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ENVIRONMENTAL MONITORING AND SURVEILLANCE
IN SUPPORT OF THE CHEMICALS MANAGEMENT PLAN

Perfluorooctane Sulfonate in the Canadian Environment



Canada 

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Perfluorooctane sulfonate (PFOS) is a synthetic substance belonging to a larger class of organic fluorochemicals that are partially or completely saturated with fluorine. PFOS and its precursors can be commonly used as water, oil, soil and grease repellents for paper and packaging, carpets, and fabrics, as well as in aqueous film-forming foam to fight fuel fires and in specialized industrial applications. These substances can be released into the environment both directly and indirectly (through degradation of its precursors) during manufacture, use and/or disposal of products containing them. PFOS is exceptionally persistent and subject to long-range transport, and is ubiquitous in the environment. It is of ecological concern, given this widespread occurrence, its bioaccumulation, and developmental toxicity, immunotoxicity and hepatotoxicity in animals. The use of PFOS and its precursors in Canada is limited to specific products and niche applications, which are exempt from the prohibition on PFOS put in place through the *Perfluorooctane Sulfonate, its Salts and Certain Other Compounds Regulations* published in June 2008. However, widespread global use since the 1950s has led to its ubiquitous presence in the Canadian environment. In order to understand the current risks posed by PFOS, the Government of Canada has been monitoring it in the environment and in certain waste streams across Canada. This document summarizes the monitoring programs for PFOS and provides information on its spatial and temporal distribution in Canada from 1979 to 2011, and compares measured PFOS concentrations to draft Federal Environmental Quality Guidelines.

Monitoring Under the Chemicals Management Plan

Monitoring (a system of long-term standardized measurements) and surveillance (focused short-term measurements) are key elements of the Government of Canada's Chemicals Management Plan (CMP) and are essential for identifying and tracking environmental concerns and health risks. Monitoring information feeds into science-based decision-making processes and is used for the evaluation of the effectiveness of risk management measures, including regulations.

Environment Canada scientists collect data on chemical substances in air,¹⁻³ freshwater,^{4,5} sediments,⁶ aquatic biota^{5,7} and wildlife⁸⁻¹¹ across Canada. Recognizing that many chemicals of concern are found in products that are ultimately disposed of in waste and wastewater, monitoring at landfills and wastewater treatment systems¹²⁻¹⁴ is also conducted under the CMP Environmental Monitoring and Surveillance Program. Also under the CMP, Health Canada conducts human biomonitoring and monitoring in other media of concern to human health including house dust, indoor air and drinking water.¹⁵

Background on PFOS

PFOS is a synthetic fluorocarbon that contains eight carbon atoms in which all of the carbon-hydrogen (C-H) bonds are replaced by carbon-fluorine (C-F) bonds (Figure 1). The C-F bond is thermodynamically the strongest bond known, which makes this compound extremely persistent in the environment. PFOS also contains a reactive sulfonyl group (SO₃H), which, together with the fluorocarbon chain, imparts the ability

to repel both oil and water. PFOS can exist in anionic, acid and salt forms. However, under normal environmental conditions of approximately neutral pH, the anionic form (i.e., $C_8F_{17}SO_3^-$) dominates, resulting in very low volatility and high water solubility. PFOS also belongs to a larger family of fluoro-organic compounds that includes perfluorooctanoic acid (PFOA) as well as more volatile precursor compounds that are commonly used in commercial products and ultimately degrade to compounds such as PFOS and PFOA.

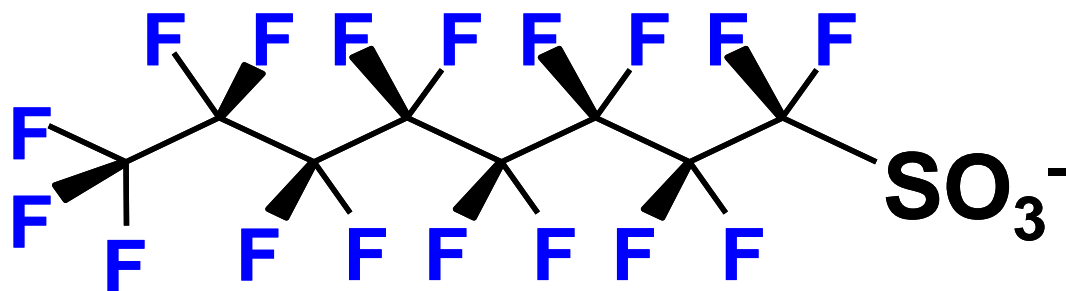


Figure 1. Molecular structure of PFOS.

Owing to its chemical and physical properties, PFOS is typically found at higher concentrations in water compared with air, and can travel long distances by oceanic currents. In contrast, PFOS precursors are more volatile and can be transported through air to areas far from initial release, where they are subsequently degraded to PFOS. PFOS is bioaccumulative and readily taken up by aquatic and terrestrial animals. However, in contrast to well-known legacy contaminants such as polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDT), which are stored predominantly in the fatty tissues of organisms, PFOS binds to proteins in blood and liver.

There are no known natural sources of PFOS, its salts or its precursors. PFOS and its precursors were never manufactured in Canada, but instead were imported as raw chemicals, products, formulations and in manufactured articles. In 2002, the primary manufacturer of PFOS phased out worldwide production. Prior to 2002, PFOS and its precursors were released into the Canadian environment during the manufacture and use of products such as paper, packaging, carpets and fabrics, where PFOS and its precursors were applied to repel water, oil, soil and grease. Currently, PFOS and its precursors are released into the Canadian environment during the use and disposal of products, such as firefighting foam, that are exempt from regulations until May 2013. PFOS or its precursors may also enter the Canadian environment through long-range transport from foreign sources.

Through risk assessment activities under the *Canadian Environmental Protection Act, 1999* (CEPA 1999), the Government of Canada concluded that PFOS, its salts, and precursors pose a risk to the environment but not to human health.^{18,19} Based on these conclusions, PFOS, its salts and precursors were added to Schedule 1 of CEPA 1999, the List of Toxic Substances. PFOS and its salts were also added to the Virtual Elimination List compiled under CEPA 1999, which demonstrates the Government of Canada's commitment to virtually eliminate PFOS and to meet the requirements of the *Perfluorooctane Sulfonate Virtual Elimination Act*.²⁰

A use pattern survey published in 2005 indicated that, with the exception of approximately three tonnes of PFOS present in stockpiles of aqueous film-forming foam, most supplies in Canada had been depleted.²¹ Regulations published in 2008 in Canada prohibit the manufacture, use, sale and import of PFOS, its salts and its precursors. Under these Regulations, five-year exemptions ending in 2013 were provided for aqueous film-forming foam and PFOS-based fume suppressants used in the metal plating industry to allow for the transition to alternatives. Ongoing exemptions in niche applications allow for use in photolithography processes, photographic materials and aviation hydraulic fluids. In the U.S., the Environmental Protection Agency requires that manufacturers and importers provide notification at least 90 days before new manufacture or import of these substances. Internationally, PFOS has been added to several agreements, such as the Stockholm Convention on Persistent Organic Pollutants, which aim to reduce production and use of PFOS on an international scale. Long-term monitoring studies and surveillance work are being conducted to determine PFOS levels in various environmental media over time.

Federal Environmental Quality Guidelines for PFOS

Environment Canada has developed draft Federal Environmental Quality Guidelines (FEQGs) to help assess the significance of PFOS concentrations in the environment (Table 1²²). These draft FEQGs for PFOS are based on studies that directly link laboratory exposure to adverse effects in animals. The FEQGs include a margin of safety to account for uncertainties associated with a lack of data (e.g., studies used a limited number of animal species). When environmental concentrations of PFOS are below the FEQG, immediate adverse effects on aquatic life or animals consuming aquatic life are not likely. Concentrations above the FEQGs indicate an increased likelihood that adverse effects in the environment may occur. However, an exceedance does not mean that adverse effects are automatically expected. Further investigation such as field sampling of animal communities would be required to confirm whether negative impacts are occurring.

Table 1: Draft Federal Environmental Quality Guidelines for PFOS.

Air	Sediment	Water (ng/L)	Fish Tissue (ng/g wet weight)	Wildlife Diet (ng/g wet weight food)		Bird Egg (ng/g wet weight)
				Mammalian	Avian	
N/A		6000	8300	4.6	8.2	1900

Monitoring Results

Results for air, sediment, water, fish and wildlife are presented, with both a geographic analysis of recent (2006–2011) PFOS concentrations across Canada (Figure 2) and an analysis of PFOS levels in Canada over time (1979–2010, Figures 3-8). Monitoring results for landfill and wastewater from 2008 to 2010 are also described. When more than one data point for a given medium and location was available, the average (geometric mean) is reported, except for comparisons to the draft FEQGs, where the maximum value is used.

Geographic Analysis

The spatial distribution of PFOS in air (gas and particle phase), sediment, fish and birds across Canada generally correlates to human activity (Figure 2). In many cases, elevated PFOS concentrations were observed near cities, especially in southern Ontario. Other sources may include airports, where use of aqueous film-forming foam is permitted until May 2013. However, it is difficult to identify the dominant sources for each site with the information that is currently available. PFOS was also detected in rural and remote locations, albeit at concentrations lower than in urban centres. The PFOS in source regions is transported to background sites through atmospheric transport of its precursor compounds and/or transport of PFOS through river and ocean currents. PFOS concentrations in media where environmental quality guidelines exist (i.e., water, fish tissue and bird eggs) were below the draft FEQGs. However, PFOS concentrations in fish and bird eggs exceeded draft FEQGs for the protection of mammals and birds that eat the fish and bird eggs, suggesting that this compound could represent a current risk to wildlife predators.

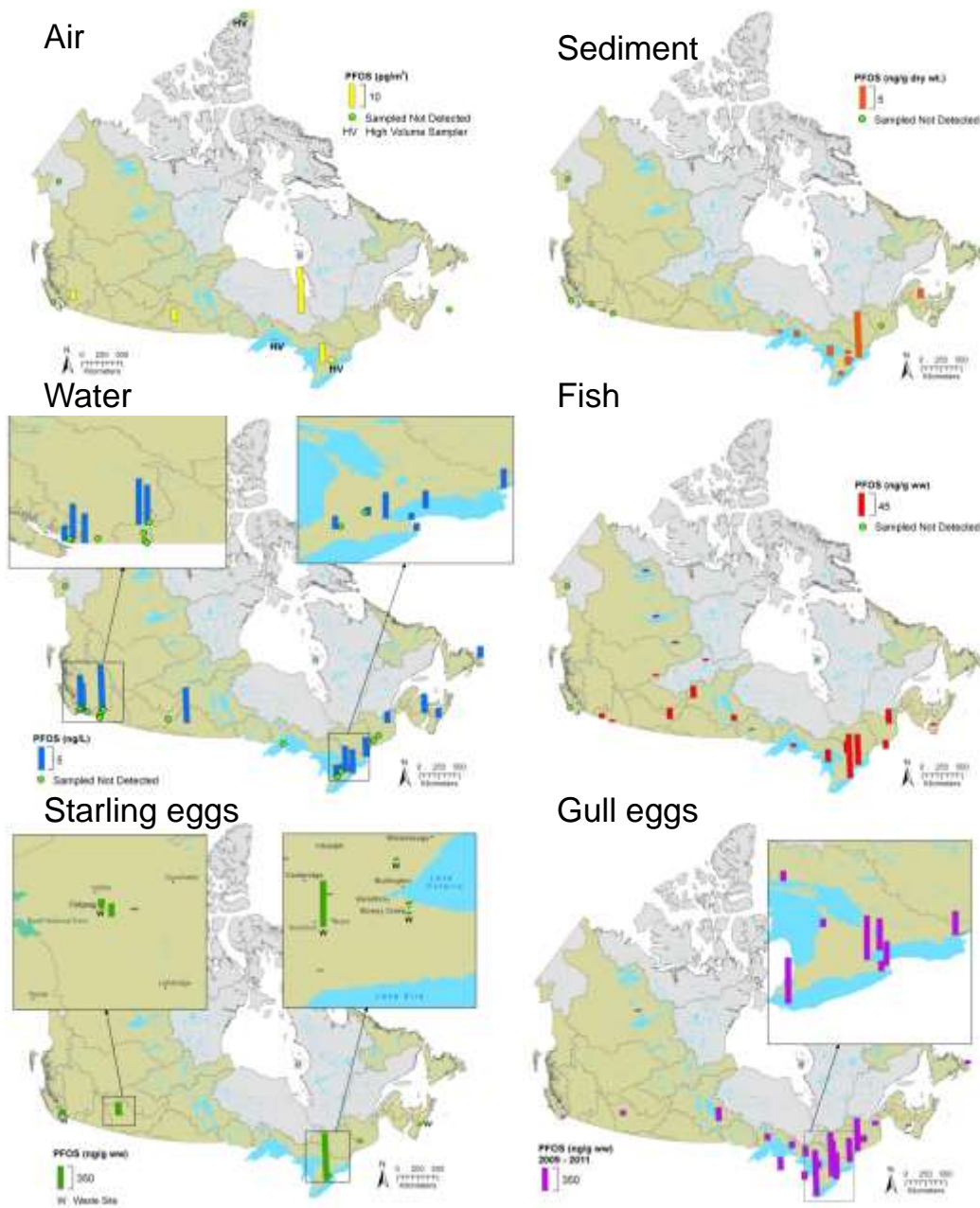


Figure 2. PFOS concentrations in air, sediment, water, fish, and wildlife (European Starling and Herring Gull eggs) across Canada in 2006–2011. For air, PFOS concentrations are either for passive or high-volume samplers (denoted as HV), collected in 2009. Sediment samples were collected in 2008. Water samples were collected between 2007 and 2010 and fish samples were collected between 2006 and 2010. Starling eggs were collected as pooled samples in 2009, the sites denoted with a W were collected from waste sites (i.e., landfills). Gulls, eggs were collected as pooled samples in 2009–2011. The spatial trends for individual gull samples collected in 2008 are similar and not shown. The green circles represent sites where PFOS concentrations were not detected. Where there was more than one data point available for a given media/location, the average (geometric mean) value was plotted on the maps.

Air: Monitoring PFOS in air across Canada provides information on PFOS levels within the country as well as quantities entering Canada from international sources. Air measurements have been obtained using two methods: high-volume air sampling^{1,2} and passive air sampling.³ High-volume air samplers measure a larger volume of air and are better for detecting the low PFOS concentrations often found in the environment. However, passive air samplers are able to gather information on long-term exposure, and can be advantageous under many circumstances because of their simplicity, ease of transport to remote sites and non-reliance on a power source.

Sampling using high-volume samplers was conducted at three locations in Canada in 2009, and it was observed that PFOS concentrations (geometric mean) were more than three times higher in Toronto (1.5 pg/m³) compared with Lake Superior air (0.43 pg/m³). PFOS was below the detection limit of 0.2 pg/m³ at the Canadian High Arctic station of Alert, Nun.; however, its precursors were detected up to several pg/m³.



Photo: © Environment Canada, Pat Roach

Sampling using passive samplers was conducted at eight locations across Canada over a three-month period in 2009. PFOS concentrations were detected in Toronto, Ont. (8 pg/m³), an agricultural site in Saskatchewan (5 pg/m³), Whistler, B.C. (4 pg/m³), and Alert, Nun. (2 pg/m³). One site in northern Ontario had elevated PFOS concentration of 18 pg/m³. However, these data points are based on only one sample. PFOS was

not detected at the other Canadian sites. The PFOS levels measured in Canada using passive samplers were substantially lower than in Paris, France (150 pg/m³), but comparable to Sydney, Florida (3.4 pg/m³), Tudor Hill, Bermuda (6.1 pg/m³), Malin Head, Ireland (3.3 pg/m³), and Hilo, Hawaii (6.6 pg/m³).³

In general, the results showed that PFOS air concentrations in urban locations (e.g. Toronto) were on the same order of magnitude as more remote sites (e.g. Lake Superior), demonstrating the widespread distribution of PFOS in the Canadian atmosphere. FEQGs do not exist for PFOS in air.

Sediment: In 2008, 65 surface sediment samples were collected at 18 sites across Canada. The highest PFOS concentration in sediments was found in Lake Ontario (geometric mean = 10 ng/g dry weight). PFOS was also detected in the open-water sediment of the other Great Lakes at concentrations of 0.89, 2.2 and 1.4 ng/g dry weight in Lake Erie, Lake Huron and Lake Superior, respectively. Sediment PFOS concentrations at Hamilton and Toronto harbours (in Lake Ontario) and near Thunder Bay (in Lake Superior) were 0.64, 1.9 and 0.54 ng/g dry weight. The PFOS concentration in Lake Simcoe, Ont., sediment (geometric mean = 0.76 ng/g dry weight) was comparable to the Great Lakes sites, except Lake Ontario.²³ Downstream of the Great Lakes watershed, the PFOS concentration in Lake Saint-Pierre, Que., was 0.16 ng/g dry weight. In the Atlantic provinces, PFOS was detected in the Nappan River, an industrial site in New Brunswick (2 ng/g dry weight), Kejimikujik Lake, N.S. (0.28 ng/g dry weight), and at Little Sackville, N.S. (0.19 ng/g dry weight). In western Canada, PFOS was found only in Osoyoos Lake, B.C. (0.36 ng/g dry weight). PFOS was non-detectable at the other sites monitored.

Overall, although the highest PFOS concentration in sediment was observed in the urbanized Lake Ontario, levels were not always associated with human population. For example, relatively low PFOS concentrations were found in the heavily developed Lake Erie, as well as the Hamilton and Toronto harbours, which were comparable to more remote sites (e.g. Lake Superior). FEQGs for PFOS do not exist for sediment.

Water: Water was sampled for PFOS in the Great Lakes, as well as in streams and rivers across the country^{4,5} from 2007 to 2010. PFOS was highest at a site in Mill Creek, located in Kelowna, B.C. (geometric mean = 10 ng/L). This section of Mill Creek is urbanized and influenced by urban stormwater. In addition, Wascana Creek, in Regina, Sask., had a relatively elevated PFOS concentration (geometric mean = 7.8 ng/L). This site in Wascana Creek is located 8.5 km downstream of a wastewater treatment plant (WWTP) outfall and is the water collection station most impacted by WWTP inputs. Detectable values (>2 ng/L) were also observed in southern Ontario (Hamilton Harbour, Niagara River at Fort Erie, Lake Ontario at Wolfe Island, Grand River and Thames River), St. Lawrence River at Quebec City, Vancouver, British-Columbia (Still Creek and Serpentine River), Abbotsford, British-Columbia (Fishtrap Creek), and at the three Atlantic sites (Napan River, N.B., Sackville River, N.S., and Waterford River, N.L.).

Many of the rivers and streams containing relatively elevated levels of PFOS were located in cities, and thus are influenced by urban activities. In comparison, PFOS concentrations were mostly not detected in water bodies from non-urban regions and background sites. The draft FEQG for PFOS in water is 6000 ng/L, which is 200 times greater than the highest measured water concentration in Canada (31 ng/L in Mill Creek, Kelowna, B.C.). Therefore, current PFOS levels in water at the selected Canadian sampling sites are of low risk to aquatic life.^{1*}

Fish: Top predator fish (e.g., lake trout and walleye) were collected at 21 sites across Canada from 2006 to 2010. PFOS levels varied considerably, with the highest concentrations observed in lake trout from Lake Erie (geometric mean = 90 ng/g wet weight) and Lake Ontario (geometric mean = 62 ng/g wet weight). Relatively elevated PFOS concentrations (geometric mean) were also found in walleye from the St. Lawrence River (30 ng/g wet weight), Codette Reservoir, Sask. (24 ng/g wet weight) and Lake Diefenbaker, Sask. (23 ng/g wet weight), and in lake trout from Peninsula Harbour, Ont. (24 ng/g wet weight) and Lake Champlain (17 ng/g wet weight). Levels in fish were mostly low (<3 ng/g wet weight) in the water bodies located in northern Canada, Pacific and Atlantic regions, and Lake Superior.

In general, the results for fish indicated relatively elevated PFOS concentrations in urban areas, particularly in southern Ontario, compared to the more remote lakes sampled. The draft FEQG for fish tissue is 8300 ng/g wet weight, which is 12 times greater than the highest measured fish concentration in Canada (189 ng/g wet weight in Lake Erie). This suggests a low probability of adverse effects to fish related to PFOS exposure. In contrast, the PFOS levels could represent a potential risk to the fishes' wildlife predators in some of the systems (draft FEQG = 4.6 ng/g wet weight and 8.2 ng/g wet weight for mammalian and avian predators, respectively).

^{1*} Draft FEQG for water is not designed to protect against bioaccumulation – see corresponding dietary and tissue residue FEQGs.



Photo : © Environment Canada, Mandi Clark

Wildlife: PFOS is currently monitored in the eggs of two types of birds: gulls and European Starlings. Gulls often eat fish and provide an indication of contamination in the aquatic environment. Although gull sampling focussed on Herring Gulls, when they were not available, other related species (i.e., California Gull, Ring-billed Gull and Glaucous-winged Gull) were monitored. In 2008, gull eggs were measured individually, whereas between 2009 and 2011, the gull eggs were measured as pooled samples.⁸ The results between individual and pooled eggs often differ, and they are therefore reported separately here. For the individual gull eggs, relatively elevated PFOS concentrations (geometric mean) were found at urbanized areas of the Great Lakes and the St. Lawrence River, with levels greater than 260 ng/g wet weight. Concentrations were lower (geometric means ranged from 7–115 ng/g wet weight) in non-urban areas as well as at marine colonies on both the Atlantic and Pacific coasts. A similar result of elevated concentrations in the Great Lakes were also found in the pooled gull eggs collected between 2009 and 2011, with the highest levels observed in Lake Erie (676 ng/g wet weight). In contrast to gulls, European Starling eggs provide information on terrestrial systems, and European Starlings feed lower on the food web. European Starlings were collected from waste (i.e., landfills) and non-waste sites in 2009 and were measured as pooled samples. The highest geometric mean PFOS concentration (703 ng/g wet weight) was found in Starling eggs collected at the Brantford, Ont., landfill, located in a highly urbanized region in southern Ontario.

Relatively elevated PFOS concentrations (geometric mean = 148 ng/g wet weight) was also found in starling eggs collected at the Calgary landfill. However, other than these two landfill sites, PFOS concentrations were not higher at the waste sites compared to non-waste sites. For example, PFOS concentrations (geometric mean) were higher in the starlings collected from urbanized communities of Indus, Alta. (199 ng/g wet weight), Delta, B.C. (75 ng/g wet weight) and Hamilton, Ont. (41 ng/g wet weight) compared with landfill sites located in Langley, B.C. (5.6 ng/g wet weight), Halton, Ont. (29 ng/g wet weight), Stoney Creek, Ont. (28 ng/g wet weight) and Otter Lake, N.S. (18 ng/g wet weight).

As shown above, the spatial trends of PFOS concentrations in gull eggs were related to human population. In comparison, for starling eggs, although the highest PFOS concentration was observed in the heavily industrialized landfill site of Brantford, Ont., levels were not always higher in eggs from urbanized/industrialized locations compared to areas that were more remote. The draft FEQG for bird eggs (1900 ng/g wet weight) was 2.3 times greater than the highest PFOS concentration observed in gulls (811 ng/g wet weight in Lake Erie). When the Brantford, Ont., landfill site was excluded, the draft FEQG for bird eggs was 7.5 times greater than the highest PFOS concentration in



Photo: © Environment Canada, Chip Weseloh

starlings (254 ng/g wet weight at Indus, Alta.). The draft FEQG for bird eggs was 1.6 times greater than the PFOS concentrations in starling eggs at the Brantford, Ont., landfill site (maximum = 1184 ng/g wet weight). These results suggest that PFOS represents little risk to the birds themselves. However, guideline exceedances were common for their wildlife consumers (draft FEQG = 4.6 ng/g wet weight for mammalian predators and 8.2 ng/g wet weight for avian predators).

Temporal Analysis

The temporal trends of PFOS have been studied in air, suspended sediment, sediment cores, lake trout and Herring Gull eggs. The majority of temporal trend data is for Lake Ontario; however, Herring Gull eggs were evaluated for PFOS in colonies from each of the five Great Lakes, and Arctic air was assessed for PFOS precursors. For the most part, levels of PFOS increased markedly until the late 1990s/early 2000s, corresponding to increasing production volumes. However, in recent years, concentration trends varied by media and location. More time may be needed before ongoing shifts in North American and global uses and releases of PFOS and its precursors result in clear trends in various environmental media and locations.

Air: At the Canadian High Arctic station of Alert, Nun., PFOS and its precursors were sampled for with a high-volume air sampler starting in 2006. PFOS was below the detection limit of 0.2 pg/m³ at Alert, Nun., however, PFOS precursors were detected. One such precursor is methyl perfluorooctane sulfonamidoethanol (MeFOSE) (Figure 3). MeFOSE is easier to detect in air as a result of its higher volatility compared

to PFOS. The concentrations of this PFOS precursor oscillated from below detection to 2.6 pg/m^3 and are showing general declining trends. Continued measurements are required to examine what factors influence transport of PFOS and its precursors to the Arctic in order to understand the long-range transport ability of these chemicals.

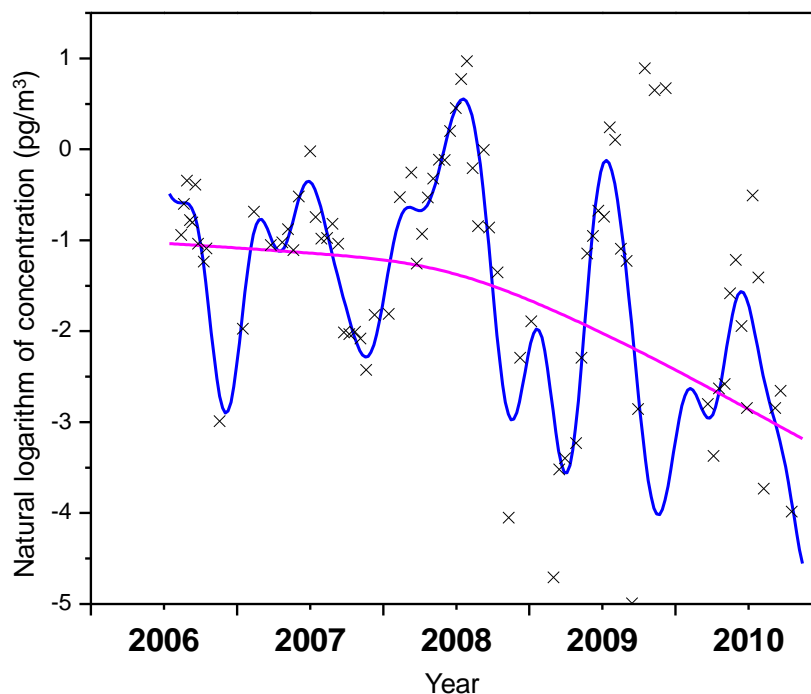


Figure 3: Concentrations of the PFOS precursor compound, methyl perfluorooctane sulfonamidoethanol, in air (pg/m^3) at Alert, Nun., between 2006 and 2010.

Suspended Sediment: Suspended sediment has been collected annually, since the 1980s, from Niagara River water flowing into Lake Ontario. The samples were analyzed for PFOS at the Ontario Ministry of the Environment.⁶ The Niagara River represents the most significant input of water to Lake Ontario, accounting for approximately 80% of the total tributary inflow into the lake. The concentrations of PFOS in suspended sediment increased from the early 1980s (0.47 ng/g dry weight) until 2001, when a peak concentration of 1.1 ng/g dry weight was reached (Figure 4). After this time, PFOS decreased continually to a concentration of 0.48 ng/g dry weight in 2006. The long-term time trends of PFOS in suspended sediment more closely resemble assumed North American production volumes and the timing of the 2002 PFOS production phase-out by the primary supplier, compared to other media. This may not be surprising, considering that suspended sediments were collected from filtered water samples and thus are likely representative of direct loadings into the lake.

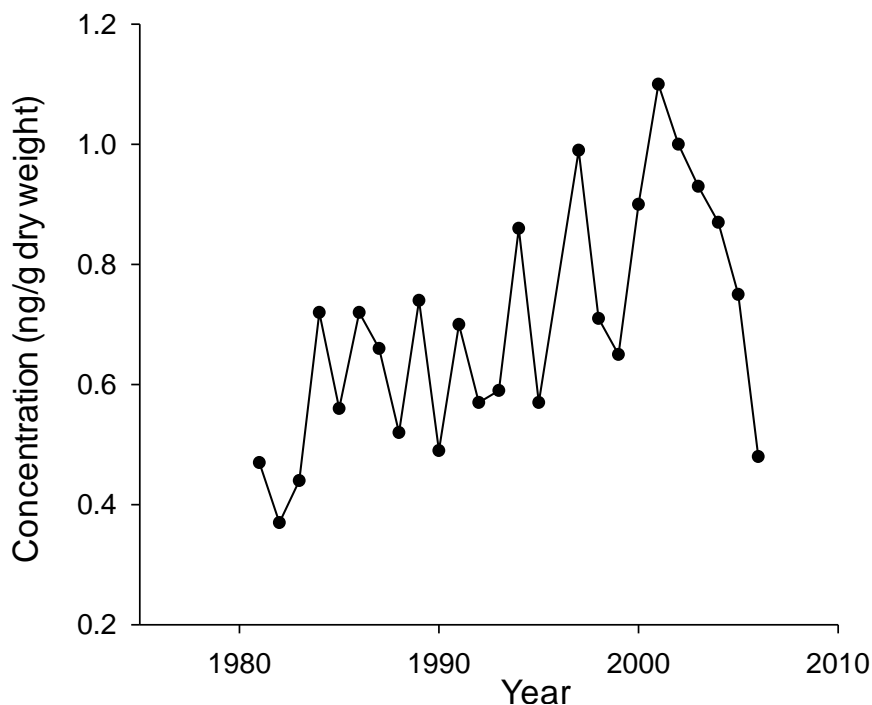


Figure 4: Concentrations of PFOS (ng/g dry weight) in Niagara River suspended sediment.

Sediment Core: Three sediment cores were collected from Lake Ontario in 2006, dated using radioisotope methods and analyzed for PFOS at the Ontario Ministry of the Environment.⁶ Figure 5 shows the results of one of these sediment cores. The trends for the other two cores are similar and thus not shown. PFOS increased in the Lake Ontario sediment cores from the start of data collection until 2004, and did not reflect the 2002 phase-out by the primary supplier. This lack of correspondence between the sediment core data with assumed loadings patterns could be a result of the sediment core trend being based on only five measurements dated between 1980 and 2004. This time trend only includes one data point following the 2002 PFOS production phase-out by the primary supplier. It should be noted that better resolution would be difficult to achieve due to the slow rate at which particles are deposited and incorporated into Lake Ontario sediment. Continued monitoring of sediment cores is required, as it may take more years before the reduction in PFOS use is reflected in this media.



Photo: © Environment Canada, Suzie Proulx

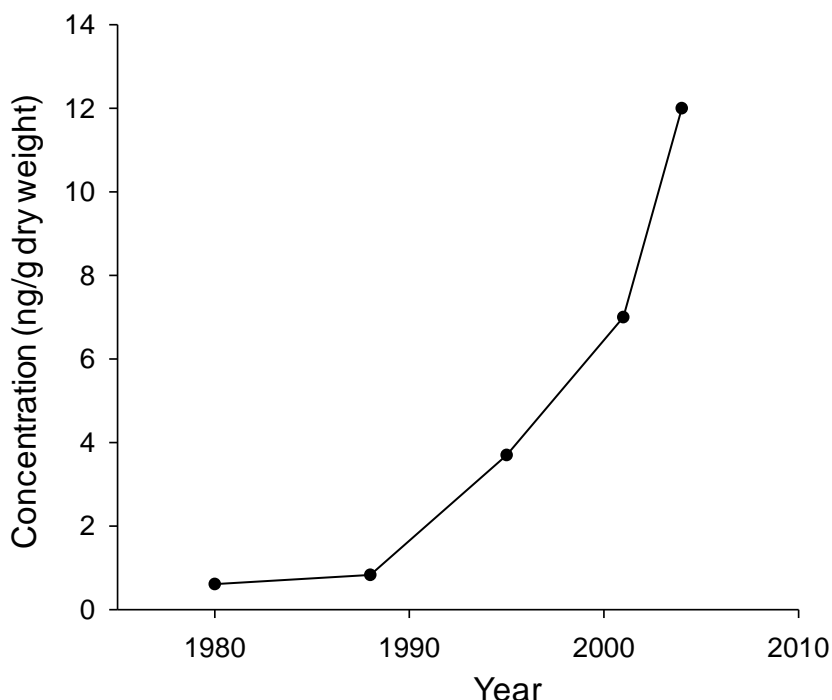


Figure 5: Concentrations of PFOS (ng/g dry weight) in a Lake Ontario sediment core sample collected in 2006.

Fish: To provide a long-term perspective of PFOS in Lake Ontario lake trout, annual measurements made by Environment Canada (1997–2010)⁷ were combined with PFOS concentrations that Furdui and co-workers^{24,25} determined in archived lake trout samples (1979–2004). These archived samples were also collected in Lake Ontario by Environment Canada and the Department of Fisheries and Oceans and were analyzed for PFOS by the Ontario Ministry of the Environment. PFOS concentrations in Lake Ontario lake trout showed an overall increase between 1979 and 2000 (Figure 6). However, after this time, concentration trends stabilized, with geometric mean levels oscillating between 44 and 109 ng/g wet weight. These results suggest that although PFOS in Lake Ontario lake trout may have stopped increasing in response to the 2002 PFOS production phase-out by the primary supplier, corresponding concentration declines in fish have not been observed. The lack of recent decline may be a result of the large number of processes, in addition to chemical loadings, that affect the accumulation of PFOS in biota such as lake trout. For example, the amount of PFOS in fish is dependent on its diet, the accumulation rate of PFOS and its precursors from water and food, and the rate at which precursors are transformed to PFOS in the fish, its food and the environment. As such, the voluntary and regulatory measures may not be reflected in PFOS concentrations in Lake Ontario lake trout for years to come. In all years, observed concentrations in lake trout were at least an order of magnitude below the draft FEQG for fish tissue (8300 ng/g wet weight), but were between 1.5- and 27-fold higher than the draft FEQG for wildlife diet. Therefore, although PFOS does not represent a risk to the Lake Ontario lake trout themselves, it is present at levels that are potentially hazardous to the wildlife consumers of the fish.

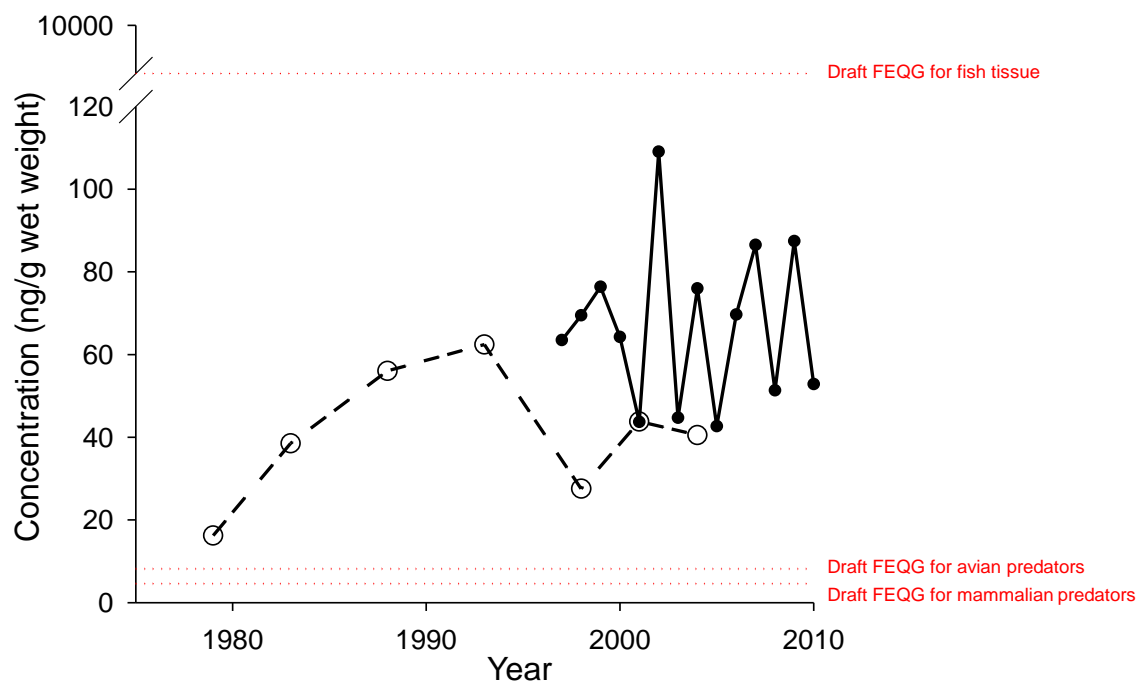


Figure 6: Geometric mean concentrations of PFOS in Lake Trout (ng/g wet weight) from Lake Ontario, 1979 to 2010. The dashed line represents data reported by Furdui *et al.* 2007 and 2008, and the solid line represents Environment Canada data. The draft Federal Environmental Quality Guidelines (FEQGs) for fish tissue and for avian and mammalian wildlife diet are shown for comparison (red dotted lines).

Wildlife: Herring Gull eggs were monitored for PFOS in 1990 and in all years between 1997 and 2010 at seven colonies throughout the Great Lakes. The data for gulls collected from the more urbanized regions of southern Ontario are shown in Figure 7. Likewise, Figure 8 shows PFOS levels in gull eggs collected from three more remote colonies in lakes Huron and Superior. The average PFOS concentrations from the more urbanized colonies oscillated between approximately 150 and 930 ng/g egg wet weight. However, consistent with trends found in Lake Ontario lake trout, PFOS levels have not shown consistent declines in response to the 2002 PFOS production phase-out by the primary supplier. PFOS levels in the gull eggs collected from the more remote colonies also varied considerably between years (80–375 ng/g wet weight); however, in contrast to the urbanized colonies, an overall decline was evident. These results show that temporal trend patterns can vary between locations, even for the same media or species. The PFOS concentrations in Herring Gull eggs were below the draft FEQG for bird eggs (1900 ng/g wet weight) in all years and locations; but were 10- to 200-fold higher than the draft FEQG for wildlife diet. Therefore, similar to the case of fish, although PFOS does not represent a risk to the Herring Gull eggs themselves, it is present at levels that are potentially hazardous to the gull’s wildlife predators.

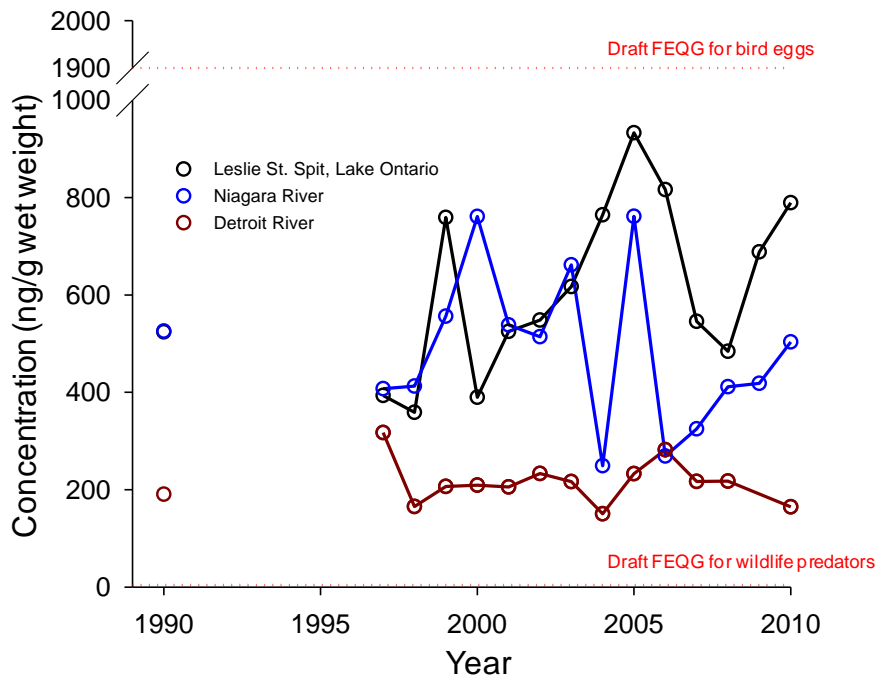


Figure 7: PFOS concentrations in Herring Gull eggs (ng/g wet weight) from Lake Ontario (Leslie Street Spit), Niagara River and Detroit River (Fighting Island), from 1990 to 2010. The draft Federal Environmental Quality Guidelines (FEQGs) for bird eggs and wildlife diet are shown for comparison (red dotted lines).

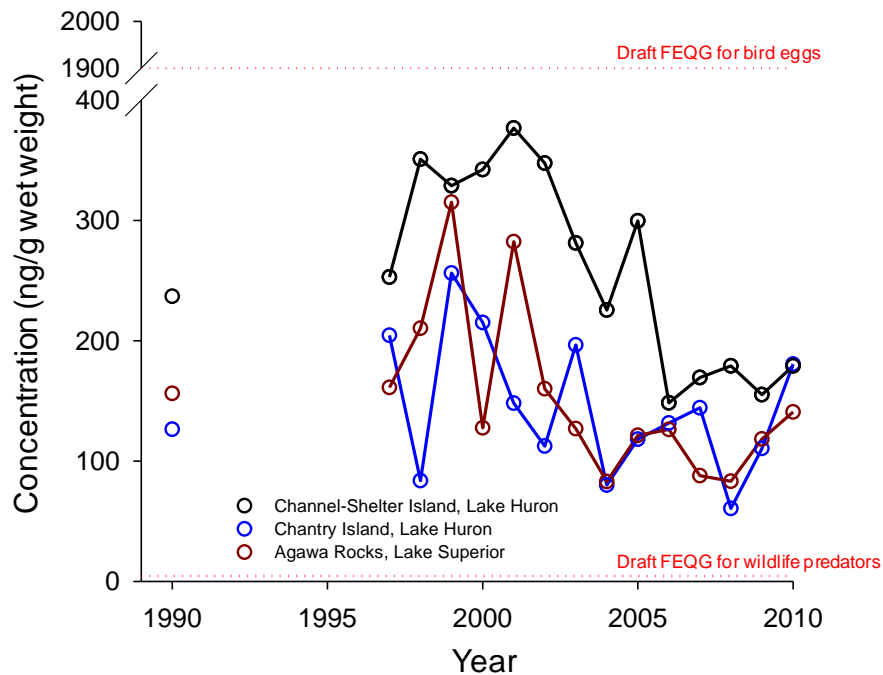


Figure 8: PFOS concentrations in Herring Gull eggs (ng/g wet weight) from Lake Huron (Channel-Shelter and Chantry Islands) and Lake Superior (Agawa Rocks), from 1997 to 2010. The draft Federal Environmental Quality Guidelines (FEQGs) for bird eggs and wildlife diet are shown for comparison (red dotted lines).

Wastewater and Landfill Monitoring

The wastewater treatment component of the CMP monitoring and surveillance program provides information on the significance of wastewater effluent discharges and land application of treated biosolids as sources of PFOS to the environment and on changes in PFOS levels from these sources over time. In 2009–2010, 20 municipal wastewater systems representing typical wastewater treatment processes in Canada were sampled in summer and winter. Raw influent PFOS concentrations across all wastewater systems ranged from below the method reporting limit (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%. PFOS concentrations in final effluent ranged from below the method reporting limit (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%. Preliminary analysis indicates that PFOS concentrations in final effluent increased in the systems monitored by the program. This increase may be due to PFOS being produced through precursor breakdown during the wastewater treatment processes. Results from wastewater solids analysis showed median PFOS concentrations of 13.6 ng/g dry weight in primary sludge (n=111, detection frequency of 31%), 36.8 ng/g dry weight in waste biological sludge (n=78, detection frequency of 90%), and 13.7 ng/g dry weight in treated biosolids (n=107, detection frequency of 91%). These preliminary results indicate that PFOS is consistently present in wastewater solids as well as effluents. Levels in these treated biosolids (ppb) are three orders of magnitude higher than levels in effluents (ppt).



Photo: © Environment Canada, Shirley Anne Smyth

In order to monitor the potential release of PFOS from a segment of the solid waste sector, landfill leachate was collected from 10 Canadian municipal solid-waste landfill sites in 2009 and 2010. The landfills all receive municipal waste, and some also receive construction waste, industrial waste and sewage sludge. Samples were collected prior to on-site treatment at all 10 landfill sites. Treated leachate samples were obtained from 3 of the 10 landfills. Concentrations of PFOS in raw leachate samples ranged from below the method reporting limit (9.5 to 44 ng/L) to 744 ng/L, with a median of 22 ng/L and a detection frequency of 48%. Concentrations in the treated leachate samples ranged from below the method reporting limit (9.8 to 20 ng/L) to 2070 ng/L, with a median value of 20 ng/L and a detection frequency of 40%. In some cases, PFOS concentrations increased following treatment, which is likely a result of precursor compound breakdown, similar to the WWTP monitoring described above. Approximately 87% of the leachate generated in Canada is treated by wastewater treatment plants.

The wastewater and landfill monitoring programs for PFOS have focused on emissions to the aquatic environment and biosolids. In contrast, there is little information on the potential for the WWTPs and landfills to emit PFOS to the atmosphere. To fulfill this need, the air at one Ontario WWTP and two landfill sites were monitored for PFOS and volatile PFOS precursor compounds between June and September 2009, using passive and active air samplers.^{13,14} For the WWTP, concentrations of PFOS and the PFOS precursor compounds were seven and four times higher, respectively, compared with upwind and downwind background locations. Similarly, for the landfills, the concentrations of PFOS and PFOS precursor compounds were approximately three and two times greater, respectively, than the upwind sites.

Conclusion

The levels of PFOS were generally higher in urban and industrialized locations across Canada than in rural and remote locations. Consistent with other studies, these data indicate that human activities such as the use and disposal of consumer products containing PFOS and discharge to wastewater continue to be sources of PFOS to the environment. Other sources may include airports, where use of aqueous film-forming foam is permitted until May 2013, as well as other fire training areas where legacy contamination may be a continuing source to surface water. Atmospheric transport of precursor compounds or transport of PFOS through oceanic currents are likely important routes of exposure to background sites. Elevated concentrations of PFOS were detected in water, biosolids and air at WWTPs and in leachate and air of landfill sites. This highlights the contributions of WWTPs and landfills as sources of PFOS to aquatic systems and the atmosphere.

For the most part, levels of PFOS increased markedly from the early 1980s (or the start of data collection) until the late 1990s/early 2000s, corresponding to increased production volumes during this time. However, in recent years, concentration trends varied by media and location. More time may be required before the domestic and international measures related to PFOS are reflected consistently in all environmental media and locations. Continued input from PFOS-containing products still in use

and continued use of PFOS products outside of North America may also be preventing decreases of concentrations in the environment.

Through comparison to the draft FEQGs, current PFOS concentrations that have been measured present a low potential for adverse effects on the organisms examined. However, PFOS in fish and bird eggs tended to exceed dietary guidelines for the protection of non-human mammalian and avian consumers, suggesting that this compound could represent a current risk to their wildlife predators. However, wildlife population health assessments are required to determine whether negative impacts are actually occurring. These results provide an important piece of information to be used by the Government of Canada in evaluating the risk management strategy for PFOS and considering how best to approach the risk management for similar substances of concern.

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References

- (1) Ahrens, L.; Shoeib, M.; Del Vento, S.; Codling, G.; Halsall, C. Polyfluoroalkyl compounds in the Canadian Arctic atmosphere. *Environ. Chem.* **2011**, *8*, 399-406.
- (2) Ahrens, L.; Shoeib, M.; Harner, T.; Lane, D. A.; Guo, R.; Reiner, E. J. Comparison of annular diffusion denuder and high volume air samplers for measuring per- and polyfluoroalkyl substances in the atmosphere. *Anal Chem.* **2011**, *83*, 9622-9628.
- (3) Genualdi, S.; Lee, S. C.; 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*, 5534-5539.
- (4) De Silva, A. O.; Backus, S. M.; Gewurtz, S. B.; McGoldrick, D. J.; Gledhill, M.; Sekela, M.; Syrgiannis, J.; Struger, J.; Rondeau, M.; Pomeroy, J. A spatial survey of perfluorinated compounds in surface water in Canada. **2012**, In Preparation.
- (5) De Silva, A. O.; Spencer, C.; Scott, B. F.; Backus, S. M.; Muir, D. C. G. Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate, in the Great Lakes of North America. *Environ. Sci. Technol.* **2011**, *45*, 8060-8066.
- (6) Myers, A. L.; Crozier, P. W.; Helm, P. A.; Brimacombe, C.; Furdui, V. I.; Reiner, E. J.; Burniston, D.; Marvin, C. H. Fate, distribution, and contrasting temporal trends of perfluoroalkyl substances (PFASs) in Lake Ontario, Canada. *Environ. Int.* **2012**, *44*, 92-99.

- (7) Gewurtz, S. B.; De Silva, A. O.; Backus, S. M.; McGoldrick, D. J.; Keir, M. J.; Small, J.; Melymuck, L.; Muir, D. C. G. Perfluoroalkyl substances in Lake Ontario Lake Trout: Detailed examination of current status and long-term trends. *Environ. Sci. Technol.* **2012**, *46*, 5842-5850.
- (8) Gebbink, W. A.; Letcher, R. J.; Burgess, N. M.; Champoux, L.; Elliott, J. E.; Hebert, C. E.; Martin, P.; Wayland, M.; Weseloh, D. V. C.; Wilson, L. 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.* **2011**, *37*, 1175-1182.
- (9) Gebbink, W. A.; Letcher, R. J.; Hebert, C. E.; Weseloh, D. V. Twenty years of temporal change in perfluoroalkyl sulfonate and carboxylate contaminants in Herring Gull eggs from the Laurentian Great Lakes. *J. Environ. Monit.* **2011**, *13*, 3365-3372.
- (10) Gebbink, W. A.; Letcher, R. J. 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*, 40-47.
- (11) de Solla, S. R.; De Silva, A. O.; Letcher, R. J. Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada. *Environ. Int.* **2012**, *39*, 19-26.
- (12) Conestoga Rovers & Associates *Sampling for Chemicals Management Plan Challenge Substances from the Waste Sector: 2010 Field Sampling Program*; CRA Project number 054555 (5); Conestoga Rovers & Associates in a report prepared for Environment Canada: Waterloo, ON, Canada, 2011.
- (13) Ahrens, L.; Shoeib, M.; Harner, T.; Lee, S. C.; Guo, R.; Reiner, E. J. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environ. Sci. Technol.* **2011**, *45*, 8098-8105.
- (14) Vierke, L.; Ahrens, L.; Shoeib, M.; Reiner, E. J.; Guo, R.; Palm, W.-U.; Ebinghaus, R.; Harner, T. Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant. *Environ. Chem.* **2011**, *8*, 363-371.
- (15) Shoeib, M.; Harner, T.; M. Webster, G.; Lee, S. C. Indoor sources of poly- and perfluorinated compounds (PFCs) in Vancouver, Canada: Implications for human exposure. *Environ. Sci. Technol.* **2011**, *45*, 7999-8005.
- (16) Butt, C. M.; Berger, U.; Bossi, R.; Tomy, G. T. Levels and trends of poly- and perfluorinated compounds in the Arctic environment. *Sci. Total Environ.* **2010**, *408*, 2936-2965.
- (17) Ahrens, L. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J. Environ. Monit.* **2011**, *13*, 20-31.

- (18) Environment Canada *Ecological Screening Assessment Report on Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C8F17SO2 or C8F17SO3 or C8F17SO2N Moiety*; 2006; www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=98B1954A-1.
- (19) Health Canada *State of the Science Report for a Screening Health Assessment on Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C8F17SO2 or C8F17SO3 Moiety*; 2006; www.ec.gc.ca/lcpe-cepa/09F567A7-B1EE-1FEE-73DB-8AE6C1EB7658/HC_SOS_PFOS-eng.pdf.
- (20) Environment Canada. *Perfluorooctane Sulfonate Virtual Elimination Act*. 2008 <http://laws-lois.justice.gc.ca/eng/acts/P-8.3/page-1.html>
- (21) Government of Canada Notice with respect to perfluorooctane sulfonate (PFOS), its salts and its precursors. *Canada Gazette Part I* 2005, Vol. 139, No. 3.
- (22) Environment Canada *Federal Environmental Quality Guidelines for Perfluorooctane Sulfonate (PFOS). Draft for Review*; National Guidelines and Standards Office: Gatineau, QC, 2013.
- (23) Helm, P. A.; Milne, J.; V., B.-H.; Crozier, P. W.; Kolic, T.; Lega, R.; Chen, T.; MacPherson, K.; Gewurtz, S. B.; Winter, J. G.; Myers, A.; Marvin, C. H.; Reiner, E. J. Lake-wide distribution and depositional history of current- and past-use persistent organic pollutants in Lake Simcoe. *J. Great Lakes Res.* 2011, 37, 132-141.
- (24) Furdui, V. I.; Helm, P. A.; Lucaciu, C.; Reiner, E. J.; Marvin, C. H.; Whittle, D. M.; Mabury, S. A.; Tomy, G. T. Temporal trends of perfluoroalkyl compounds with isomer analysis in Lake Trout from Lake Ontario (1979-2004). *Environ. Sci. Technol.* 2008, 42, 4739-4744.
- (25) Furdui, V. I.; Stock, N. L.; Ellis, D. A.; Butt, C. M.; Whittle, D. M.; Crozier, P. W.; Reiner, E. J.; Muir, D. C. G.; Mabury, S. A. Spatial distribution of perfluoroalkyl contaminants in Lake Trout from the Great Lakes. *Environ. Sci. Technol.* 2007, 41, 1554-1559.

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The Chemicals Management Plan and Monitoring Program

- The Chemicals Management Plan:
www.chemicalsubstanceschimiques.gc.ca/plan/index-eng.php
- Monitoring and Research under the Chemicals Management Plan:
www.chemicalsubstanceschimiques.gc.ca/fact-fait/monitor-surveill-eng.php
- Chemicals Management Plan Monitoring Factsheet Website:
www.ec.gc.ca/scitech/default.asp?lang=En&n=7AC5DC36-1

Risk Assessment and Management of PFOS

- Ecological Screening Assessment Report on Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C₈F₁₇SO₂ or C₈F₁₇SO₃ or C₈F₁₇SO₂N Moiety:
www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=98B1954A-1
- PFOS Health Canada Screening Assessment Report:
www.ec.gc.ca/lcpe-cepa/09F567A7-B1EE-1FEE-73DB-8AE6C1EB7658/HC_SOS_PFOS-eng.pdf
- CEPA 1999 Schedule 1 – List of Toxic Substances:
www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=0DA2924D-1&wsdoc=4ABEFFC8-5BEC-B57A-F4BF-11069545E434
- Risk Management Strategy for Perfluorooctane Sulfonate (PFOS), Its Salts and Its Precursors:
www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=2AD798EA-1
- *Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations:*
www.ec.gc.ca/lcpe-cepa/eng/regulations/detailReg.cfm?intReg=107

Health Canada's Activities

- Environmental Contaminants and Human Biomonitoring:
www.hc-sc.gc.ca/ewh-semt/contaminants/index-eng.php
- Maternal-Infant Research on Environmental Chemicals:
www.mirec-canada.ca/

Other Environmental Monitoring Programs

- The Northern Contaminants Program:
www.aadnc-aandc.gc.ca/eng/1100100035611/1100100035612
www.science.gc.ca/Northern_Contaminants_Program-WS7A463DBA-1_En.htm
- The National Air Pollution Surveillance Program:
www.ec.gc.ca/rnspa-naps/default.asp?lang=En&n=5C0D33CF-1
- The Integrated Atmospheric Deposition Network:
www.ec.gc.ca/rs-mn/default.asp?lang=En&n=BFE9D3A3-1
- The Global Atmospheric Passive Sampling Network:
www.ec.gc.ca/rs-mn/default.asp?lang=En&n=22D58893-1
- Great Lakes Surveillance Program:
www.ec.gc.ca/scitech/default.asp?lang=en&n=3F61CB56-1

- National Fish Contaminants Monitoring and Surveillance Program:
www.ec.gc.ca/scitech/default.asp?lang=en&n=828EB4D2-1
- National Freshwater Quality Monitoring and Surveillance:
www.ec.gc.ca/eaudouce-freshwater/Default.asp?lang=En

Federal Environmental Quality Guidelines

- Environment Canada. 2013. Federal Environmental Quality Guidelines for Perfluorooctane Sulfonate (PFOS). Draft for Review. National Guidelines and Standards Office, Gatineau QC.

www.ec.gc.ca

Additional information can be obtained at:

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