 2009 and 2010 (Conestoga Rovers and Associates, 2011). In addition, the air at two Ontario landfill sites and one WWTP (secondary activated sludge treatment) were monitored for PFAAs and volatile fluorinated precursor compounds using passive air samplers between June and September 2009 (Ahrens et al., 2011c). Additional air sampling at a different secondary activated sludge WWTP was undertaken in 2010 using both passive air samplers and high volume air samplers (Vierke et al., 2011). Further details on the waste sector monitoring programs are provided in the Appendix.

2.2. Summary of analytical methods

Analytical methods for each media have been previously reported (Ahrens et al., 2011a, 2011c; Conestoga Rovers and Associates, 2011; De Silva et al., 2010, 2011, 2012; Furdui et al., 2008b; Gebbink and Letcher, 2012; Gebbink et al., 2009, 2011a, 2011b; Genualdi et al., 2010; Gewurtz et al., 2012; Helm et al., 2011; Myers et al., 2012; Shoeib et al., 2011; Vierke et al., 2011) and are summarized in the Appendix.

2.3. QA/QC protocols and data reporting

Even though comparable instrumental techniques were used for all media with quantification performed using isotope-labeled internal standards, as described above and in the Appendix, there is uncertainty regarding the comparability of data sets generated from different laboratories and at different times, which likely introduces error into the spatial and temporal trends analyses, especially with regard to comparison between media. Temporal trend analyses on archived samples are less affected by this issue because samples are generally analyzed at the same laboratory and time. To optimize consistency between datasets, extensive QA/QC procedures were conducted during the analysis of each media, as described in the Appendix. Well-defined native standards and mass-labeled internal standards were used in each laboratory. In addition, procedure blanks, duplicate samples, and spiked reference materials were run with each batch of samples. Each of the laboratories are participating in laboratory or field intercomparison studies (e.g., Dreyer et al., 2010; Gebbink et al., 2009; Myers et al., 2012; Reiner et al., 2012). The Lab Services Section and the Organic Contaminants Research Laboratory at NWRC, the analytical laboratory at the Canada Center for Inland Waters Center, and the OMOE are participants in specific PFAA QA/QC exercises such as the Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME) and interlaboratory analyses organized by the National Institute of Standards and Technology and by the Northern Contaminants Program. The OMOE and AXYS Analytical Services (AXYS) have been accredited by the Canadian Association for Laboratory Accreditation (CALA) for their analytical PFAA methods.

Due to small sample sizes, for the purpose of calculating summary statistics, detection limit substitutions with one half of the method detection limit (MDL) were made when greater than 40% of the samples for a particular media/compound/location/time period were above the detection level (Clarke, 1998). Otherwise, a zero value was attributed to the sample for data presentation. For the spatial assessment of PFAAs in the maps (Figs. 1, 2, 4, and 5), geometric mean (geomean) was used to represent central tendency because sample variance was not included for simplicity of presentation and the geomean is less sensitive to outliers compared with the arithmetic mean. However, additional information on sample dispersion is presented in Figs. 3 and 6. For all other reporting, data are presented as mean ± standard error of the mean, unless otherwise noted.

3. Results and discussion

3.1. Spatial trends

3.1.1. PFOS

The spatial distribution of PFOS in air, water, sediment, fish, and birds across Canada generally relates to urbanization (Figs. 1, 2, and 3). In many cases, higher concentrations were observed near cities, especially in southern Ontario, suggesting that urban and industrial centers are the primary sources of PFOS in the environment. These results correspond to previous studies (Adams et al., 2008; Houde et al., 2006; O'Connell et al., 2010) and are likely indicative of ongoing losses from consumer products during use and disposal (Paul et al., 2009). The influence of consumer product use and disposal was tested through analysis of samples in the indoor environment and WWTP effluents and landfill leachate, as discussed below. We next discuss results for each media separately.

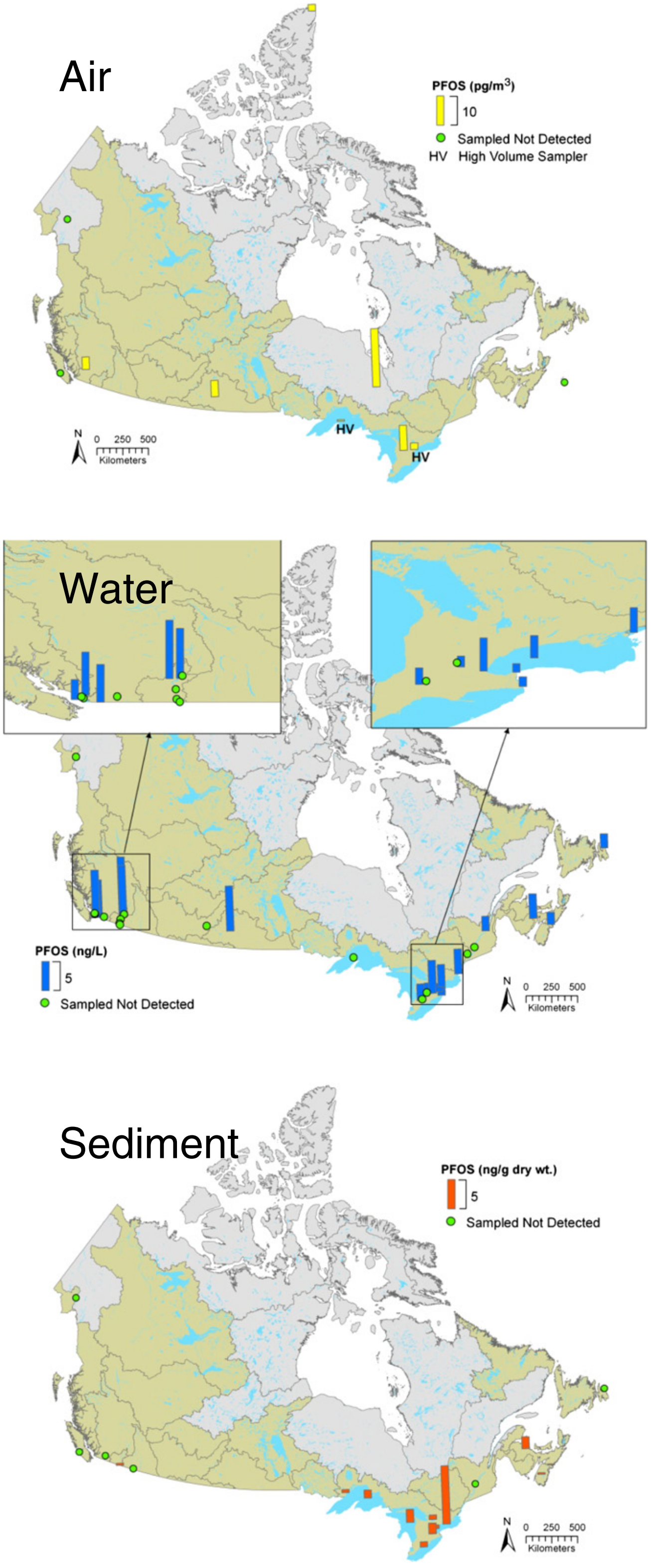
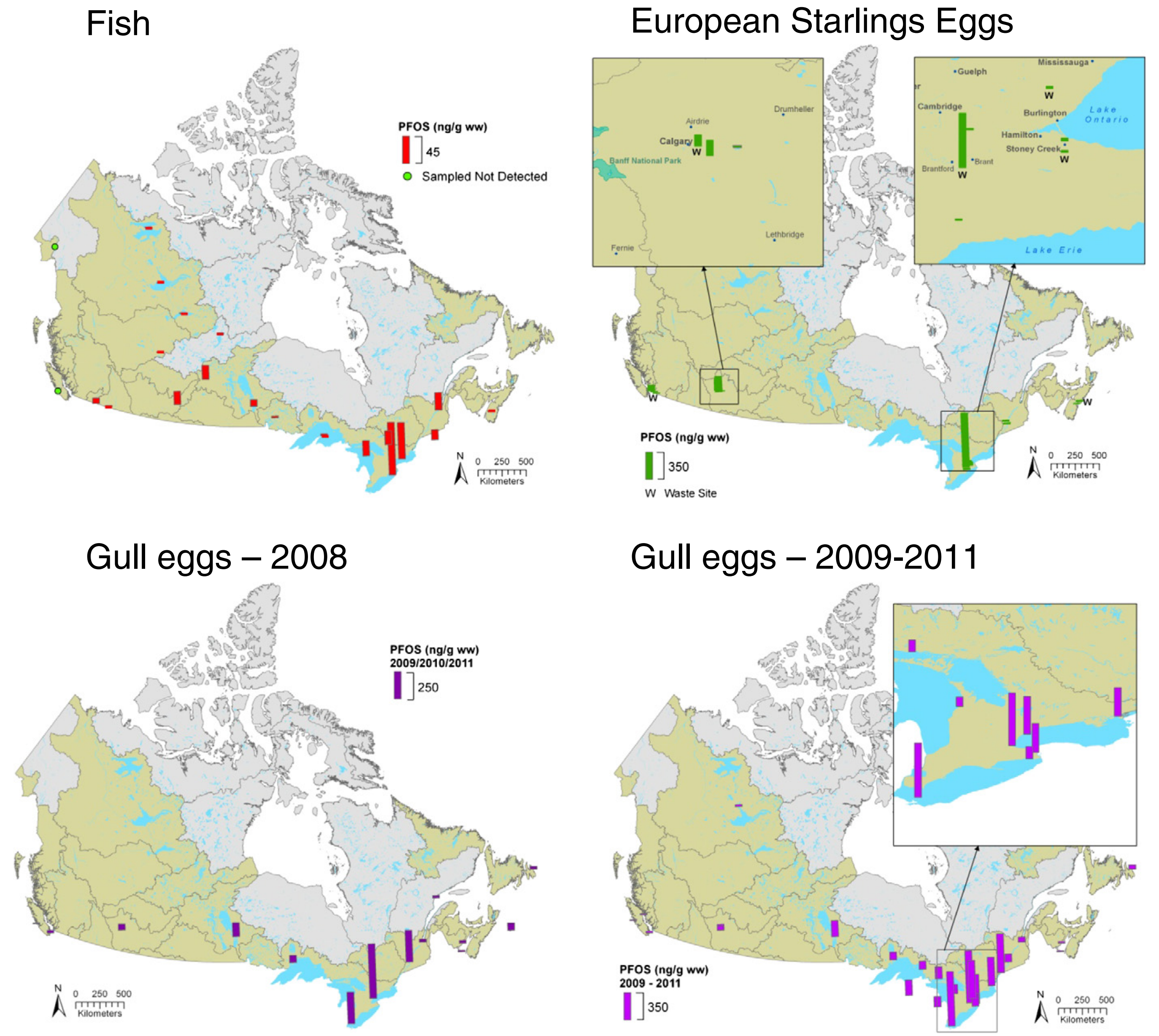


Fig. 1. PFOS concentrations (geomean for replicate measurements) in air, sediment, and water across Canada. For air, PFOS concentrations are either for passive or high volume samplers (denoted as HV). The green circles represent sites where PFOS concentrations were not detected.


Fish

European Starlings Eggs

Gull eggs – 2008

Gull eggs – 2009-2011

Fig. 2. PFOS concentrations (geomean for replicate measurements) in fish, European Starling eggs, and Gull eggs across Canada. For European Starling eggs, the sites denoted with a W were collected from waste sites (i.e., landfills). For Gulls, eggs sampled in 2008 were collected as individuals whereas those sampled in 2009–2011 were collected as pooled samples. The green circles represent sites where PFOS concentrations were not detected.

The geomean PFOS concentration in Toronto air (1.5 pg/m^3) measured using high volume samplers (sum of gas and particulate phases) in 2009 was more than three times greater than over Lake Superior (0.43 pg/m^3). In contrast, air measured using passive samplers in 2009 showed elevated PFOS concentration at a background site in northern Ontario. However, this data point was based on only one sample. In addition, the passive air sampler has a lower detection frequency for PFOS, due to a lower volume of air sampled, compared to the high volume sampler (Ahrens et al., 2011b; Genualdi et al., 2010; Jahnke et al., 2007; Klanova et al., 2008). Additional differences between high volume and passive samplers are discussed in Vierke et al. (2011).

Many of the rivers and streams sampled across Canada are located in cities and/or by WWTPs, and thus are influenced by urban and industrial activities. PFOS was highest in water collected at a site in Mill Creek, located in Kelowna, BC, where a geomean concentration of 10 ng/L was found. This section of Mill Creek is urbanized and influenced by urban stormwater. In addition, Wascana Creek, in Regina, Saskatchewan, had a relatively high PFOS geomean concentration of 7.8 ng/L compared to the other sampling sites. Wascana Creek is located 8.5 km downstream of a major WWTP outfall and is the water collection site most impacted by WWTP inputs (De Silva et al., In Prep.). Detectable values (>2 ng/L) were also observed in water samples from southern Ontario (Hamilton Harbour, Fort Erie, Wolfe Island, Grand River (downstream of Waterloo, ON), and Thames River (downstream of London, ON)), Quebec City, QC, Vancouver, BC (Still Creek and Serpentine River), Abbotsford, BC (Fishtrap Creek), and at the three Atlantic region sites (Napan River, NB, Sackville River, NS, and Waterford River, NF). PFOS concentrations were mostly not detected in water bodies from non-urban regions (e.g., background sites on the Fraser River, Mill Creek, and the Okanagen River, BC, Kusawa Lake, YT, Lake Superior (three open water sites and one site located near Thunder Bay, ON), Grand River (upstream of Waterloo, ON), and Thames River (upstream of London, ON)).

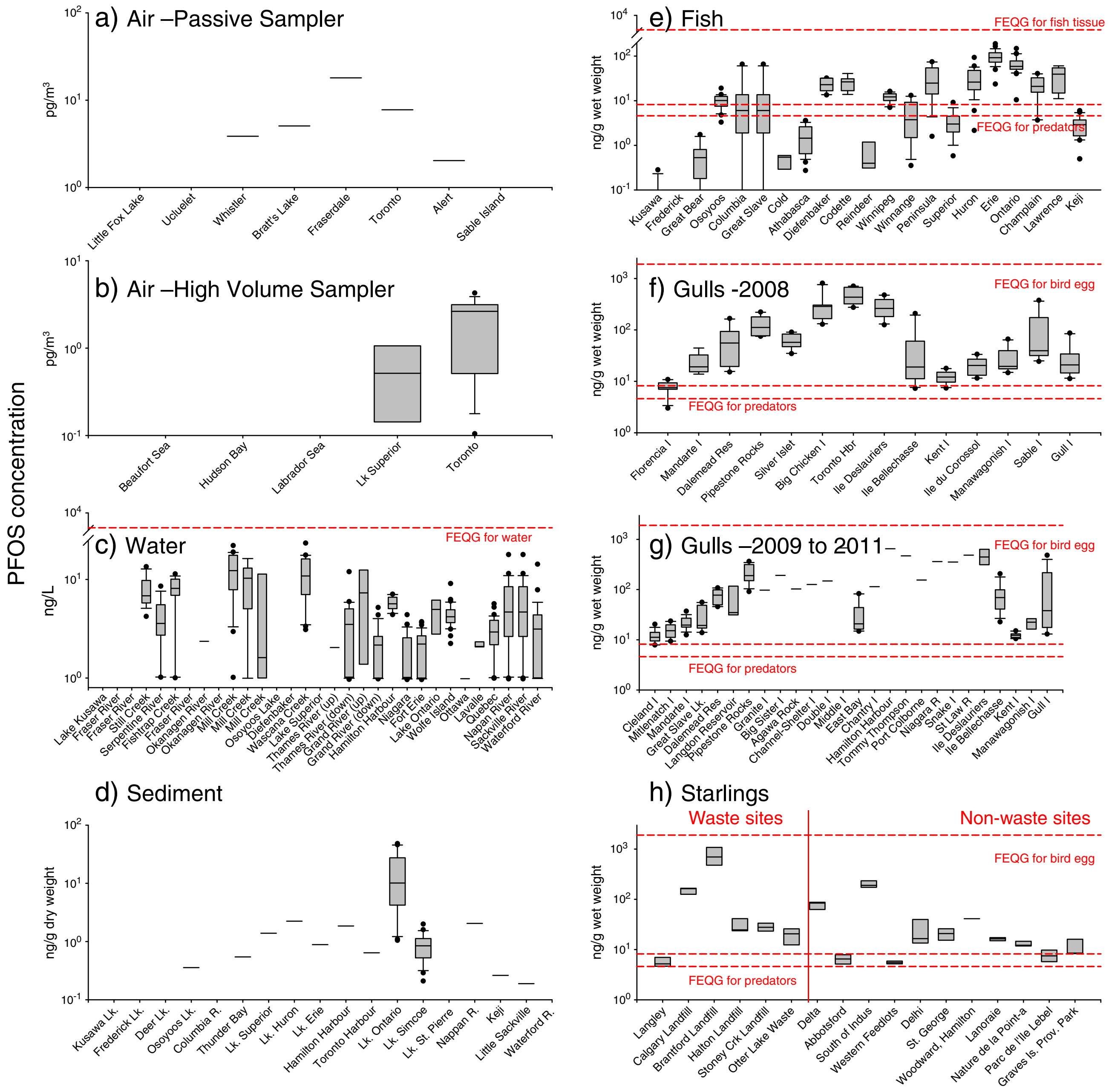


Fig. 3. Box and whisker plots of PFOS concentrations a) air (passive sampler), b) air (high volume sampler — sum of gas and particle phases), c) water, d) sediment, e) fish, f) Gulls collected in 2008, g) Gulls collected from 2009–2011, and h) Starlings (waste and non-waste sites). Sites are generally plotted from west to east. The line within the boxes indicates median, the boxes indicate 25th and 75th percentiles, the whiskers (error bars) below and above the boxes indicate 10th and 90th percentiles, and the closed circles indicate outliers. Draft Federal Environmental Quality Guidelines (FEQGs) are also displayed as red dashed lines for those media where guidelines exist.

For sediment, the highest PFOS concentration was found in Lake Ontario (geomean = 10 ng/g dry weight). PFOS was also detected in sediment from the other Great Lakes with concentrations ranging from 0.5 ng/g dry weight in Lake Superior by Thunder Bay, ON to 2 ng/g dry weight in Lake Huron. The PFOS concentrations in Lake Simcoe, ON sediment (geomean = 0.76 ng/g dry weight) were comparable to the Great Lakes sites, except Lake Ontario. A relatively elevated PFOS geomean sediment concentration of 2 ng/g dry weight was also found at an industrial site in New Brunswick (Nappan River). PFOS was present at relatively low concentrations (<0.4 ng/g dry weight) or was non-detectable in sediment at the other sites monitored.

With regard to fish, the highest geomean PFOS concentrations were observed in Lake Trout (*Salvelinus namaycush*) from Lake Erie (90 ng/g wet weight) and Lake Ontario (62 ng/g wet weight). Relatively elevated PFOS concentrations were also found in Walleye (*Sander vitreus*) from the St. Lawrence River, QC (30 ng/g wet weight), Codette Reservoir, SK (24 ng/g wet weight), and Lake Diefenbaker, SK (23 ng/g wet weight), and Lake Trout from Peninsula Harbour, ON (24 ng/g wet weight) and Lake Champlain, QC (17 ng/g wet weight). Levels were mostly low (<3 ng/g wet weight) in fish from the systems located in northern Canada, Pacific, and Atlantic regions, and Lake Superior. Differences in PFOS concentrations observed in fish could be a function of the different species used. However, concentrations of PFOS and other PFAAs in fish are generally not related to indicators of food web structure or diet such as stable isotopes of nitrogen and carbon, or fish lipid, size, age, and growth (Gewurtz et al., 2012; Guo et al., 2012).

For Starling eggs, the highest PFOS concentration (geomean = 703 ng/g wet weight) was found at the Brantford, ON, landfill, located

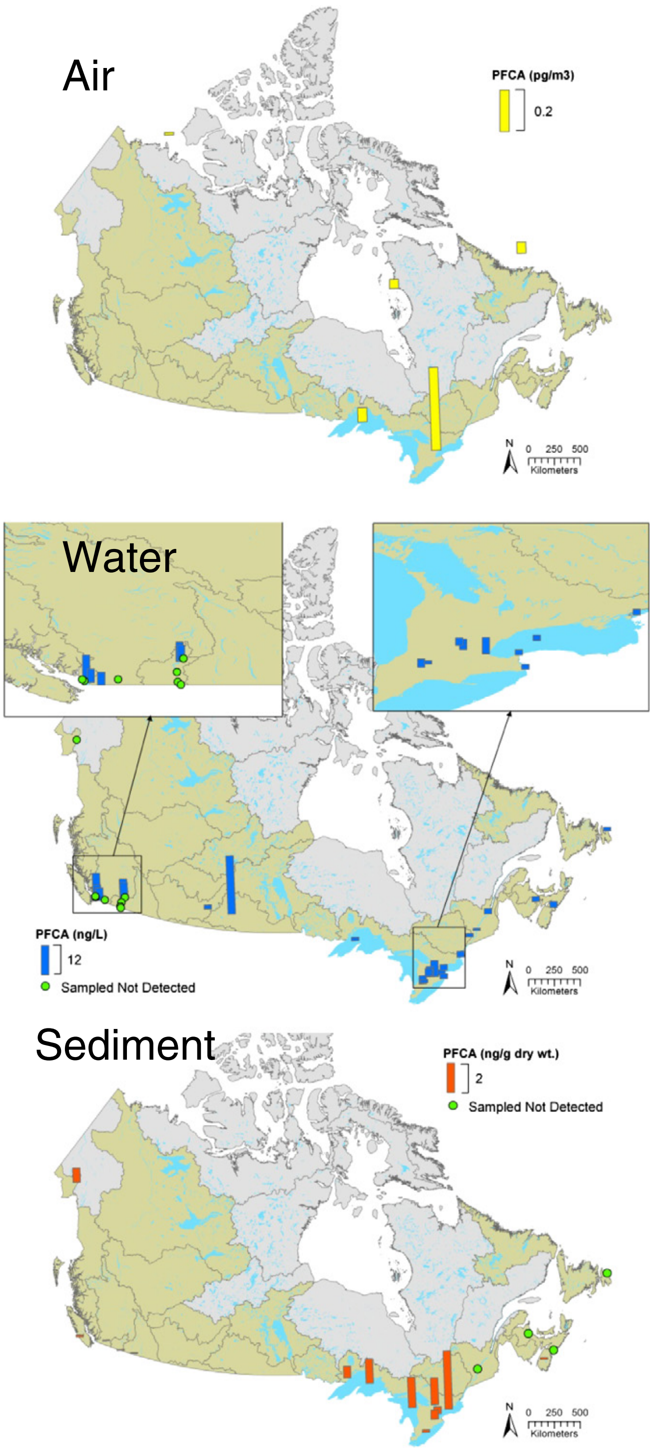


Fig. 4. Sum of five perfluorocarboxylates (PFOA, PFNA, PFDA, PFUnA, PFDoA) in air (measured using high-volume air samplers), water, and sediment across Canada. Geometric mean values were plotted when there were replicate measurements. The green circles represent sites where PFOS concentrations were not detected.

in a highly urbanized region in southern Ontario. Relatively elevated PFOS levels (geomean = 148 ng/g wet weight) were also found in Starling eggs at the Calgary, AB landfill. However, other than these two landfill sites, there was no trend of higher PFOS concentrations observed in Starling eggs at the waste compared to non-waste sites (Figs. 2 and 3). It is interesting to note that PFOS levels in Starling eggs from Graves Island Provincial Park, NS (11 ng/g wet weight), a relatively remote location, was comparable to more urbanized locations such as Abbotsford, BC (6.3 ng/g wet weight) and Nature de la Pointe-aux-Prairies, an urban park in Montreal, QC (13 ng/g wet weight), suggesting the influence of a non-local source. Graves Island Provincial Park is downwind of major North American urban and industrial centers (Desjardins et al., 2004; Wyn et al., 2010) and Starling eggs from this location are likely influenced by contaminants originating from these areas.

With regard to Gull eggs, relatively elevated PFOS concentrations were found in colonies located in urbanized areas of the Great Lakes and the St. Lawrence River with levels greater than 260 ng/g wet weight. Concentrations were lower (7–30 ng/g wet weight) in non-urban areas as well as at marine colonies on both the Atlantic and Pacific coasts.

3.1.2. PFCAs

The spatial distribution of the sum of five PFCAs (PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), and perfluorododecanoate (PFDoA)) in air (high volume samplers), water, sediment, and biota are shown in Figs. 4, 5 and 6. In Fig. 6, for air measured using passive samplers, we show fluorotelomer alcohols (FTOHs) (sum of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH) rather than PFCAs, because PFCAs were not detected, likely because of their low volatility, and because the FTOHs are PFCA precursors (Buck et al., 2011; Prevedouros et al., 2006; Young and Mabury, 2010). We center the following discussion on the sum of PFCAs because the longer-chained PFCAs are typically found at higher concentrations than PFOA in biota (due to greater bioaccumulation) and therefore their levels are more reliable (Houde et al., 2011). In contrast, PFOA tends to be the most dominant PFCA in water (Butt et al., 2010; Furdui et al., 2008a; Scott et al., 2010).

Similar to PFOS, concentrations of PFOA and other PFCAs were generally associated with urban areas, although more exceptions were observed. With regard to air, the concentrations of the sum PFCAs measured using high volume samplers were highest in Toronto, ON (geomean = 0.44 pg/m^3) in 2009, followed by Lake Superior (geomean = 0.075) in 2009 and the remote Arctic sites (geomean = 0.06 pg/m^3, 0.050 pg/m^3, and 0.014 pg/m^3 for Labrador Sea (2007), Hudson Bay (2007), and Beaufort Sea (2008), respectively). For the passive samplers, the sum of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were relatively elevated in Toronto, ON air (geomean = 64 pg/m^3) in 2009, with lower but detectable concentrations (geomean = 3.4 to 16 pg/m^3) observed in air at the other locations, which are less urbanized (Genualdi et al., 2010).

In water, the highest PFCA concentration was observed in Wascana Creek, SK (geomean = 23 ng/L). As discussed above, the monitoring site for this creek is located 8.5 km downstream of the WWTP outfall of the city of Regina, and was the water collection site most impacted by WWTP inputs. Relatively elevated water concentrations of PFCAs (geomean > 5 ng/L) were also observed at Still Creek, in Vancouver, BC, Mill Creek, in Kelowna, BC, Hamilton Harbour, ON, and Serpentine River in Surrey, BC. Similar to PFOS, PFCA concentrations were generally not detected in water bodies from non-urban regions (e.g., background sites along the Fraser River, Mill Creek, and the Okanagen River, BC, and Kusawa Lake, YT).

Elevated PFCAs were observed in Lake Ontario sediment (geomean = 3.1 ng/g dry weight) compared to other sites. Lakes Huron and Superior also had comparably elevated PFCA sediment concentrations (geomean = 1.8 and 1.4 ng/g dry weight, respectively) as well as Kusawa, YT (geomean = 0.84 ng/g dry weight), and Thunder Bay, Ontario (geomean = 0.68 ng/g dry weight). Surprisingly, relatively low PFCA concentrations were observed in sediment from Hamilton, ON and Toronto, ON Harbours (geomean = 0.52 and 0.36 ng/g dry weight, respectively) and PFCAs were not detectable in Lake Erie. Relatively low PFCA (<0.6 ng/g dry weight) or non-detectable concentrations were also found in sediment at the other sites monitored.

In fish, although the highest geomean PFCA concentration was observed in Lake Trout from Lake Erie (15 ng/g wet weight), surprisingly

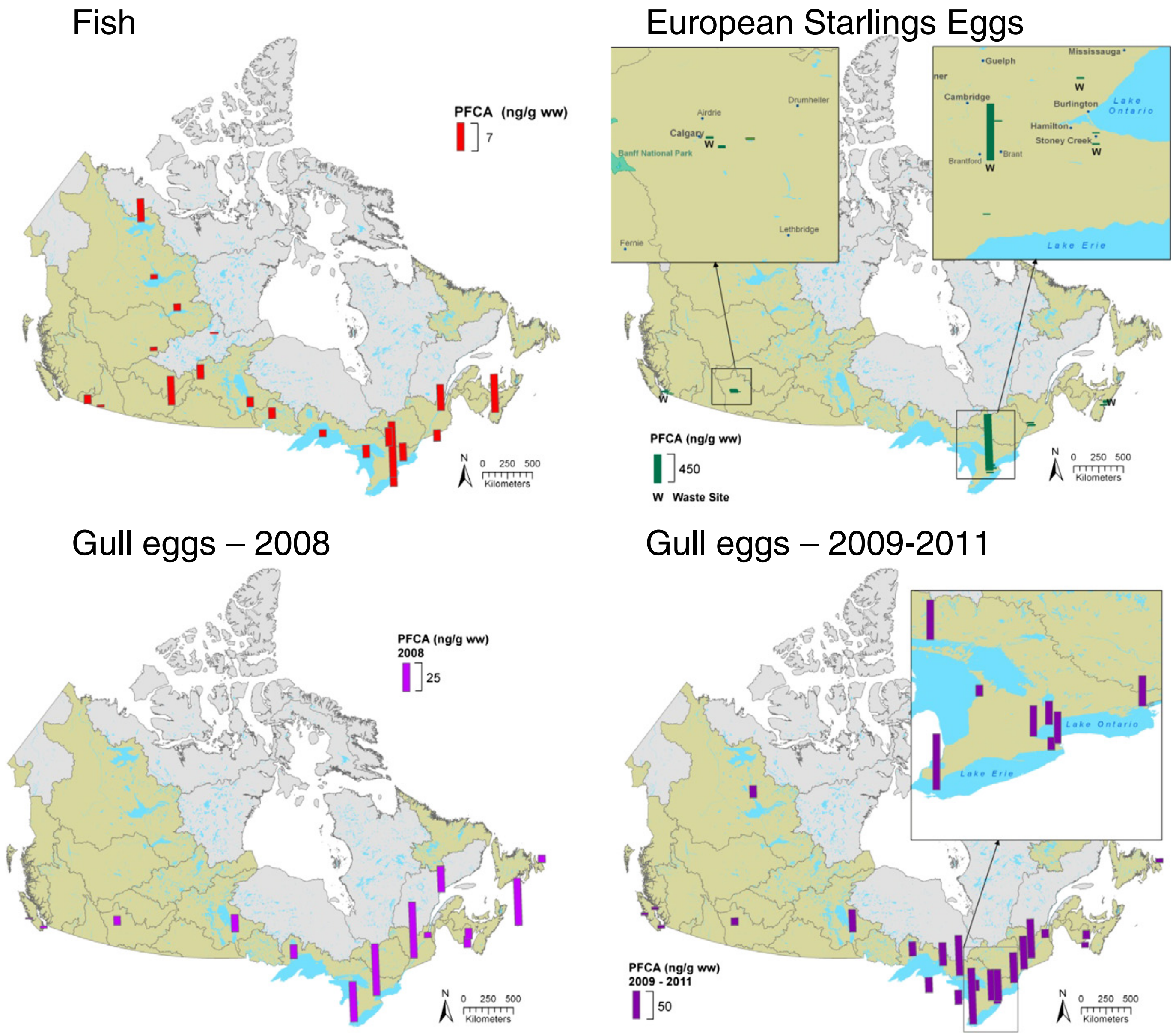


Fig. 5. Sum of five perfluorocarboxylates (PFOA, PFNA, PFDA, PFUnA, PFDoA) in fish, European Starling eggs, and Gull eggs across Canada. For European Starling eggs, the sites denoted with a W were collected from waste sites (i.e., landfills). For Gulls, eggs sampled in 2008 were collected as individuals whereas those sampled in 2009–2011 were collected as pooled samples. Geometric mean values were plotted when there were replicate measurements. The green circles represent sites where PFOS concentrations were not detected.

elevated PFCA concentrations were also found in fish from less populated areas, such as Brook Trout (*Salvelinus fontinalis*) from Kejimkujik Lake, NS (geomean = 10 ng/g wet weight), Walleye from Lake Diefenbaker, SK (geomean = 7.7 ng/g wet weight), and Lake Trout from Great Bear Lake, NT (geomean = 5.6 ng/g wet weight). The reason for this pattern is unknown and currently under more detailed study.

For Starlings, the trends for PFCAs were generally similar to PFOS, with the highest PFCA concentration (910 ng/g wet weight) found at the Brantford, ON landfill. Further, there was no trend of higher PFCAs in waste compared with non-waste sites.

For Gulls, similar to PFOS, relatively elevated PFCA concentrations were found in urbanized areas of the Great Lakes and the St. Lawrence River with levels greater than 40 ng/g wet weight. PFCA concentrations in Gull colonies located in less populated regions, including marine colonies, were generally lower (1.1 to 69 ng/g wet weight) compared to the urbanized systems (Gebbink et al., 2009).

For Lake Erie, the fact that PFAA concentrations were relatively elevated in Lake Trout and Gull eggs but low in sediment is surprising. The data for Lake Erie sediment were based on only one sample. However, Helm et al. (2007) found similar results, in that concentrations of PFOS and PFOA at nearshore sampling sites throughout the Canadian side of Lake Erie (maximum concentrations = 0.47 and 0.07 ng/g dry weight for PFOS and PFOA, respectively), were lower than in Lake Ontario (maximum concentrations = 1.2 and 0.77 ng/g dry weight, respectively), and Lake Huron/Georgian Bay (maximum concentrations = 1.7 and 0.71 ng/g dry weight, respectively), but comparable to Lake Superior (maximum concentrations = 0.44 and 0.29 ng/g dry weight, respectively). In contrast to sediment, De Silva et al. (2011) found that water concentrations of PFOA were higher in Lake Erie (5.5 ng/L) compared to any of the other Great Lakes (range from 0.65 ng/L in Lake Superior to 4.3 ng/L in Lake Ontario). PFOS concentrations in Lake Erie water (2.8 ng/L) were higher than Lake Superior (0.26 ng/L) and Lake

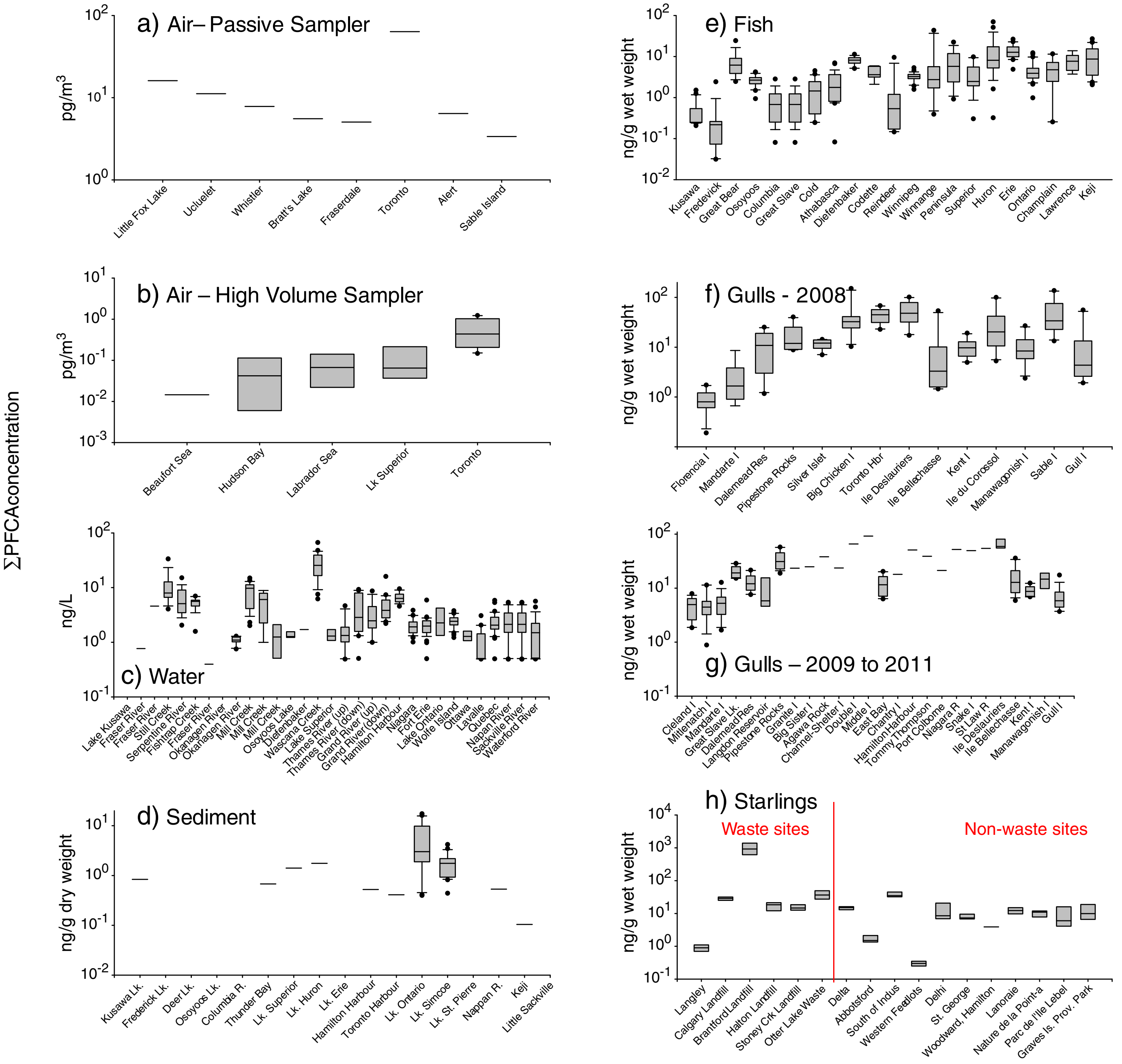


Fig. 6. Box and whisker plots of the sum of three fluorotelomer alcohol (6:2 FTOH, 8:2 FTOH, and 10:2 FTOH) concentrations in a) air measured using passive samplers and the sum of five perfluorocarboxylate (PFOA, PFNA, PFDA, PFUnA, PFDoA) concentrations in b) air measured through high volume samplers (sum of gas and particle phases), c) water, d) sediment, e) fish, f) Gulls collected in 2008, g) Gulls collected from 2009 to 2011, and h) Starlings (waste and non-waste sites). The line within the boxes indicates median, the boxes indicate 25th and 75th percentiles, the whiskers (error bars) below and above the boxes indicate 10th and 90th percentiles, and the closed circles indicate outliers.

Huron (2.2 ng/L) but lower than Lake Ontario (5.5 ng/L). With regard to biota, De Silva et al. (2011) and Furdui et al. (2007) also found that whole Lake Trout samples from Lake Erie had the highest PFOS and PFCAs concentration in the Great Lakes, and Guo et al. (2012) determined that concentrations of PFOS and PFCAs in Lake Trout (fillet) from Lakes Erie and Ontario were generally comparable and significantly greater ($p < 0.05$) than the other Great Lakes. Differences in PFAA concentrations between sediment and water/biota emphasize differences in the processes controlling the fate and transport of PFAAs between these media and require further study. The differences could also be an artifact of the different laboratories used. However, the trends for sediment corresponded in two separate laboratories (i.e., data from this study which were measured by AXYS and data from Helm et al. (2007)). Furthermore, the trends for biota were similar for data generated from multiple analytical laboratories (De Silva et al., 2011; Furdui et al., 2007; Gebbink et al., 2009; Guo et al., 2012).

As PFAAs detected in the Canadian environment may originate outside of Canada's borders, it is interesting to compare the concentrations reported in this review to those measured in other parts of the world. Such a comparison is hampered by the fact that a variety of techniques (for abiotic media) or tissue types (for biota) have been used in different studies. Nonetheless, it is evident from recent reviews and global-scale studies that PFAA concentrations observed in the Canadian environment span the range of those observed in the literature (Butt et al., 2010; Genualdi et al., 2010; Houde et al., 2006, 2011; Suja et al., 2009).

3.2. Comparison of PFOS concentrations to Draft Federal Environmental Quality Guidelines

Draft Federal Environmental Quality Guidelines (FEQGs) developed by Environment Canada exist for PFOS in water, fish tissue, bird eggs, and wildlife (mammalian and avian) diet. The FEQGs are currently in review and thus are denoted as draft throughout this paper. When environmental concentrations of PFOS are below the draft FEQG, adverse effects on aquatic life or animals consuming aquatic life are not likely. Concentrations above the draft FEQGs indicate an increased likelihood that adverse effects in the environment may occur but are not automatically expected.

PFOS concentrations in all media were below their respective guideline levels (Fig. 3). The draft FEQG for water is 6000 ng/L which is over two orders of magnitude greater than the highest measured water concentration (23 ng/L in Wascana Creek, SK). Similarly, for fish, the draft FEQG (8300 ng/g wet weight) is 44-times greater than the highest measured PFOS concentration in fish (189 ng/g in Lake Erie Lake Trout). The bird egg FEQG (1900 ng/g wet weight) was 2.3-times the highest measured concentration in Gulls (811 ng/g wet weight at Big Chicken Island, Lake Erie) and 1.6-times the highest measured concentration in Starling eggs (1184 ng/g wet weight at the Brampton, ON landfill site). If eggs from Brampton are excluded, the FEQG was 7.5-times greater than the highest PFOS measurement in Starlings (254 ng/g wet weight near Indus, AB). In contrast, the FEQGs for wildlife diet (4.6 ng/g wet weight food for mammalian predators and 8.2 ng/g wet weight food for avian predators) were consistently exceeded in fish and birds (Fig. 3). Taken together, these results suggest that PFOS concentrations present a low potential of adverse effects to the organisms examined in this paper. However, PFOS in fish and bird eggs tended to exceed guidelines for the protection of mammalian and avian consumers, suggesting that this compound could represent a potential risk to their wildlife predators. Wildlife population health assessments are required to determine whether negative impacts are actually occurring. As discussed below, PFOS concentrations have mostly stabilized or decreased, suggesting that the extent of these exceedances will decrease over time.

3.3. Multimedia comparison of PFAA profiles

We next evaluated the multimedia PFAA profiles at locations where three or more media were sampled and where each of these media had at least one compound above the detection limit. In Kejimkujik Lake, NS, we also included Gull and Starling samples from nearby locations (Kent Island, NB and Graves Island Park, NS for Gulls and Starlings, respectively). Such an analysis helps to identify differences in routes of exposure (Houde et al., 2006) and to ascertain whether unexpected patterns in biota (e.g., in Kejimkujik Lake as discussed above) are due to loadings or food web processes. We examined PFAA compounds that were quantified in all media, i.e., PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, and PFOS and plotted each PFAA as a percent of the total of these seven compounds (Figs. 7 and 8).

For the systems shown in Fig. 7, i.e., Lake Erie, Hamilton Harbour, Toronto Harbour, Lake Ontario, and the St. Lawrence River, the PFAA profile was similar and typical of abiotic and food web studies e.g., (Ahrens et al., 2010; Furdui et al., 2008a; Kelly et al., 2009; Kwadijk et al., 2010; Labadie and Chevreuil, 2011; Martin et al., 2003a, 2003b, 2004). All of these systems are located in southern Ontario and heavily influenced by urban, industrial, and agricultural (especially Lake Erie) activities. In these five systems, PFOS and PFOA were dominant in water (each encompassing between 30 and 60% of the total PFAA profile). This is not surprising as larger quantities of PFOS and PFOA have been used compared to the other PFAAs (Paul et al., 2009; Prevedouros et al., 2006). With regard to air in Toronto, PFOS (65%) followed by PFOA (17%) had the largest contribution to the compound profile. The fact that the percent of PFOS was greater than PFOA in air can be explained by the relatively large proportion of PFAAs found in the particulate compared with the gas-phase, especially as measured by the high volume sampler (Ahrens et al., 2011b) and because PFOS sorbs to particles to a greater extent than PFOA (Ahrens et al., 2009; Higgins and Luthy, 2006). With regard to sediment and biota, PFOS sorbs to sediment to a greater extent than PFOA (Ahrens et al., 2009; Higgins and Luthy, 2006) and is more bioaccumulative (Conder et al., 2008; Labadie and Chevreuil, 2011; Martin et al., 2003b). As such, the relative proportion of PFOA decreased or was not detected in sediment and biota, whereas PFOS dominated the PFAA profile in these media, with a relative contribution to total PFAAs greater than 60% for sediment and Starlings and greater than 80% for fish and Gulls. Longer-chained PFCAs are more bioaccumulative and have a greater sediment sorption than PFOA (Ahrens et al., 2009; Higgins and Luthy, 2006; Labadie and Chevreuil, 2011; Martin et al., 2003b). However, the fact that they are used in lower quantities compared with both PFOA and PFOS (Paul et al., 2009; Prevedouros et al., 2006), likely explains why they are less predominant in sediment and biota ($\sum$5PFCAs contributed less than 40% in sediment and biota).

For the systems shown in Fig. 8, i.e., Lakes Huron and Superior and Kejimkujik Lake, NS, different patterns were evident, with PFOS being less dominant in the contaminant profile compared to the systems shown in Fig. 7. In Lake Superior, only PFOA was detected in water and PFOA made up 20% and 24% of the PFAA profile in sediment of Lakes Huron and Superior, respectively. This is much greater than the relative contribution of PFOA in the systems presented in Fig. 7, where PFOA only made up between 2 and 10% of total PFAAs in sediment. These relatively lower concentrations of PFOS in the abiotic media from Lakes Huron and Superior were reflected in fish, whereby PFOS contributed 70% and 50% to total PFAA, respectively, with the remainder being made up of the longer-chained PFCAs. However, the PFAA profile in Lake Superior air (sum of gas and particle phase) was comparable to Toronto, with PFOS being dominant, contributing 82% to the PFAA profile (the remainder consisting of longer-chained PFCAs). For the air breathing Starlings and Gulls in Lakes Huron and Superior, PFOS contributed between 75 and 85% to total PFAAs, comparable to the patterns in Superior air.

Kejimkujik Lake had a unique PFAA profile that differed greatly from the other systems in Figs. 7 and 8, with long-chained PFCAs contributing a relatively high proportion to total PFAAs ($\sum$5PFCAs contributed 28%, 75%, 50%, and 43% to total PFAAs in sediment, fish, Starlings, and Gulls). Interestingly, De Silva et al. (2010) reported that Kejimkujik fish had the highest concentrations of long-chained PFCAs in Canada. By combining data from all media, it is evident that the source of PFAAs to Kejimkujik Lake differs from the other systems included in Figs. 7 and 8 and that the unique PFAA profile in biota (especially fish) from this lake is not due to some sort of food web process. Kejimkujik Lake is downwind of major North American urban and industrial centers and contaminants originating from these areas are likely transported and deposited to this lake (Desjardins et al., 2004; Scott et al., 2006; Wyn et al., 2010). Relatively high levels of the long-chained PFCAs have been previously noted in biota from other studies (Hart et al., 2008; Houde et al., 2011), particularly in East Asia and northern latitudes. It has been suggested that this pattern may be due to specific sources of emission in East Asia dominated by long-chained PFCAs and/or their precursors followed by long-range transport via ocean and atmospheric pathways to northern regions (Hart et al., 2008; Houde et al., 2011). In support of this hypothesis, De Silva et al. (2010) found that fish collected from northern systems also had relatively elevated concentrations of long-chained PFCAs compared to other PFAAs.

3.4. Temporal trends

In order to evaluate the temporal trends of PFAAs from a multimedia perspective, we focused on Lake Ontario, as long-term temporal trend data for this lake exists for abiotic (sediment core, suspended

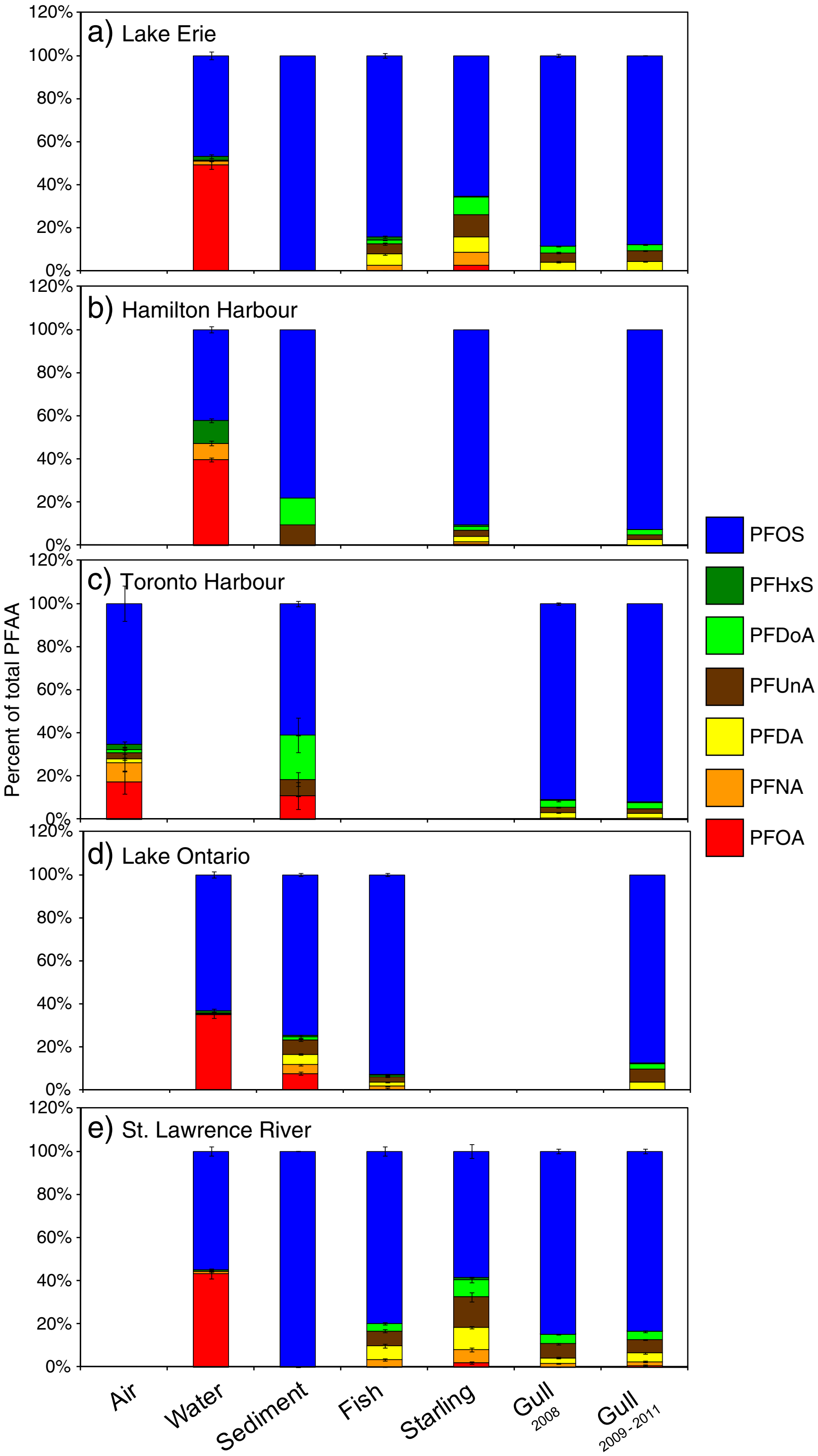


Fig. 7. Multi-media chemical patterns of PFAAs in a) Lake Erie, b) Hamilton Harbour, c) Toronto Harbour, d) Lake Ontario, and e) St. Lawrence River. PFAA compounds that were evaluated in all media (i.e., PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFOS) were included. Data are expressed as mean ± standard error percent of total PFAA. Specific sites included in this figure for Lake Erie were Fort Erie for water, open water Lake Erie for sediment, Dunkirk, ON for fish, Delhi, ON for Starlings, and Big Chicken Island for Gulls collected in 2008 and Middle Island and Port Colborne, ON for Gulls collected from 2009 to 2011. Water, sediment, and Gull data included in this figure for Hamilton Harbour were collected from within this harbour and Starlings were collected in Hamilton, ON. Data included in this figure for the Toronto Harbour were collected from Toronto, ON for air (high volume sampler, sum of gas and particulate phases), within the Toronto Harbour for sediment and Gulls collected in 2008, and Tommy Thompson Park, ON for Gulls collected in 2009–2011. Data included in this figure for Lake Ontario were collected from Wolfe Island for water, open water Lake Ontario for sediment, Niagara-On-The-Lake, ON for fish, and Snake Island for Gulls (2009–2011). Data included in this figure for the St. Lawrence River were collected from the St. Lawrence at Quebec and Lavaltrie City for water, the St. Lawrence River at St. Nicholas for fish, Parc de l'Ile Lebel and Park-Nature de la Point Aux Prairies, QC for Starlings, and Ile Deslauriers and Ile Bellechasse for Gulls collected in both 2008 and 2009–2011.

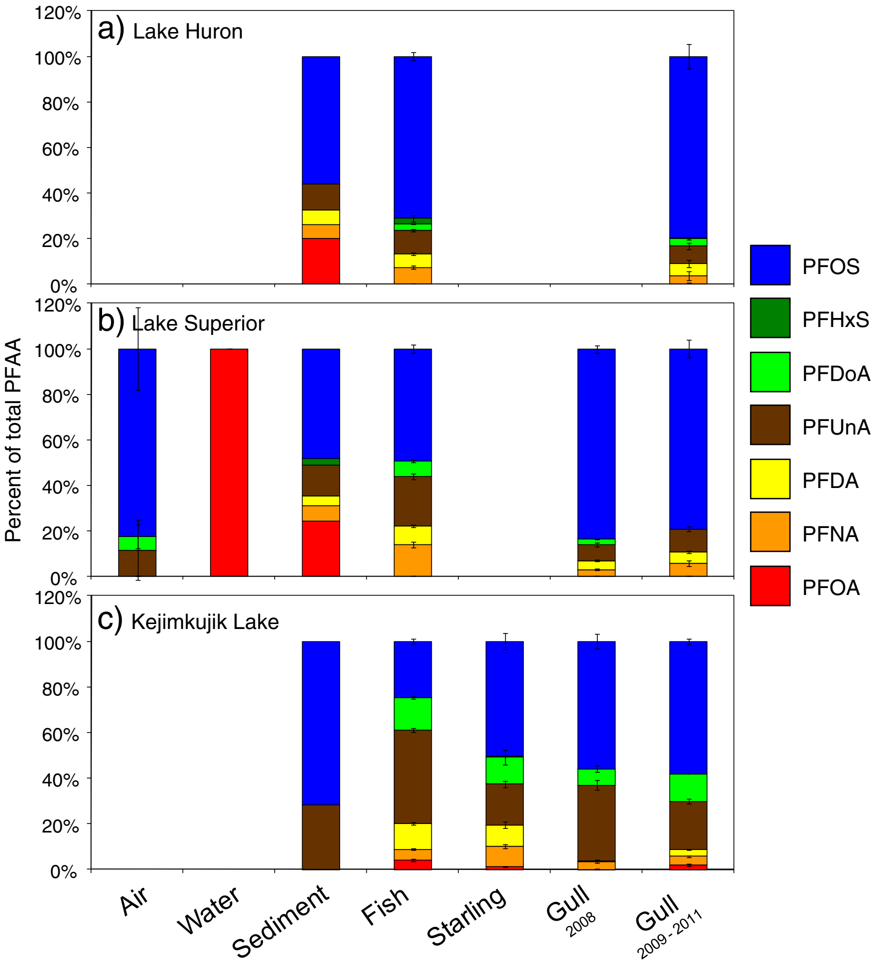


Fig. 8. Multi-media chemical patterns of PFAAs in a) Lake Huron, b) Lake Superior, and c) Kejimkujik Lake. PFAA compounds that were evaluated in all media (i.e., PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFOS) were included. Data are expressed as mean ± standard error percent of total PFAA. Data included in this figure for Lake Huron were collected from open water Lake Huron for sediment, Goderich, ON for fish, and Channel-Shelter Island, Chantry Island, and Double Island for Gulls (2009–2011). Data included in this figure for Lake Superior were collected from open water Lake Superior for air (high volume sampler, sum of gas and particle phases), water, and sediment, Marathon, ON for fish, Silver Islet for Gulls collected in 2008, and Granite Island and Agawa Rock for Gulls collected in 2009–2011. Data included in this figure for Kejimkujik Lake were collected from open water Kejimkujik Lake for sediment and fish, Graves Island Park for Starlings, and Kent Island for Gulls collected in 2008 and 2009–2011.

sediment) and biotic (Lake Trout and Herring Gull eggs) media (Table S-2). Shorter-term temporal trend data for water from Lake Ontario (collected approximately monthly from March 1997 to November 2010 at Niagara-On-The-Lake, ON) were also included for comparative purposes.

To compare temporal patterns between media on the same scale, the following was plotted on Fig. 9 a and b: percent change of PFOS concentration from 1997 to the sampling year for suspended sediment, Lake Trout, and Herring Gull eggs, and percent change of PFOS concentration from 1995 and March 5, 2007 to the sampling year for the sediment core and water, respectively. Fig. 9 c and d shows comparable data for the sum of five PFCAs (PFOA, PFNA, PFDA, PFUnA, and PFDoA).

It should be noted that with regard to Lake Trout, data from 1979 to 2004 were obtained from Furdui et al. (Furdui et al., 2007, 2008b), whereas data from 1997 to 2010 were obtained from Gewurtz et al. (2012). Gewurtz et al. (2012) discussed the comparability of the two datasets by evaluating differences in concentrations in the three years shared by the two studies, namely 1998, 2001, and 2004.

For PFOS, concentrations in all media generally increased starting from the late 1970s/early 1980s for Lake Trout, suspended sediment, and the sediment core and starting from 1990 for the Herring Gull eggs. This corresponds to estimates of production volumes for PFOS-related chemicals (Paul et al., 2009; Prevedouros et al., 2006; Smithwick et al., 2006) which increased to a peak of approximately 4500 tonnes/year. However, recent trends (from the 1990s onwards) deviated between media (Fig. 9 a and b), with concentrations stabilizing in Lake Trout and Herring Gull eggs, and decreasing and increasing in suspended sediment and the sediment core, respectively. The two additional sediment cores collected from the Mississauga and Rochester Basins of Lake Ontario showed patterns similar to the Niagara Basin presented in Fig. 9 b (Myers et al., 2012). The PFOS concentrations in water samples collected from Lake Ontario declined between 2007 and 2010. Estimates of global production volumes show that post-1990s, concentration trends stabilized and then subsequently decreased following regulatory actions and the voluntary phase-out by the primary producer in the early 2000s (Paul et al., 2009). In the past decade, China has stepped up the production of PFOS-related chemicals from 30 tonnes in 2001 to between 200 and 250 tonnes/year from 2006 to 2011 (Xie et al., 2013) and minor production continues in Europe (<42–82 tonnes/year) (Martin et al., 2010). However, based on publically available information, contemporary production volumes of PFOS-related chemicals remain less than what was historically produced up until the early 2000s.

For the $\sum 5$ PFCAs, concentration trends generally increased with time (Herring Gull eggs, suspended sediment, and the sediment core) or increased until the late 1990s and subsequently stabilized (Lake Trout) (Fig. 9 c and d). Concentrations of PFCAs in water decreased between 2007 and 2010. Although production volumes for PFOA and

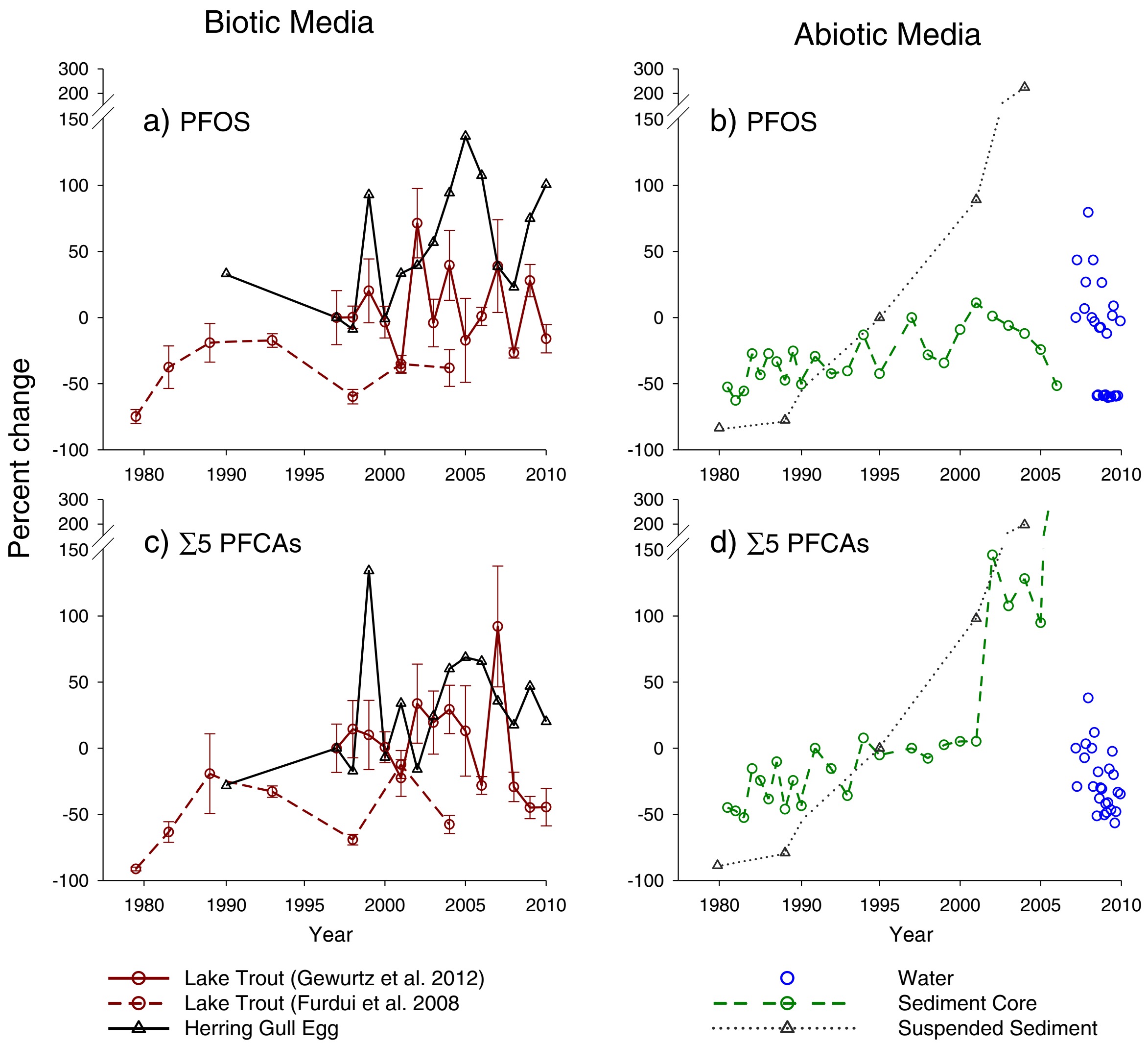


Fig. 9. Temporal patterns of PFOS in a) Lake Trout and Herring Gull eggs and b) suspended sediment, sediment core, and water collected from Lake Ontario. Comparable temporal patterns for $\sum 5$ PFCAs (PFOA, PFNA, PFDA, PFUnA, and PFDoA) in biotic and abiotic media are shown in c) and d), respectively. Data are presented as percent change from the sampling year to 1997 (for Lake Trout, Herring Gull eggs, and suspended sediment), 1995 (for the sediment core), and March 2007 (for water). Data for Lake Trout are presented as mean ± standard error of the mean.

related compounds increased between 1951 and 2004 (Paul et al., 2009), recent patterns are not as well known compared with PFOS-related compounds (Vierke et al., 2012). Regulatory actions for PFCAs are more recent compared to PFOS and are still in discussion (Government of Canada, 2010; Vierke et al., 2012).

Differences in temporal trends of PFOS and PFCAs between media could be due to a variety of factors. As discussed by Myers et al. (2012), while suspended sediment appears to reflect market changes of PFAAs, the trends in the sediment core and in biota were likely influenced by additional physico-chemical and biological factors. Using enantiospecific analysis, Asher et al. (2012) found that biotransformation of precursor compounds was a source of PFOS to invertebrates and fish (including Lake Trout) in Lake Ontario. As such, the concentrations measured in biota likely reflect the temporal trends of both PFOS and precursors, differences in their uptake and elimination rates, biotransformation rates, and food web changes. Similarly, the PFAAs measured in the sediment core are likely affected by partitioning of PFAAs between sediment particles and pore water, interactions at the sediment/water interface, and bioturbation (Ahrens et al., 2009; Myers et al., 2012).

The differences between media may also be due to the extent that exposure of PFAAs in each media is integrated over time. Suspended sediment and water likely achieve steady-state with their environment relatively quickly, and thus would respond more rapidly to loading changes. In contrast, the sediment core was collected in a depositional zone and each sub-section represented approximately 5 years of exposure (Myers et al., 2012). The time that Lake Trout and Herring Gulls integrate exposure of PFAAs under field conditions is not well known and is likely dependent on accumulation and food chain transfer of PFAAs and their precursors as well as biotransformation rates, as noted above.

Variability between years could be confounding the interpretation of long-term temporal trend patterns. This factor is particularly important for Lake Trout, Herring Gull eggs, and suspended sediment, as the time trends for these media appear to show large cyclical oscillations. With regard to Lake Trout, through a power analysis, Gewurtz et al. (2012) found that given the variability associated with the data, it would take 15 years to detect a 5% annual decrease in PFOS concentrations with an 80% power and 5% significance level with a within-year sample size of 10. This suggests that even if PFOS concentrations in the Lake Trout had started declining following the 2002 voluntary phase-out by the primary producer, there has not yet been sufficient time to achieve an 80% power for detecting a 5% decrease, although larger decreases would take less time to detect (Gewurtz et al., 2012).

The sediment core was the only media where PFOS concentrations increased exponentially with time, with no apparent leveling off or decrease in response to the voluntary and regulatory actions. Increases in PFOS concentrations in sediment cores in more recent years may be partially due to higher levels of wastewater treatment (secondary and tertiary), which appear to generate PFOS in effluent that would then partition to sediments. In addition, the sediment core trend was based on only five measurements dated between 1980 and 2004. Such few measurements can provide misleading interpretations of long-term trend data by not accounting for between-year variability (Bignert et al., 1993). It should be noted, however, that it would be difficult to obtain better resolution for sediment core data because it is controlled, in large part, by sedimentation rates. Furthermore, the last data point occurred only two years following the voluntary phase-out by the primary producer and additional sampling years are likely required before any concentration decrease occurs in this media.

The time trends of PFAAs in water between 2007 and 2010 corresponded to that in suspended sediment, with decreasing concentrations during this short time period. This is not surprising considering that the suspended sediment samples were collected by filtering bulk water samples (Myers et al., 2012). Alternatively, the trends in water could be part of the cyclical patterns observed in Lake Trout, Herring Gulls, and suspended sediment.

Overall, this comparison emphasizes the importance of long-term monitoring programs that use different types of media for assessing the temporal trends of PFAAs, similar to the case of other contaminants discussed previously (Bentzen et al., 1999; Gewurtz et al., 2011). The voluntary and regulatory actions for PFAAs appear to be reflected in suspended sediment. However, additional years of data collection are likely required before sediment and biota concentrations decrease definitively in response to market changes. Furthermore, continued inputs of PFAAs to Lake Ontario are likely a confounding factor. There continue to be specific use exemptions for PFOS, its salts, and precursors in both Canada and the U.S. (Environment Canada, 2009; Environmental Protection Agency, 2002) and PFOSF-based production continues in other countries (Martin et al., 2010; Xie et al., 2013; Zhang et al., 2012). In addition, the indoor environment and the waste sector are likely major sources of PFAAs from products that are still in use, as discussed below.

Fig. 10 shows the temporal patterns of PFOS and the sum of 8 PFCAs (PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, and PFPA) in Herring Gull eggs collected from 7 colonies throughout the Great Lakes. These data have been previously published by Gebbink et al. (2011b). Similar to Fig. 9, the percent change of PFAA concentrations from 1997 to the sampling year was plotted so that the trends could be examined on the same scale.

For PFOS in the lower Great Lakes (Fig. 10 a), there was no significant trend between 1990 and 2010 at Fighting Island in the Detroit River and in the Niagara River (Gebbink et al., 2011b). In Gull eggs from the Toronto Harbour, although PFOS levels showed a marginally

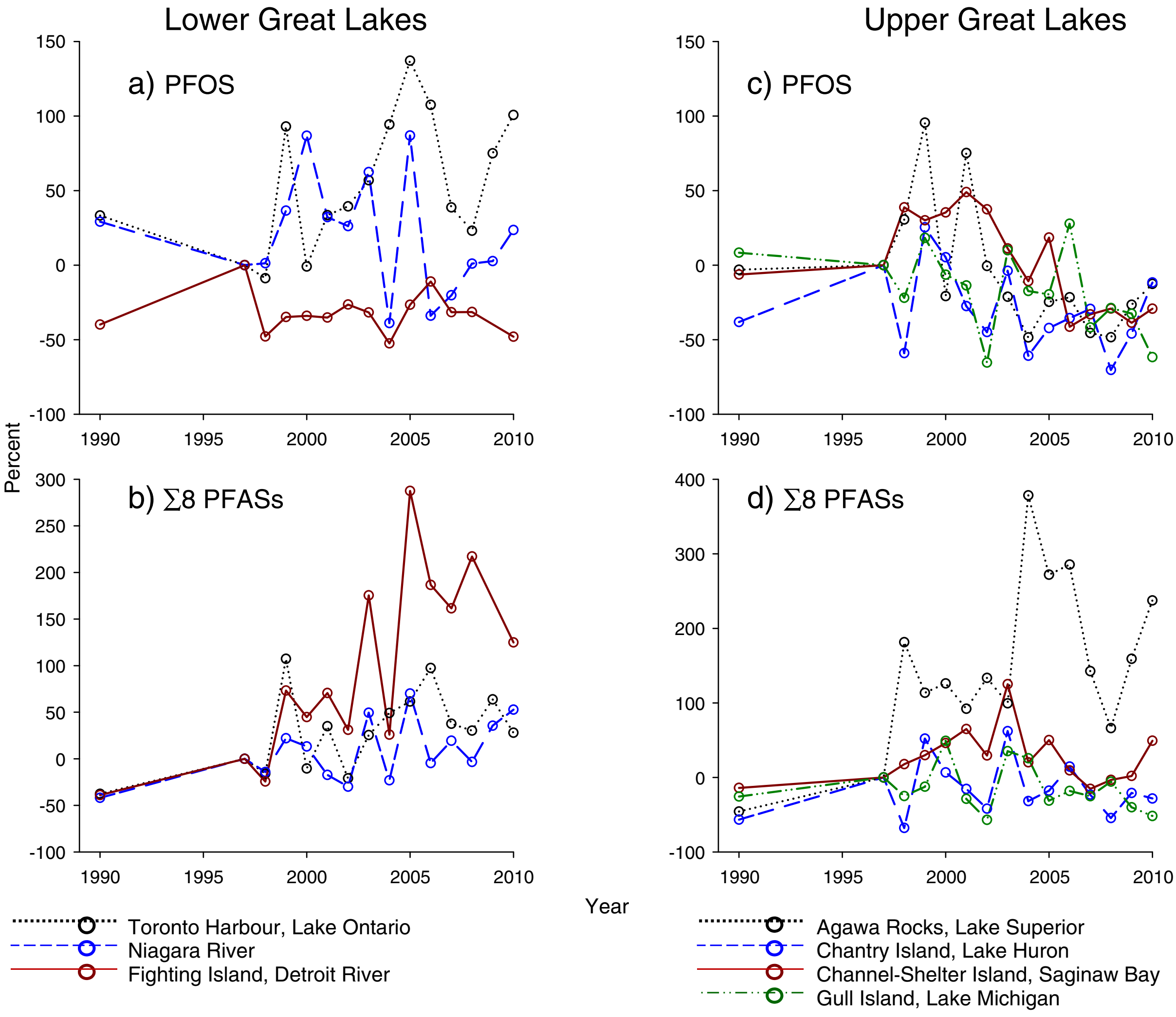


Fig. 10. Temporal patterns of a) PFOS and b) ∑8 PFCAs (PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTriA, PFTeA, and PFPA) in Herring Gull eggs from three colonies in the lower Great Lakes. Comparable temporal patterns for four upper Great Lakes colonies are shown in c) and d), respectively. Data are presented as percent change from the sampling year to 1997. Data were obtained from Gebbink et al. (2011b).

significant increasing trend ($p = 0.06$) between 1990 and 2010 (Gebbink et al., 2011b), there was no significant trend from 2000 to 2010 ($p > 0.10$, assuming log-linear regression). This corresponds to the trends in Lake Trout from Lake Ontario and suggests that while PFOS concentrations in biota from the lower (and more populated) Great Lakes have stopped increasing, they have yet to start decreasing in response to the voluntary and regulatory actions. In contrast, PFOS concentrations in the upper Great Lakes Superior, Huron, and Michigan (Fig. 10 c) generally decreased between 1990 and 2010 (Gebbink et al., 2011b), although the decline was significant ($p < 0.05$) only at Agawa Rocks (Lake Superior) and Channel-Shelter Island (Saginaw Bay, Lake Huron), and marginally significant ($p = 0.08$) at Gull Island (Lake Michigan). In contrast to PFOS, the concentrations of $\sum 8$ PFCAs increased significantly between 1990 and 2010 at all three lower Great Lakes colonies (Fig. 10 b) and at Agawa Rocks, Lake Superior (Fig. 10 d) (Gebbink et al., 2011b). However, the $\sum 8$ PFCAs showed no consistent trend with time at the Gull Island, Channel-Shelter Island, and the Chantry Island colonies (Fig. 10 d). These results correspond to other studies that show that even within the same media, temporal trends of PFAAs can vary between locations (Armitage et al., 2009; Butt et al., 2007; Houde et al., 2011). For Arctic marine biota, Armitage et al. (2009) found that a rapid decrease in PFOS concentrations following the 2000–2002 voluntary phase-out by the primary producer was only possible if the major exposure route in the food web was uptake and metabolism of volatile precursor compounds to PFOS *in vivo*. The factors influencing spatial differences in the long-term trends in inland lakes require further study.

The time trends of atmospheric concentrations of PFAA precursor compounds (8:2 and 10:2 fluorotelomer alcohols (FTOHs) and methyl and ethyl perfluorooctane sulfonamidoethanols (MeFOSEs and EtFOSEs)) at Alert, Nunavut, from 2006 until 2010, are shown in Fig. 11. The precursor concentrations oscillated from below detection to 12.3 pg/m^3. The two perfluorooctane sulfonamidoethanols showed declining trends at Alert. In contract, the FTOHs, which are not regulated, showed increasing tendencies in air at Alert (AANDC, 2012). Continued measurements of Arctic air are required to examine what factors influence the transport of PFAAs and their precursors to the Arctic. The temporal trends of PFAAs have been studied previously in a variety of other Canadian Arctic media, especially marine fish, birds, and mammals (Braune and Letcher, 2013; Butt et al., 2010; Stock et al., 2007). For these studies, in some cases concentrations of PFOS increased to the early 2000 and subsequently decreased whereas PFCAs increased through time (Braune and Letcher, 2013; Butt et al., 2010; Martin et al., 2010; Stock et al., 2007). However, similar to the Great Lakes, temporal trends across the Canadian Arctic are not consistent, even within the same media.

3.5. Monitoring in the indoor environment

In a survey of 152 homes in Vancouver, BC, indoor air was dominated by 8:2 FTOH with a geomean concentration of 2900 pg/m^3 (Shoeib et al., 2011). Among the perfluorooctane sulfonamides (FOSAs) and FOSEs, MeFOSE exhibited the highest air concentration with a geomean of 380 pg/m^3. PFOA was the major PFAA chemical measured and was detected in all indoor air samples with a geomean of 28 pg/m^3. PFOS was below the detection limit in indoor air; this may have been a result of its low abundance or because passive samplers have relatively elevated detection limits for PFAAs compared to high volumes samplers, as discussed above. In support of the latter hypothesis, both PFOS and PFOA were dominant in house dust, with concentrations ranging from 1.5 to 4700 and 2.0 to 1400 ng/g, respectively. In clothes dryer lint, the concentrations of all fluorinated chemicals measured were an order of magnitude lower than house dust. De Silva et al. (2012) measured concentrations of emerging organofluorine compounds in a subset of 102 dust samples. The chemicals that were analyzed included phosphorus-containing fluorinated compounds, namely polyfluoroalkyl phosphoric acid diesters (diPAP), perfluorophosphonates (PFPA), and perfluorophosphinates (PFPIA), as well as perfluoroethylcyclohexane sulfonate (PFECHS). The diPAPs (median = 2213 ng/g) dominated the dust samples, encompassing 98% of the emerging chemicals analyzed. The median concentrations of diPAPs were 30 and 67 times higher than the median concentrations of PFOS (75 ng/g) and PFOA (33 ng/g) in the same samples. These results are not surprising as diPAPs have many potential uses, such as in personal care products and cleaners, in the indoor home environment (De Silva

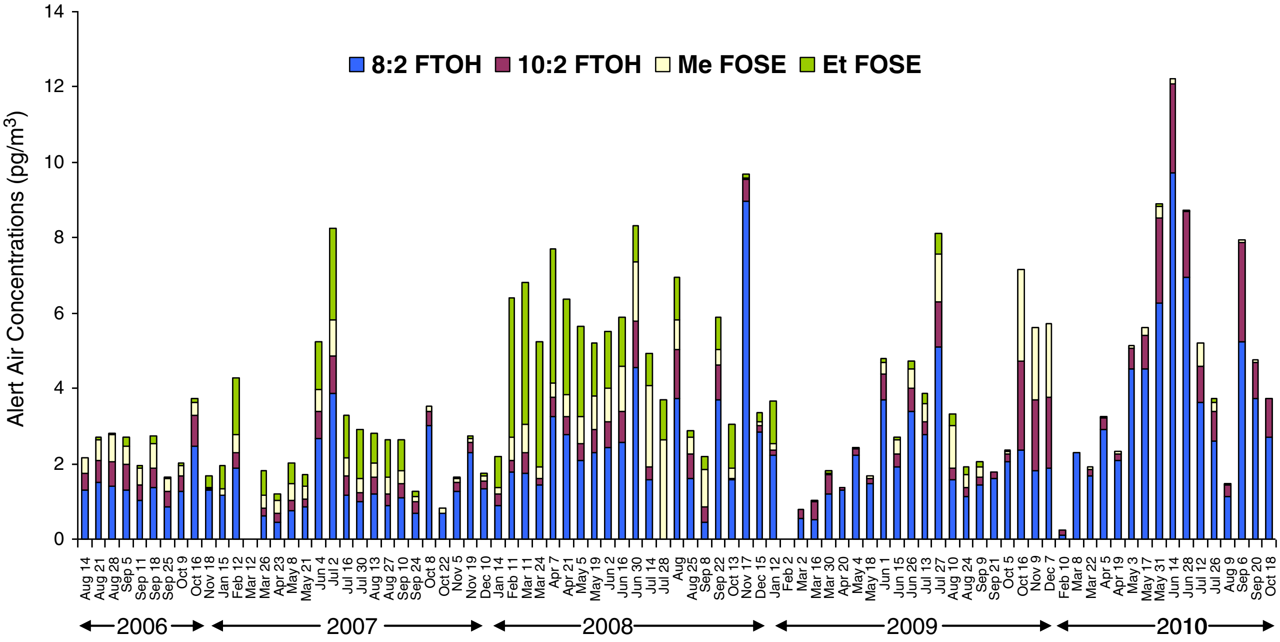


Fig. 11. Atmospheric concentrations (gas + particle phase) of PFAA precursor compounds (8:2 and 10:2 fluorotelomer alcohols (FTOHs) and methyl and ethyl perfluorooctane sulfonamidoethanols (FOSEs)) at Alert, Nunavut. The x-axis indicates start dates of weekly-integrated samples.

et al., 2012). DiPAPs are likely an indirect source of PFCAs and FTOHs to humans (D'eon and Mabury, 2011).

The concentrations of fluorinated compounds in the air outside of the Vancouver homes were approximately ~20 times lower than inside, highlighting the importance of building interiors as an emission source to the atmosphere. Other studies have also reported high indoor compared to outdoor air concentrations for PFAAs and their precursors (Goosey and Harrad, 2012; Harrad et al., 2010; Shoeib et al., 2005).

3.6. Wastewater and landfill leachate monitoring

The wastewater monitoring program provides information on the significance of wastewater effluent discharges and land application of treated biosolids as sources of chemical substances such as PFAAs to the environment (Government of Canada, 2011). For PFOS, raw influent concentrations across all wastewater systems ranged from below the MDL (1.49 to 7.92 ng/L) to 1140 ng/L, with a median value of 4.93 ng/L and a detection frequency of 60% (Guerra et al., In Prep). PFOS concentrations in effluent ranged from below the MDL (1.92 to 6.27 ng/L) to 1260 ng/L, with a median value of 5.73 ng/L and a detection frequency of 81%. All final effluent measurements were in the same range or higher compared to water PFOS concentrations measured in urban areas, as discussed above. For PFOA, raw influent concentrations across all wastewater systems ranged from <1.04 ng/L to 146 ng/L, with a median value of 5.25 ng/L. PFOA concentrations in effluent ranged from 1.86 ng/L to 142 ng/L, with a median value of 11.8 ng/L, which are also in the same range or higher compared to water concentrations measured in urban areas. Previous WWTP monitoring efforts showed higher concentrations of PFOS and PFCAs in effluent compared to influent, and may be due to PFAAs being produced via precursor breakdown during the wastewater treatment processes (Schultz et al., 2006; Sinclair and Kannan, 2006).

The median PFOS concentration in biosolids was 13.7 ng/g, with a detection frequency of 90%. Likewise, a median PFOA concentration of 2.74 ng/g in biosolids (detection frequency of 50%) was found. Biosolids have a relatively high organic content (60% to 70% of solids), and appear to retain PFOS and PFOA in a similar manner to sediment and biota. Recent studies have shown that municipal biosolids containing PFAAs can contaminate agricultural fields following land application (Lindstrom et al., 2011a; Sepulvado et al., 2011) and the compounds may be mobilized by rainfall (Gottschall et al., 2010).

The total daily discharge of PFAAs from wastewater and biosolids in all of Canada was calculated, with values ranging from 0.043 g/day to 177 g/day (Guerra et al., In Prep). Generally, the highest input was from the wastewater stream and PFOA was the most discharged compound followed by PFOS. It should be noted that these values are underestimated as they do not consider discharge of PFAA precursor compounds, which can be transformed to PFAAs following release from WWTPs into the environment.

With respect to landfill leachate monitoring, concentrations of PFOS and PFOA in untreated leachate samples ranged from <9.5 to 744 ng/L with a detection frequency of 48% and 50.3 to 1590 ng/L (100% detection frequency), respectively. Concentrations of PFOS and PFOA in the treated samples ranged from <9.8 to 2070 ng/L with a detection frequency of 40% and 42 to 4750 ng/L (100% detection frequency), respectively (Conestoga Rovers and Associates, 2011). Similar to the wastewater monitoring program described above, on-site leachate treatment did not decrease the concentrations of PFOS or PFOA. Rather, concentrations tended to increase following treatment (Conestoga Rovers and Associates, 2011), likely due to generation of PFAAs through precursor compounds (Benskin et al., 2012). About 90% of landfill leachate in Canada is sent to WWTPs (Government of Canada, 2011) while the rest is treated at the landfill site and/or discharged to the environment through natural attenuation. Landfill leachate was estimated to be responsible for the generation of 1.6 g/day and 0.27 g/day of PFOS and PFOA, respectively (Conestoga Rovers and Associates, 2011). However, similar to the case of WWTPs, these values do not consider PFAA precursors and thus these loading estimates are underestimated.

Most WWTP and landfill sector monitoring programs for PFAAs, including those described above, have focused on emissions to the aquatic environment and biosolids. In contrast, there is little information on the potential for WWTPs and landfills to emit PFAAs to the atmosphere. To fulfill this need, the air at two Ontario landfill sites and one secondary activated sludge WWTP were monitored for PFAAs and volatile precursor compounds between June and September 2009 (Ahrens et al., 2011c). Reference site concentrations of PFAAs were usually in the range reported for both urban and more remote locations throughout the world (Ahrens et al., 2011c; Genualdi et al., 2010). For the WWTP, mean air concentrations of ΣFTOH, ΣFOSA/FOSE, PFOS, and ΣPFCAs were 11, 4, 7, and 2 times higher within the plant compared to reference locations, respectively. The two landfill sites showed similar results, especially for ΣFTOH, which had substantially higher concentrations (5–36 times) on-site of the landfills compared to the upwind (reference) samples. In comparison, ΣFOSA/FOSE concentrations were only 2–3 times higher on-site compared to upwind reference locations, reflecting lower landfill emission strength for the FOSA and FOSE classes. The mean concentrations of ΣPFCAs and PFOS were about 3 times higher at the landfill sites compared to the upwind sites. The yearly emissions were estimated to be 2423, 30.8, 45, and 62 g/year for ΣFTOH, ΣFOSA/FOSE, PFOS, and ΣPFCAs at the WWTP, 92, 2.3, 0.1, and 4.6 g/year for ΣFTOH, ΣFOSA/FOSE, PFOS, and ΣPFCAs at landfill site 1, and 984, 4.3, 0.2, and 12.5 g/year for ΣFTOH, ΣFOSA/FOSE, PFOS, and ΣPFCAs at landfill site 2.

Vierke et al. (2011) further explored air concentrations of PFAAs at the aeration tank and secondary clarifier sites of a different WWTP in 2010. Similar to Ahrens et al. (2011c), they found that PFAA concentrations in the WWTP, especially in the aeration tank, were elevated compared to urban areas. These two air sampling campaigns highlight the important role of the wastewater sector (especially the aeration process of the WWTP) as an emission source of PFAAs and their precursors to the atmosphere.

4. Conclusions

The concentrations of PFOS in a variety of media in the Canadian environment were generally higher in heavily populated urban and industrialized locations, especially in southern Ontario, than in more remote locations. Consistent with other studies conducted throughout the world (Houde et al., 2006, 2011; Suja et al., 2009), this pattern indicates that activities associated with human population, such as the use and disposal of PFAA containing consumer products, continue to be important sources of PFAAs to the Canadian environment. However, other sources, such as airports, where use of aqueous film forming foam is permitted until July 2013, as well as other fire training areas, also likely contribute to the elevated PFAA concentrations in urban/industrial centers as well as result in unexpectedly elevated concentrations in some remote locations. The PFAAs found in source regions are transported to other more distant sites through atmospheric transport of precursor compounds and/or transport of PFAAs through rivers and oceanic currents. As a result, this compound is also detected at locations far from obvious point sources, albeit at lower concentrations.

Through comparison to draft FEQGs, the PFOS data suggest that concentrations have low potential of adverse effects with respect to the organisms examined. However, PFOS in fish and bird eggs tended to exceed guidelines for the protection of mammalian and avian consumers, and thus there may be exposure risks to the health of their mammalian and avian wildlife consumers. Because FEQGs are preventive, and not predictive, wildlife population health assessments would be necessary to determine whether negative impacts are actually occurring.

Long-term temporal trends for suspended sediment, sediment cores, Lake Trout, and Herring Gull eggs from Lake Ontario suggest that while PFOS concentrations consistently increased from the start of data collection until the 1990s, consistent with production volumes (Martin et al., 2010; Paul et al., 2009; Xie et al., 2013), recent trends varied between media. For PFCAs, concentrations generally increased with time for Herring Gull eggs, suspended sediment, and sediment cores in correspondence with assumed market trends (Myers et al., 2012; Paul et al., 2009; Vierke et al., 2012), or increased until the late 1990s and subsequently stabilized (Lake Trout). The lack of correspondence between media for recent trends may be due to a variety of factors such as partitioning of PFAAs from sediment particles to pore water and bioturbation in sediment cores, biotransformation of precursor compounds and food web interactions in biota, differences in the time that each media integrates exposure, influence of between year variability on long-term trends, and continued production in Asia. Continued long-term data collection may be required before voluntary and regulatory actions are reflected consistently in all environmental media and locations.

Measurements of PFAAs in indoor air and dust, in air, water, and biosolids of Canadian WWTPs, and in leachate and air of Canadian landfill sites illustrate that current-use products (from the indoor environment) and the waste and wastewater sectors are sources of PFAAs to the environment. The importance of the waste and wastewater sectors as sources of PFAAs was illustrated in the elevated PFAAs found in water (Wascana Creek) located 8.5 km from a major WWTP in Regina, SK, and in Starling eggs collected from Brantford, ON and Calgary, AB landfills. However, it should be noted that for Starlings, other than the elevated PFAAs observed at the Brantford and Calgary landfills, there was no trend of higher concentrations observed at the waste compared to non-waste sites. This suggests that the waste sector, although important, is not always the dominant source of PFAAs across sites in Canada.

Much has been learned about PFAAs since PFOS was first reported in wildlife by Giesy and Kannan (2001). We now know that PFAAs are widely distributed throughout the Canadian environment, are persistent, are susceptible to long-range transport (although the dominant mechanisms for such transport are not clear), and that PFAAs are accumulating in fish and wildlife. The results of this project can be used to guide future work on the study of PFAAs in Canada. For example, additional work is needed to generate toxicity information on PFAAs other than PFOS (including precursor compounds) so that FEQGs can be developed for other compounds. Furthermore, although this study identified major sources of PFAAs to the Canadian environment, more work is needed quantify the relative importance of these sources, and the importance of PFAA precursors, to the concentrations of PFAAs observed at different locations in order to assess the potential effectiveness of control measures. More work is also needed to understand discrepancies in the spatial and temporal trends between media. For example, Lake Erie had relatively high PFAA concentrations in Lake Trout, Gull eggs, and water, but low PFAA concentrations in sediment. Furthermore, recent temporal trends varied between media and locations.

It is evident that continued multi-media monitoring is essential for determining the response of environmental PFAA concentrations to voluntary and regulatory actions into the future. Currently, there are eight locations across Canada where more than three media were monitored and PFAAs were detected. A multi-media comparison of PFAA profiles showed that the unexpectedly high concentrations of the longer-chained PFCAs in Kejimkujik Lake, NS, biota was likely due to source patterns rather than some sort of food web process. This would have been difficult to tease out with an assessment of the PFAA concentrations in biota alone. We recommend multi-media sampling at other sites, especially Arctic locations, such as Great Bear Lake, NT, which also had surprisingly elevated concentrations of the long-chained PFCAs that were unexpected based on its remote northern location.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2013.05.008.

References

3M Company. 3M's Phase Out and New Technologies. http://solutions.3m.com/wps/portal/3M/en_US/PFOS/PFOA/Information/phase-out-technologies/, 2012.

AANDC. Aboriginal affairs and northern development Canada. In: Muir D, Kurt-Karakus PB, editors. Canadian arctic contaminants assessment report III; 2012.

Adams J, Houde M, Muir D, Speakman T, Bossart G, Fair P. Land use and the spatial distribution of perfluoroalkyl compounds as measured in the plasma of bottlenose dolphins (*Tursiops truncatus*). Mar Environ Res 2008;66:430–7.

Ahrens L, Yamashita N, Yeung LWY, Taniyasu S, Horii Y, Lam PKS, et al. Partitioning behavior of per- and polyfluoroalkyl compounds between pore water and sediment in two sediment cores from Tokyo Bay. Japan Environ Sci Technol 2009;43:6969–75.

Ahrens L, Taniyasu S, Yeung LWY, Yamashita N, Lam PKS, Ebinghaus R. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay. Japan Chemosphere 2010;79:266–72.

Ahrens L, Shoeib M, Del Vento S, Codling G, Halsall C. Polyfluoroalkyl compounds in the Canadian Arctic atmosphere. Environ Chem 2011a;8:399–406.

Ahrens L, Shoeib M, Harner T, Lane DA, Guo R, Reiner EJ. Comparison of annular diffusion denuder and high volume air samplers for measuring per- and polyfluoroalkyl substances in the atmosphere. Anal Chem 2011b;83:9622–8.

Ahrens L, Shoeib M, Harner T, Lee SC, Guo R, Reiner EJ. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. Environ Sci Technol 2011c;45:8098–105.

Armitage JM, Schenker U, Scheringer M, Martin JW, Macleod M, Cousins IT. Modeling the global fate and transport of perfluorooctane sulfonate (PFOS) and precursor compounds in relation to temporal trends in wildlife exposure. Environ Sci Technol 2009;43:9274–80.

Asher BJ, Wang Y, De Silva AO, Backus S, Muir DCG, Wong CS, et al. Enantiospecific perfluorooctane sulfonate (PFOS) analysis reveals evidence for the source contribution of PFOS-precursors to the Lake Ontario foodweb. Environ Sci Technol 2012;46:7653–60.

Beach S, Newsted J, Coady K, Giesy JP. Ecotoxicological evaluation of perfluorooctanesulfonate (PFOS). Rev Environ Contam Toxicol 2006;186:133–74.

Benskin JP, Li B, Ikonomou MG, Grace JR, Li LY. Per- and polyfluoroalkyl substances in landfill leachate: patterns, time trends, and sources. Environ Sci Technol 2012;46:11532–40.

Bentzen E, Mackay D, Hickie BE, Lean DRS. Temporal trends of polychlorinated biphenyls (PCBs) in Lake Ontario fish and invertebrates. Environ Rev 1999;7:203–23.

Bignert A, Gothberg A, Jensen S, Litzen K, Odsjo T, Olsson M, et al. The need for adequate biological sampling in ecotoxicological investigations: a retrospective study of twenty years pollution monitoring. Sci Total Environ 1993;128:121–39.

Braune BM, Letcher RJ. Perfluorinated sulfonate and carboxylate compounds in eggs of seabirds breeding in the Canadian Arctic: temporal trends (1975–2011) and interspecies comparison. Environ Sci Technol 2013;47:616–24.

Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, de Voogt P, et al. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr Environ Assess Manag 2011;7:513–41.

Butt CM, Muir DCG, Stirling I, Kwan M, Mabury SA. Rapid response of Arctic ringed seals to changes in perfluoroalkyl production. Environ Sci Technol 2007;41:42–9.

Butt CM, Berger U, Bossi R, Tomy GT. Levels and trends of poly- and perfluorinated compounds in the Arctic environment. Sci Total Environ 2010;408:2936–65.

Carloni D. Perfluorooctane sulfonate (PFOS) production and use: past and current evidence. United Nations Industrial Development Organization. http://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/POPs/DC_Perfluorooctane%20Sulfonate%20Report.PDF, 2009.

Clarke JU. Evaluation of censored data methods to allow statistical comparisons among very small samples with below detection limit observations. Environ Sci Technol 1998;32:177–83.

Conder JM, Hoke RA, De Wolf W, Russell MH, Buck RC. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. Environ Sci Technol 2008;42:995–1003.

Conestoga Rovers and Associates. Sampling for chemicals management plan challenge substances from the waste sector: 2010 field sampling program. Conestoga Rovers & Associates in a report prepared for Environment Canada, CRA project number 054555 (5). ON, Canada: Waterloo; 2011.

De Silva AO, Gledhill M, Sekela M, Syrgiannis J, Evans MS, Armellin A, et al. Perfluorinated chemicals in freshwater fish in Canada. Organohalogen Compd 2010;72:1277–80.

De Silva AO, Spencer C, Scott BF, Backus SM, Muir DCG. Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate, in the Great Lakes of North America. Environ Sci Technol 2011;45:8060–6.

De Silva AO, Allard CN, Spencer C, Webster GM, Shoeib M. Phosphorus-containing fluorinated organics: polyfluoroalkyl phosphoric acid diesters (diPAPs), perfluorophosphonates (PFPAs), and perfluorophosphinates (PFPIAs) in residential indoor dust. Environ Sci Technol 2012;46:12575–82.

D'eon JC, Mabury SA. Is indirect exposure a significant contributor to the burden of perfluorinated acids observed in humans. Environ Sci Technol 2011;45:7974–84.

Desjardins MJ, Telmer K, Beauchamp S. Apportioning atmospheric pollution to Canadian and American sources in Kejimkujik National Park, Nova Scotia, using Pb isotopes in precipitation. Atmos Environ 2004;38:6875–81.

Dreyer A, Shoeib M, Fiedler S, Barber J, Harner T, Schramm K-W, et al. Field intercomparison on the determination of volatile and semivolatile polyfluorinated compounds in air. Environ Chem 2010;7:350–8.

Environment Canada. Perfluorooctane sulfonate (PFOS), its salts and its precursors. Gatineau, Quebec, Canada. http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=98E80CC6-1&xml=ECD5A576-CEE5-49C7-B26A-88007131860D&printerversion=true, 2009.

Environmental Protection Agency. Perfluoroalkyl sulfonates; significant new use rule; final rule and supplemental proposed rule. Federal register, vol. 67; 2002 [No. 47].

Furdui VI, Stock NL, Ellis DA, Butt CM, Whittle DM, Crozier PW, et al. Spatial distribution of perfluoroalkyl contaminants in Lake Trout from the Great Lakes. Environ Sci Technol 2007;41:1554–9.

Furdui VI, Crozier PW, Reiner EJ, Mabury SA. Trace level determination of perfluorinated compounds in water by direct injection. Chemosphere 2008a;73:S24–30.

Furdui VI, Helm PA, Lucaciu C, Reiner EJ, Marvin CH, Whittle DM, et al. Temporal trends of perfluoroalkyl compounds with isomer analysis in Lake Trout from Lake Ontario (1979–2004). Environ Sci Technol 2008b;42:4739–44.

Gebbink WA, Letcher RJ. Comparative tissue and body compartment accumulation and maternal transfer to eggs of perfluoroalkyl sulfonates and carboxylates in Great Lakes Herring Gulls. Environ Pollut 2012;162:40–7.

Gebbink WA, Hebert CE, Letcher RJ. Perfluorinated carboxylates and sulfonates and precursor compounds in herring gull eggs from colonies spanning the Laurentian Great Lakes of North America. Environ Sci Technol 2009;43:7443–9.

Gebbink WA, Letcher RJ, Burgess NM, Champoux L, Elliott JE, Hebert CE, et al. Perfluoroalkyl carboxylates and sulfonates and precursors in relation to dietary source tracers in the eggs of four species of gulls (Larids) from breeding sites spanning Atlantic to Pacific Canada. Environ Int 2011a;37:1175–82.

Gebbink WA, Letcher RJ, Hebert CE, Weseloh DV. Twenty years of temporal change in perfluoroalkyl sulfonate and carboxylate contaminants in Herring Gull eggs from the Laurentian Great Lakes. J Environ Monit 2011b;13:3365–72.

Genualdi S, Lee SC, Shoeib M, Gawor A, Ahrens L, Harner T. Global pilot study of legacy and emerging persistent organic pollutants using sorbent-impregnated polyurethane foam disk passive air samplers. Environ Sci Technol 2010;44:5534–9.

Gewurtz SB, Backus SM, Bhavsar SP, McGoldrick DJ, de Solla SR, Murphy EW. Contaminant biomonitoring programs in the Great Lakes region: a review of approaches and critical factors. Environ Rev 2011;19:162–84.

Gewurtz SB, De Silva AO, Backus SM, McGoldrick DJ, Keir MJ, Small J, et al. Perfluoroalkyl substances in Lake Ontario lake trout: detailed examination of current status and long-term trends. Environ Sci Technol 2012;46:5842–50.

Giesy JP, Kannan K. Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 2001;35:1339–42.

Goosey E, Harrad S. Perfluoroalkyl substances in UK indoor and outdoor air: spatial and seasonal variation, and implications for human exposure. Environ Int 2012;45:86–90.

Gottschall N, Topp E, Edwards M, Russell P, Payne M, Kleywegt S, et al. Polybrominated diphenyl ethers, perfluorinated alkylated substances, and metals in tile drainage and groundwater following applications of municipal biosolids to agricultural fields. Sci Total Environ 2010;408:873–83.

Government of Canada. Perfluorooctane sulfonate and its salts and certain other compounds regulations. Canada Gazette Part II, vol. 142; 2008 [No. 12].

Government of Canada. Publication after screening assessment of long-chain perfluorocarboxylic acids (PFCAs) that contain from 9 to 20 carbon atoms, their salts and their precursors. Canada Gazette Part I, vol. 144. ; 2010 [No. 44].

Government of Canada. Monitoring and research under the chemicals management plan. http://www.chemicalsubstanceschimiques.gc.ca/fact-fait/monitor-surveill-eng.php, 2011.

Guo R, Reiner E, Bhavsar S, Helm P, Mabury S, Braekevelt E, et al. Determination of polyfluoroalkyl phosphoric acid diesters, perfluoroalkyl phosphonic acids, perfluoroalkyl phosphinic acids, perfluoroalkyl carboxylic acids, and perfluoroalkane sulfonic acids in lake trout from the Great Lakes region. Anal Biochem 2012;1–11.

Harrad S, de Wit CA, Abdallah MA-E, Bergh C, Bjorklund JA, Covaci A, et al. Indoor contamination with hexabromocyclododecanes, polybrominated diphenyl ethers, and perfluoroalkyl compounds: an important exposure pathway for people? Environ Sci Technol 2010;44:3221–31.

Hart K, Kannan K, Tao L, Takahashi S, Tanabe S. Skipjack Tuna as a bioindicator of contamination by perfluorinated compounds in the oceans. Sci Total Environ 2008;403:215–21.

Helm PA, Crozier PW, Reiner EJ, Howell ET, Marvin CH. Spatial distribution of perfluorinated compounds in sediments and surface waters of the Great Lakes and temporal trends in Lake Ontario sediment core. Milwaukee, WS, USA: Society of Environmental Toxicology and Chemistry; 2007.

Helm PA, Milne J, V., B.-H., Crozier PW, Kolic T, Lega R, et al. Lake-wide distribution and depositional history of current- and past-use persistent organic pollutants in Lake Simcoe. J Gt Lakes Res 2011;37:132–41.

Higgins CP, Luthy RG. Sorption of perfluorinated surfactants on sediments. Environ Sci Technol 2006;40:7251–6.

Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DCG. Biological monitoring of polyfuoroalkyl substances: a review. Environ Sci Technol 2006;40:3463–73.

Houde M, De Silva AO, Muir DCG, Letcher RJ. Monitoring of perfluorinated compounds in aquatic biota: an updated review. Environ Sci Technol 2011;45:7962–73.

Jahnke A, Berger U, Ebinghaus R, Temme C. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 degrees N–33 degrees S). Environ Sci Technol 2007;41:3055–61.

Kelly BC, Ikonomou MG, Blair JD, Surridge B, Hoover D, Grace R, et al. Perfluoroalkyl contaminants in an arctic marine food web: trophic magnification and wildlife exposure. Environ Sci Technol 2009;43:4037–43.

Klanova J, Eupr P, Kohoutek J, Harner T. Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers. Environ Sci Technol 2008;42:550–5.

Kwadijk CJAF, Korytar P, Koelmans AA. Distribution of perfluorinated compounds in aquatic systems in the Netherlands. Environ Sci Technol 2010;44:3746–51.

Labadie P, Chevreuil M. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environ Pollut 2011;159:391–7.

Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A, Seed J. Perfluoroalkyl acids: a review of monitoring and toxicological findings. Toxicol Sci 2007;99:366–94.

Letcher RJ, Bustnes JO, Dietz R, Jenssen BM, Jorgensen EH, Sonne C, et al. Exposure and effects assessment of persistent organohalogen contaminants in arctic wildlife and fish. Sci Total Environ 2010;408:2995–3043.

Lindstrom AB, Strynar MJ, Delinsky AD, Nakayama SF, McMillan L, Libelo EL, et al. Application of WWTP biosolids and resulting perfluorinated compound contamination of surface and well water in Decatur, Alabama, USA. Environ Sci Technol 2011a;45:8015–21.

Lindstrom AB, Strynar MJ, Libelo EL. Polyfluorinated compounds: past, present, and future. Environ Sci Technol 2011b;45:7954–61.

Martin JW, Mabury SA, Solomon KR, Muir DCG. Bioconcentration and tissue distribution of perfluorinated acids in Rainbow Trout (*Oncorhynchus mykiss*). Environ Toxicol Chem 2003a;22:196–204.

Martin JW, Mabury SA, Solomon KR, Muir DCG. Dietary accumulation of perfluorinated acids in juvenile Rainbow Trout (*Oncorhynchus mykiss*). Environ Toxicol Chem 2003b;22:189–95.

Martin JW, Whittle DM, Muir DCG, Mabury SA. Perfluoroalkyl contaminants in a food web from Lake Ontario. Environ Sci Technol 2004;38:5379–85.

Martin JW, Asher BJ, Beesoon S, Benskin JP, Ross MS. PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? J Environ Monit 2010;12:1979–2004.

Myers AL, Crozier PW, Helm PA, Brimacombe C, Furdui VI, Reiner EJ, et al. Fate, distribution, and contrasting temporal trends of perfluoroalkyl substances (PFASs) in Lake Ontario, Canada. Environ Int 2012;44:92–9.

O'Connell SG, Arendt M, Segars A, Kimmel T, Braun-Mcneill J, Avens L, et al. Temporal and spatial trends of perfluorinated compounds in juvenile Loggerhead Sea Turtles (*Caretta caretta*) along the east coast of the United States. Environ Sci Technol 2010;44:5202–9.

Paul AG, Jones KC, Sweetman AJ. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environ Sci Technol 2009;43:386–92.

Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. Sources, fate and transport of perfluorocarboxylates. Environ Sci Technol 2006;40:32–44.

Reiner J, O'Connell S, Butt C, Mabury S, Small J, De Silva A, et al. Determination of perfluorinated alkyl acid concentrations in biological standard reference materials. Anal Bioanal Chem 2012;404:2683–92.

Schultz MM, Barofsky DF, Field JA. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry — characterization of municipal wastewaters. Environ Sci Technol 2006;40:289–95.

Scott BF, Spencer C, Mabury SA, Muir DCG. Poly and perfluorinated carboxylates in North American precipitation. Environ Sci Technol 2006;40:7167–74.

Scott BF, De Silva AO, Spencer C, Lopez E, Backus SM, Muir DCG. Perfluoroalkyl acids in Lake Superior water: trends and sources. J Gt Lakes Res 2010;36:277–84.

Sepulvado JG, Blaine AC, Hundal LS, Higgins CP. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. Environ Sci Technol 2011;45:8106–12.

Shoeib M, Harner T, Wilford B, Jones KC, Zhu J. Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: occurrence, partitioning, and human exposure. Environ Sci Technol 2005;39:6599–606.

Shoeib M, Harner TM, Webster G, Lee SC. Indoor sources of poly- and perfluorinated compounds (PFCs) in Vancouver, Canada: implications for human exposure. Environ Sci Technol 2011;45:7999–8005.

Sinclair E, Kannan K. Mass loadings and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ Sci Technol 2006;40:1408–14.

Smithwick M, Norstrom RJ, Mabury SA, Solomon K, Evans TJ, Stirling I, et al. Temporal trends of perfluoroalkyl contaminants in polar bears (*Ursus maritimus*) from two locations in the North American Arctic, 1972–2002. Environ Sci Technol 2006;40:1139–43.

Stock NL, Furdui VI, Muir DCG, Mabury SA. Perfluoroalkyl contaminants in the Canadian arctic: evidence of atmospheric and local contamination. Environ Sci Technol 2007;41:3529–36.

Suja F, Pramanik BK, Zain SM. Contamination, bioaccumulation and toxic effects of perfluorinated chemicals (PFCs) in the water environment: a review paper. Water Sci Technol 2009;60:1533–44.

Vecitis CD, Wang Y, Cheng J, Park H, Mader BT, Hoffmann MR. Sonochemical degradation of perfluorooctanesulfonate in aqueous film-forming foams. Environ Sci Technol 2010;44:432–8.

Vierke L, Ahrens L, Shoeib M, Reiner EJ, Guo R, Palm W-U, et al. Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant. Environ Chem 2011;8:1–9.

Vierke L, Staude C, Biegel-Engler A, Drost W, Schulte C. Perfluorooctanoic acid (PFOA) — main concerns and regulatory developments in Europe from an environmental point of view. Environ Sci Eur 2012;24:1–11.

Wyn B, Kidd KA, Burgess NM, Curry RA, Munkittrick KR. Increasing mercury in yellow perch at a hotspot in Atlantic Canada, Kejimkujik National Park. Environ Sci Technol 2010;44:9176–81.

Xie S, Wang T, Liu S, Jones KC, Sweetman AJ, Lu Y. Industrial source identification and emission estimation of perfluorooctane sulfonate in China. Environ Int 2013;52:1–8.

Young CJ, Mabury SA. Atmospheric perfluorinated acid precursors: chemistry, occurrence, and impacts. Rev Environ Contam Toxicol 2010;208:1–109.

Zhang L, Liu J, Hu J, Liu C, Guo W, Wang Q, et al. The inventory of sources, environmental releases and risk assessment for perfluorooctane sulfonate in China. Environ Pollut 2012;165:193–8.