Perfluoroalkyl Substances (PFASs) in the Canadian Freshwater Environment.

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Abstract

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic substances that are very stable in the receiving environment. PFASs are persistent and resistant to typical environmental degradation processes and therefore are distributed across all trophic levels and environmental compartments (soil, air, water). Since most uses of PFOS, PFOA and LC-PFCAs are banned in Canada, alternative PFASs have been in use for a number of years. Twenty-nine sites across Canada were sampled for PFASs to determine concentrations and trends. Overall, 13 PFASs were measured in 566 Canadian freshwater samples from 2013- 2020 with a range from below the detection limit of the laboratory to a maximum of 138 ng/L (for PFBS). While PFOS and PFOA concentrations are declining significantly over time, other compounds such as PFPeA and PFBA have increased significantly over 2013-2020. Overall the range of concentrations found in this study were similar to that of other Canadian and international studies. However, this study also found a higher frequency of detections of the replacement PFASs than that of the other, older, Canadian studies.

Introduction

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic substances that are very stable in the receiving environment. Due to their chemical structures, these fluorinated compounds repel both water and oil. They are used extensively in consumer products and industrial applications such as treatments on carpets and clothing, coatings on paper, cardboards and non-stick coatings on cookware, industrial surfactants and emulsifiers and firefighting foams (OECD 2013). Since these products are fabricated, their release to the environment are from industrial manufacturing and the use and/or disposal of PFSA-containing products. Some PFASs are also formed by environmental degradation of related PFSA or precursor compounds (OECD 2013; ATSDR 2018).

PFASs are persistent and resistant to typical environmental degradation processes and therefore are distributed across all trophic levels and environmental compartments (soil, air, and water). Although PFASs are not considered volatile they readily associate with particulates and may contribute PFASs to surface water through precipitation (OECD 2013; Gewurtz et al 2019) and have high long range transport potential (OECD 2021). PFASs as a group contain more than 4700 substances with PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid) the two most frequently measured. They are two main types of PFASs; long and short chain with long chains defined as having 6 or more perfluoroalkyl carbons (OECD 2021). The long chain PFASs include such compounds as PFOS, PFAS, PFNA, PFHxS. The length of the carbon chain may result in different bioaccumulative, toxicity and persistence tendencies in the environment (OECD 2021). Myers et al (2012) depicted short chain PFASs as more common in urban and industrial watersheds.

In the US, the longer chain PFASs (PFOS and PFOA) have historically have been produced in the largest quantities (ATSDR 2018) and were both phased out in part due to the groundwater contamination affecting millions of its citizens (EPA 2017). Risk reduction measures on PFOA/ PFOS including bans are

in place throughout the world (China, Japan, Korea, Sweden, Russia, Australia etc.) (OECD 2021). The Canadian government has deemed PFOS, PFOA and LC-PFCAs, their salts and precursors toxic to the environment, persistent and bio accumulative (Longpré et al. 2020). Furthermore, PFOS, PFOA and LC-PFCAs (Perfluorocarboxylic acids) (and their salts and precursors) are also prohibited from manufacture, use, sale, offer for sale or import. More recent scientific evidence indicates that some replacement PFAS, which are being used in place of the already prohibited compounds, may also be associated with adverse environmental effects. These replacement PFASs include such compounds as PFBA, PFBS, PFPeA, PFHxA, and PFHpA, and are shorter chain compounds than their predecessors. Nevertheless, Longpré et al (2020) and Gewurtz et al (2019) suggested that current and past uses of any PFAS-containing products, as well as long-range transport deposition, may continue to contribute those substances the Canadian environment. In fact, Goodrow et al (2020) detected those shorter chain PFASs in the majority of surface water samples in the United States.

The objectives of this project were to assess the frequency of detection of PFASs in Canadian freshwaters, to quantify their concentrations, and to assess trends over time of both long and short chain PFASs. This PFAS monitoring work was intended to assess concentrations in a variety of ambient surface waters in the country, and not to target specific releases from industrial sources.

Methods

Monitoring strategy

Sampling sites for this study were selected to reflect a range of population densities across Canada and a focus was on areas where PFASs would be released from into the environment (Table 1 in Supplemental Information and Figure 1). Twenty-nine sampling sites across Canada were sampled between 2013 and 2020. Sampling sites were categorized in four groupings based on dominant activities occurring upstream in the watershed; reference, mixed development (mixture of urban, agricultural and/or forested areas), urban and municipal wastewater treatments plants (MWWTP) associated sites (Table 1 in supplementary information (SI)). Where sampling was associated with municipal wastewater effluent discharges, they were not collected at end of pipe, nor within the mixing zone. Those sites were well downstream of MWWTPs and represent ambient surface water conditions in areas that are influenced by wastewater discharges. The reference category only contained one site, mixed use had 11 sites, urban and MWWTP-associated had 9 and 8 sites respectively (Table 1 in SI). The reference site was chosen in an area devoid of all human disturbance except for atmospheric transport of contaminants.

Sample collection

Water samples were collected by wading into the waterbody or by using a sampling pole from the shoreline while a smaller fraction were obtained from the middle portion of bridges or from a boat. All samples were collected in 1L contaminant free (trace clean) wide mouth plastic bottles, immediately

placed in coolers packed with ice and delivered to the analytical laboratory within 24 – 48 hours post collection. Trace Clean bottles were achieved by following EPA cleaning procedures listed in the OSWER Directive 9240.0-05A "Specifications and Guidance for Contaminant-Free Sample Containers" (EPA 1992).

From 2012 to 2020, quality assurance and control samples comprised twelve field blanks and fifteen sets of triplicate samples. The field blank consisted of a 1L plastic bottle filled with ultra-pure water (using Millipore Sigma water purification systems), which was exposed for 20 seconds on site. Triplicate samples were obtained using a single 4L amber glass bottle, which was mixed gently and sub-sampled, into three 1L bottles.

Laboratory Analysis

Laboratory analyses were conducted by AXYS Analytical Services Ltd. in Sidney, BC, according to AXYS method MLA-060 and MLA-110b (AXYS 2020 and 2021 respectively) by liquid chromatography- tandem mass spectrometry (LC-MS/MS).

Water samples are extracted by solid phase extraction (SPE) using weak anion exchange cartridge (AXYS 2021). Sample extracts are then treated with carbon powder, spiked with recovery standards (7 individual standards) and analyzed by LC-MS/MS (AXYS 2021). Sample analysis is performed on an ultrahigh performance liquid chromatography reversed phase C18 column using a solvent gradient. The column is coupled to a triple quadrupole mass spectrometer run at unit mass resolution in the multiple reaction monitoring (MRM) in negative electrospray ionization mode.

A mid level calibration is also analyzed after every 12 hours (AXYS 2020). Sample concentrations are determined by the isotope dilution/ internal standard method quantification procedures (AXYS 2021). Sample detection limit are determined by converting the area equivalent to 3.0 times the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations (AXYS 2021). The MS acquisition rate was at least ten data points per peak (AXYS 2020).

Spiked reference samples and laboratory blank samples are also analyzed for each batch of samples collected for quality assurance and quality control issues. Each batch may contain up to twenty samples, one procedural blank and one spiked matrix sample (AXYS 2020). Samples were deemed acceptable if the recovery of the spiked samples ranged from 70 to 130% (AXYS 2020) and laboratory blanks were below the detection limit of the laboratory (range from <0.4 to <1.6 ng/ sample depending on the compound) (AXYS 2020). Spiked reference samples are processed alongside samples and used to demonstrate on-going method precision and recovery. All values used in this paper were deemed acceptable against both laboratories quality control specifications.

AXYS analytical laboratory is accredited by the Canadian Association for Laboratory Accreditation (CALA) to the standard ISO/IEC 17025 and it also holds analysis accreditation with the NELAC (National Environmental Laboratory Accreditation) Institute.

Statistical treatment

All statistical analyses were produced using Systat™ 13 and R (2013). Since a high proportion of the dataset of this study were under the detection limit of the laboratory (censored value), (Table 1) it is important to use statistical tools which include all values. Helsel (2005) describes how a mere substitution of the censored value by some fraction of the detection limit (DL) (such as $\frac{1}{2}$ DL) has resulted in inadequate summary statistics and may obscure patterns and trends in the data and suggests instead the use of non parametric methods to describe such datasets. The methods used to analyse this dataset are included in the non-detects and data analysis (NADA and NADA2) user-written package for R. The details of these methods are described in the books by Helsel (2005, 2012, 2020). The NADA package uses survival analysis methods to estimate descriptive statistics.

Helsel and Lee (2006) suggested that the censored maximum likelihood (MLE) method may be used when the dataset contain more than 50 detected observations to estimate summary statistics such as the median, mean and standard deviation. The medians depicted in Figure 1 were calculated using MLE in the NADA package. Censored box plots were created with NADA and the lower portions of the boxplots (below the reporting limit) are estimated using ROS (Helsel 2012). ROS is obtained by calculating a linear regression on the logarithmic of the uncensored data versus their normal scores, the order statistic of the normal distribution is equal to the rank of the observation where ranking accounts for censored data (Helsel 2012). Censored data were also used to calculate trend lines using the Arritts-Theil-Sen non parametric regression on log-normalized concentrations of the different PFASs using the cenken function of the NADA package (Helsel 2012).

The type of sampling site (mixed, urban and MWWTP-associated) and watershed areas (Atlantic Ocean, Great Lakes, Hudson Bay, Pacific Ocean) were tested using the “cen1way” command of the NADA package to determine if PFASs concentration varies depending on the type of waterbody sampled. This non-parametric test does not assume any normal distribution of the data and utilized both the censored and uncensored dataset. A post hoc pairwise comparison using the Peto-Peto test was also conducted to determine which pairs differed significantly.

Results And Discussion

Overall, 13 different PFAS chemicals were detected in 566 Canadian freshwater samples from 2013-2020. Concentration of PFASs ranged from below the detection limit of the laboratory to a maximum of 138 ng/L (for PFBS, Table 1). The median and standard deviations below were calculated using both censored and uncensored values for those compounds which contained enough detections; PFBA, PFHxA, PFOA, PFOA, PFHpA and PFPeA. The other ten compounds listed in Table 1 only had detection frequencies ranging from <1 to 18%. Such small frequency of detections does not permit the use of censored methods to calculate summary statistics. Therefore, the median and standard deviations for those compounds only included values reported over the detection limit of the laboratory.

The PFASs with the highest frequency of detections were PFBA followed closely by PFHxA and PFOA. PFOS was also detected in 43% of the samples (Table 1) and no samples were above the Canadian water quality guideline for PFOS of 6800 ng/L. Similar to the results of our study, MacInnis *et al* (2019) also detected a high frequency of detection for PFBA in the high arctic due to atmospheric deposition while Goodrow *et al* (2020) detected PFOA, PFHpA and PFPeA at all sampling sites in New Jersey. Wang *et al* (2019) reported PFBA as the dominant compounds detected in urban lakes and rivers in Beijing (China) which is similar to our results where PFBA had the highest detection frequency (Table 1). The study by Gewurtz *et al* (2019) also showed detection greater than 30% for the same six PFASs in the Canadian Great Lakes samples although that study also showed higher detections for PFNA, PFDA, PFUnA and PFDoA.

The subsequent result and discussion on temporal and spatial trends will focus on the six PFASs products, which occurred more frequently: PFBA, PFHxA, PFOA, PFOS, PFHpA and PFPeA (Table 1).

Table 1
Summary statistics of the PFAS compounds measured in Canadian freshwater sites.

Compound	Number of detections	% censored	Maximum (ng/L)	Median (ng/L)	Standard deviation (ng/L)
PFAS compounds with high detection frequencies					
PFBA	378	32	73	2.64	5.4
PFHxA	375	34	137	1.96	9.3
PFOA	350	38	24.4	1.52	4.2
PFOS	325	43	27.6	2.3	5.9
PFHpA	300	47	32.7	1.16	2.9
PFPeA	266	53	47.8	1.3	6.4
PFAS compounds with low detection frequencies					
PFHxS	102	82	24.4	2.5	5.3
PFBS	80	86	138	2.6	15.8
PFDA	70	88	10.7	2.2	2.5
PFNA	69	88	44.6	1.1	5.4
PFOSA	17	97	1.7	0.9	0.4
PFUnA	5	99	9.9	1.4	3.8
PFDoA	1	>99	1.4	1.4	1.4

Temporal analysis

Box plots using both censored and uncensored data were created for the 6 PFASs which had the highest detection frequencies (Figures 2a-f). The majority of values range from 0.2 ng/L to 5 ng/L with a few outliers above 50 ng/L (PFBA, PFHxA, Figures 2a and 2f). A visual analysis of the possible increasing or decreasing trends of figures 2a-f does not reveal any obvious patterns. However, the dataset contains 8 years of data and therefore is suitable to be analysed using trend analysis. Figure 2c clearly shows how the maximum value of PFOS in this study is well below the Canadian guideline of 6800 ng/L by two orders of magnitude.

Censored Kendall trends were performed on the six PFASs compounds that had the highest detection frequencies (Table 2). Table 2 below presents the results of these trends (slope, intercept Tau and p values). There was not enough data in each “seasons” to run any seasonal trend analysis. Apart from PFHxA, the other five compounds all had statistically significant trends although the direction of the trends varied by compounds (Table 2). From the Kendall calculations, PFBA, and PFPeA concentrations are increasing significantly in the years of this study while PFOS, PFOA and PFHpA concentrations are decreasing (Table 2).

The decreases in PFOS and PFOA concentrations are not surprising, as these compounds have been managed extensively in Canada since 2008 and 2010 respectively. Furthermore, these substances are also controlled through the Stockholm convention on Persistent Organic Pollutants. Similar decreasing trends in PFOS/ PFOA have been reported in other Canadian and international studies (Gewurtz et al 2019; Nguyen et al. 2019; Land et al 2018, Hong et al 2015). As for the significant decline in PFHpA in our study, Kirchgeorg et al (2013) also measured a significant decrease overtime of this compound in snow from the Alps and noted the decline was probably due to the change from longer to shorter chain PFASs.

The increase in PFBA and PFPeA might be attributed to an increase in the use and disposal of products containing these substances in lieu of the traditional PFOS/PFOA. An increase in PFBA was also detected in Great Lakes samples in the Gewurtz et al (2019) study while a significant increase in PFPeA was detected in MWWTP influent in Australia (Nguyen et al. 2019). Morales-McDevitt et al (2021) also suggest that the prevalence of PFBA in water samples in Bangladesh probably stems from the textile industry’s switch to shorter chain PFAS alternatives.

Urban streams in China and the United States also contained high detection of PFPeA and PFHxA and the concentrations were attributed to MWWTP, runoff from land use and landfill and not manufacturing (Moller et al. 2011; Bai and Sun 2021; Xu et al. 2021). A meta analysis of time series of PFASs across all media did not yield enough detections in the studies analysed for PFBA, PFHxA and PFPeA to determine an overall time series trend (Land et al. 2018).

Table 2
Censored Kendall trends results for PFAS at all sampling stations.

Compounds	Slope	Intercept	Tau	p value
PFBA	0.205278	-410.926	0.063596	0.02496
PFHpA	-0.10458	211.9609	-0.07095	0.011509
PFHxA	-0.03689	76.2428	-0.01523	0.587707
PFOS	-0.27462	556.0784	-0.08466	0.002574
PFOA	-0.165	334.142	-0.08167	0.003643
PFPeA	0.389608	-784.015	0.102524	0.000259

Spatial Analysis

Sampling sites and frequencies changed during the course of this study and this may influence the calculations of the previous trends per compound (Table 2). For example, sampling at mixed-used sites declined in the later years of this study. Careful consideration of the dataset revealed that there were five sites in particular that had been sampled for 6 to 8 years at a frequency ranging from four to seven occurrence per year. A subsequent trend analysis of those five sites (Highland Creek, Red River (at Selkirk), Taylor Creek, Wascana Creek (downstream of MWWTP) and St Lawrence River) was undertaken and is presented below. Censored Kendall trends were performed on the six PFASs compounds at those five sites, which had the highest frequency of sampling and resulted in 30 individual trend results. Of those 30 trend calculations, only three were statistically significant (Table 2 SI). There were two statistically significant increasing trends for PFPeA at Taylor and Wascana Creek (downstream) and a statistically significant decreasing trend for PFOS at Wascana Creek (downstream) (Table 2 SI).

The site at Red River did not yield any statistically significant trends. However, it is interesting to note that every single sample obtained at this site since 2014 contained a measurable value of PFBA while the majority of the concentrations reported for the other five main PFASs were below the detection limit of the laboratory. This also occurs for the St Lawrence site, which with the Red River, are the sites with the highest discharge volumes/watershed size of this study. This result may be explained by the results from the Gewurtz et al (2019) study which suggested that wet deposition is contributing to PFBA in Canadian freshwater.

The St Lawrence River site had the highest number of observations of all the sites of this study spread over 8 years of sampling. All of the trends calculated were non-significant (Table 2 SI). Comparing the results of this site to that of the other four sites in Table 2 SI it becomes evident that a vast majority of the samples obtained at this site contained a concentration less than the detection limit of the laboratory. Interestingly the substance PFBA that was seldom detected in 2014 and 2015 becomes prevalent in the last few years of sampling at this site. Since PFBA are both persistent and a short-chain PFAS it is likely

that the increase in concentration might be attributed to the replacement of longer chain PFOS/PFAS with PFBA. In a 2005-2008 study, Scott et al. (2009) did not measure any concentration of PFBA in 38 Canadian rivers including the very same site on the St Lawrence River. PFBA was also characterised a potential breakdown product of other in-use PFASs which would also support some of our results. (MDH 2017). PFBA are often the PFAS most frequently detected in air samples, snowpack, glacial melt water and surface waters (Kirchgeorg et al 2013, Kwok et al 2013, MacInnis et al. 2019 Muir et al 2019) in the high Arctic which gives indication that PFBA are uniformly distributed in the northern hemisphere due to long range transport.

The Highland Creek site did not yield any statistically significant trends. While PFOS and PFAS detections at this site were reported in approximately half of the samples, PFBA, PFHxA and PFPeA were detected in almost all of the samples obtained. Although the upward trend of PFPeA was statistically non-significant ($p=0.07$), the trend slope shows an increase that should be re-evaluated in the next few years to determine if the trend becomes statistically significant. The site at Taylor Creek did yield one statistically significant upward trend for PFPeA ($p=0.042$). Similarly, to Highland Creek, the vast majority of samples from this site had detectable concentrations even for PFOS and PFOA although none of the PFSA had a significant trend to report. Urban streams throughout the world have shown high detection frequencies of these PFASs mostly due to runoff from land and not necessarily PFAS manufacturing plants located in the watershed (Goodrow et al 2020, Bai and Sun 2021, Xu et al 2021).

The Wascana Creek site had two statistically significant trends (Table 2 SI). Of all the sites samples in this study, this is the location where WWTP discharge influence the natural environment the most. The sampling site on Wascana Creek is located approximately 8.5 km downstream of a MWWTP serving a population of over 190 000 (Table S1). The discharge of this river fluctuates from < 5 to $60 \text{ m}^3/\text{s}$ depending on rain, spring freshet. Wascana Creek is known to receive a high proportion of its flow from a wastewater treatment plant during dry spells (Waiser et al 2011). While it was expected that PFOS concentrations are decreasing over time due to the legislation in Canada, the statistically increasing concentration of PFPeA was novel. While PFPeA concentrations are mostly under the detection limit of the laboratory from 2013-2015, it becomes ubiquitous from 2016-2019. This might be a reflection in the change of PFAS compounds in industrial and commercial uses and its ultimate discharge to the MWWTP located upstream of the sampling site

PFASs as a function of land use type

All six of the PFAS chemicals had statistically significant different ($p<0.05$) concentrations between the categories of major land use types. The post hoc pairwise comparison (Peto-Peto) revealed that all pairs for all six PFASs were statistically different from each other. The censored box plots (Figures 3a-f) reveal an overall trend with 5 of the 6 PFASs having the lowest concentrations measured at mixed sites and the highest at urban sites. It is interesting to note that urban waterbodies had significantly higher concentrations than either MWWTP-associated sites or mixed use sites. This result indicates that most of the PFASs reaching surface waters could be attributed to weathering of material containing these PFASs,

urban runoff, and wet deposition rather than through wastewater discharge or direct industrial outputs. Similarly, both Wang et al (2019) and Bai et al. (2021) detected high frequencies of PFASs in urban streams not always associated with MWWTPs. Recently, Propp et al (2021) measure significant concentrations of PFAS in landfills across Ontario that had been closed for more than 30 years. This suggests that historic landfill sites may be contributing PFAS to groundwater and possibly to the urban sites sampled during the course of this study.

Comparison to other studies

PFASs have been measured in freshwater systems around the world. Most countries, including Canada, started monitoring for long chain PFASs such as PFOS/ PFOA before refocusing on short chain PFASs especially in the last decade. The majority of studies have sampled urban or MWWTP influenced water bodies to determine the concentrations of PFASs that might be attributed to runoff or industrial wastewaters (Table 3). In addition, there has been many studies conducted in the Arctic to determine the effects of long range transport of PFASs to an environment where sources of these compounds are minimal if present at all (Table 3).

In Canada, the results from past studies are mostly within the range of concentrations found within our study (Table 3) except for the results from D'Agostino and Maybury (2017). In the D'Agostino and Maybury (2017) study, the maximum concentrations of most compounds are well above those found in this study. However, this may be related to the inclusion of sites knowingly impacted by fire fighting foams. It is also interesting to note the ubiquitous measurements of PFPeA, PFHxA and PFBA in this study that were not always detected in past Canadian studies (Table 3). This might be a reflection of new uses of these products in some manufacturing processes. Direct comparison was possible for the following sites; Hamilton Harbour, Mimico Creek, Grand and Thames rivers. In general, PFSA concentrations at the four sites have increased slightly for the majority of compounds. Although none of the increases were more than an order of magnitude. Both PFHpA and PFHxA saw the largest increases at these four sites while PFOS/ PFOA had very similar concentrations in past and present studies. This could be a reflection of the use of new PFASs in the manufacturing process and the long persistence of PFOS/ PFOA in the environment.

In international studies, the majority of compounds had higher maximum concentrations than that of this study (Table 3). However some of those international studies were meant to record the effects of industrial outputs directly related to PFASs such as the 3M facility on the Mississippi River (Newsted et al 2017) or heavily industrialized waterways such as the River Rhine (Moller et al. 2010) (Table 3). Even some Arctic stream may contain similar PFASs concentrations to that of our study especially streams located near settlements and/or those influenced by precipitations linked to long-range atmospheric transport (Table 3).

Table 3

Maximum or *mean/median* (bold and italic in table) concentrations of PFASs in surface waters from other Canadian and international studies.

Sampling location (# of samples)	PFBA	PFHxA	PFOA	PFOS	PFHpA	PFPeA	Ref
Canada							
Great Lakes	4.9	3.9	5	7.4	2	4.1	1
Arctic lakes	1		<1		<0.5		2
Lake Ontario (1)			<3		<1		3
Mimico Creek (7)			14	22	3.3		3
Hamilton Hbr. (2)			7.2	13	1.4		3
Lake Superior (25)		0.8	1.23	0.7			4
WWTP effluent (3)	2.6	6.8	24		3.3	4.1	4
Ontario Rivers (6)		0.18	0.48	0.8	0.42		4
Ontario Rivers (20)		100	52	150	51	150	5
Grand River (1)		5.3	1.7	2.8	<2	5.8	5
Thames River (1)		3.9	1.4	5.7	<2	<5	5
United States							
Nevada brook (8)	nd	56.9	19.2	17.4	10.4	21.8	6
Nevada brook – downstream of WWTP (10)	26	187	65.5	38	32.5	170	6
Yadkin-Pee Dee river (Carolina) (5)	1.38	4.37	8.07	4.34	5.79	1.93	7
Mississippi; downstream of 3M facility (1)	650	32	220	136	75		8
New Jersey river; downstream of WWTP and/or landfill (11)	10	26	33.9	102	14.6	17.7	9
Europe							
Surface water – Arctic river (6)	1.2	0.3	0.3	0.29	0.2	1.1	10
Rhine River (36)	188	4.48	4.07	7.34	0.97	9.99	11
Ruhr River (3)	27.5	13.8	17.9	10.1	1.23	27.6	11
Other German rivers (8)	8.38	9.86	11.7	7.07	1.31	12.1	11
Lake (reference) (20)	1.37	0.13	1.78	0.23	0.42	<0.01	12

Sampling location (# of samples)	PFBA	PFHxA	PFOA	PFOS	PFHpA	PFPeA	Ref
Arctic Stream near settlement (3)	28.1	61.47	39.28	653	15.43	<0.02	12
Asia/ Australia							
Influent of a WWTP (9)	19	20	13	17	16	15	13
Rivers (7)	8.8	11.4	14.5	45.2	6	9.7	14
Urban lakes and rivers (350)	75.8	30	69	50.8	11.2	111	15
Surface water- landfill, urban (19)	110	26.24	100.1	54.78	30.3	53.18	16

Ref; References; ¹Gewurtz et al. 2019, ²MacInnis et al 2019, ³ Meyer et al 2011, ⁴ Scott et al. 2010, ⁵ D'agostino and Mabury. 2017, ⁶ Bai et al 2021, ⁷ Penland et al 2020, ⁸ Newsted et al 2017, ⁹ Goodrow et al 2020, ¹⁰ Kwok et al. 2013, ¹¹ Moller et al 2010, ¹² Skaar et al. 2019, ¹³ Nguyen et al 2019, ¹⁴ Allinson et al. 2019, ¹⁵ Wang et al 2019, ¹⁶ Xu et al 2021

Conclusion

This study has revealed that PFAS chemicals are found throughout freshwater systems in Canada. The main contributor of PFASs in our study were probably related to urban runoff and secondarily to MWWTPs. Concentrations of older PFASs, such as PFOS and PFOA are declining, likely due to regulatory measures in Canada and other countries, while some of the shorter chain PFASs are increasing, probably due to a combination of increased use and long range transport. Both Meyers et al (2012) and Gewurtz et al (2019) have suggested that sediment may play a larger role as a continual source of PFASs to surface water. It is suggested that the addition of sediment to surface water monitoring for PFSA would be beneficial to understand the different source of these compounds to the Canadian environment.

Declarations

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Statements & Declarations

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The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

References

1. Allinson M. Yamashita N. Taniyasu S. Yamazaki E. Allinson G. Occurrence of perfluoroalkyl substances in selected Victorian rivers and estuaries: An historical snapshot. *Heliyon* 5.
2. ATSDR. 2018. Toxicological profile for perfluoroalkyls. Draft for public comment. <https://www.atsdr.cdc.gov/toxprofiles/tp200.pdf>. Accessed. April 2021
3. AXYS . 2020. Analytical Procedure for the Analysis of Perfluoroalkyl Substances (PFAS) in Aqueous Samples and Solvent Extracts by LC-MS/MS. Summary of Method MLA-060 REV. 11 VER. 05.
4. AXYS . 2021. Analytical Procedure for the Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Samples, Solids, Tissues, AFFF Products, Blood/Serums and Solvent Extracts by LC-MS/MS Summary of Method MLA-110 REV. 02 VER. 11.
5. Bai X. Son Y. 2021. Perfluoroalkyl substances (PFAS) in surface water and sediments from two urban watersheds in Nevada, USA. *Sci. Tot. Env.* 751:
6. D'Agostino LA. Maybury SA. 2017. Certain Perfluoroalkyl and Polyfluoroalkyl Substances Associated with Aqueous Film Forming Foam Are Widespread in Canadian Surface Waters. *Env. Sci. Tech.* 51: 13603-13.
7. Environmental Protection Agency (EPA). 2009. Specifications and Guidance for Contaminant-Free Sample Containers. A540/R-93/051
8. Environmental Protection Agency (EPA). 2017. Technical Fact Sheet – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA). EPA 5050-F-17-001
9. Gewurtz S.B. Bradley L.E. Backus S. Dove A. McGoldrick D. Hung H. Dryfhout-clark H. 2019. Perfluoroalkyl Acids in Great Lakes Precipitation and Surface Water (2006–2018) Indicate Response to Phase-outs, Regulatory Action, and Variability in Fate and Transport Processes. *Env. Sci. Tech.* 53: 8543-52.
10. Goodrow SM. Ruppel B. Lippincott RL. Post GB. Procopio. 2020. Investigation of levels of perfluoroalkyl substances, surface water, sediment and fish tissue in New Jersey, USA. *Sci. Tot. Env.* 729.
11. Helsel D. 2005. Nondetects and data analysis: statistics for censored environmental data. Wiley, Hoboken
12. Helsel D. 2012 Statistics for censored environmental data using Minitab and R, 2nd edn. Wiley, Hoboken

13. Helsel D. Lee L. 2006) Analysis of environmental data with nondetects. In: Statistical methods for censored environmental data. ASA Workshop, Seattle, Washington. <https://www.practicalstatistics.com/nada/downloads.html>. Accessed May 2021.
14. Helsel D. 2020. Statistical methods in water resources. Techniques and methods 4-A3. Available at; <https://pubs.er.usgs.gov/publication/tm4A3>
15. Hong S, Khim Jong S, Wang T, Naile Jonathan E, Park J, Kwon B-O, Song Sung J, Ryu J, Codling G, Jones Paul D. 2015 Bioaccumulation characteristics of perfluoroalkyl acids (PFAAs) in coastal organisms from the west coast of South Korea. *Chemosphere*. 129:157–63.
16. Kirchgeorg T. Dreyer A. Gabrieli J. Kehrwald N. Sigl M Schwikowski M. Boutron C. Gambaro A. Barbante C. Ebinghaus R. 2013. Temporal variations of perfluoroalkyl substances and polybrominated diphenyl ethers in alpine snow. *Environ Pollut*. 178:367–74.
17. Kwok KY. , Yamazaki E. , Yamashita N. Taniyasu S. Murphy MB. Horii Y. Petrick G. Kallerborn R. Kannan K. Murano K. Lam PKS. 2013. Transport of Perfluoroalkyl substances (PFAS) from an arctic glacier to downstream locations: implications for sources, *Sci. Total Environ*. 447: 46-55.
18. Land M. deWit CA Bignert A. Cousins IT, Herzke D. Johansson J. Martin J. 2018. What is the effect of phasing out long-chain per- and polyfluoroalkyl substances on the concentrations of perfluoroalkyl acids and their precursors in the environment? A systematic review. *Env. Evidence*. 7(4):
19. Longpré D. Lorusso L. Levicki C. Carrier R. Cureton P. 2020. PFOS, PFOA, LC-PFCAS, and certain other PFAS: A focus on Canadian guidelines and guidance for contaminated sites. *Management. Env. Tech. Innovation* 18.
20. MacInnis JJ. Lehnher I. Muir DCG. Quinlan R. De Silva AO. 2019. Fate and transport of perfluoroalkyl substances from snowpacks into a lake in the High Arctic of Canada, *Sci. Total Environ*. 666 (2019) 414-422.
21. Meyer T. DeSilva AO. Spencer C. Wania F. 2011. Fate of perfluorinated carboxylates and sulfonates during snowmelt within an urban watershed. *Env. Sci. Tech*. 45: 8113-19.
22. Moller A. Ahrens L. Surm R. Westerveld J. van der Wielen F. Ebinghaus R. Voogt P. 2010. Distribution and sources of perfluoroalkyl substances (PFAS) in the River Rhine watershed. *Env. Poll*. 158: 3243-50.
23. Morales-McDevitt ME. Dunn M. Habib A. Vojta S. Becanova J. Lohmann. 2021. Poly- and perfluorinated alkyl substances in air and water from Dhaka, Bangladesh. *Env. Toxicol. Chem. Environmental Toxicology and Chemistry - Wiley Online Library*. Accessed November 29, 2021.
24. MDH. 2017. Contaminants and Minnesota Fish. www.health.state.mn.us/divs/eh/fish/faq.html. Accessed April 2021.
25. MDH. 2017. PFBA and drinking water. <https://www.health.state.mn.us/communities/environment/risk/docs/guidance/gw/pfbainfo.pdf>. Accessed. June 2021.
26. Muir D. Bossi R. Carlsson P. Evans M. De Silva A. Halsall C. Rauert C. Herzke D. Hung H. Letcher R. Rigt F. RoosA. 2019. Levels and trends of poly and perfluoroalkyl substances in the arctic environment – an update. *Emerging contaminants*. 5: 240-271.

27. Myers AL. Crozier PW. Helm PA. Brimacombe C. Furdui VI. Reiner EJ. Burniston D. Marvin CH. 2012. Fate, distribution, and contrasting temporal trends of perfluoroalkyl substances (PFASs) in Lake Ontario, Canada. *Env. Intl.* 44:92-99.
28. Newsted JL. Halem R. Hohenstein G. Lange C. Ellefson M. Reagen W. Wolf S. 2017. Spatial and temporal trends of poly- and perfluoroalkyl substances in fish fillets and water collected from pool 2 of the Upper Mississippi River. *Env. Toxicol. Chem.* 36(11): 3138-47
29. Nguyen HT. Kaserzon SL. Thai PK. Vijayasathya S. Braunig J. Crosbie ND. Bignert A. Mueller JF. 2019. Temporal trends of per- and polyfluoroalkyl substances (PFAS) in the influent of two of the largest wastewater treatment plants in Australia. *Emerging contaminants*. 5: 211-18.
30. OECD, Organisation for Economic Co-operation and Development. 2013. OECD/UNEP Global PFC Group, Synthesis paper on per- and polyfluorinated chemicals (PFCs), Environment, Health and Safety, Environment Directorate, OECD.
31. OECD. 2021. OECD portal on perfluorinated chemicals. Available from: http://www.oecd.org/site/0,3407,en_21571361_44787844_1_1_1_1_1,00.Html (Accessed May 27, 2021).
32. Penland TN. Cope WG. Kwak TJ. Strynar MJ. Grieshaber CA. Heise RJ. Sessions FW. 2020. Trophodynamics of Per- and Polyfluoroalkyl Substances in the Food Web of a Large Atlantic Slope River. *Environ. Sci. Tech.* 54: 6800-11.
33. Propp VR. DeSilva AO. Spencer C. Brown SJ. Catingan SD. Smith JE. Roy JW. 2021. Organic contaminants of emerging concern in leachate of historic municipal landfills. *Env. Poll.* 276: 1-12.
34. Scott BF. Spencer C. Lopez E. Muir DCG. 2009. Perfluorinated Alkyl Acid Concentrations in Canadian Rivers and Creeks. *Water Qual. Res. J. Canada.* 44(3): 263-277.
35. Scott BF. De Silva AO. Spencer C. Lopez E. Backus S. Muir DCG. 2010. Perfluoroalkyl acids in Lake Superior water: Trends and sources. *J. Great Lakes. Res.* 36: 277-284.
36. Skaar JS. Raeder EM. Lyche JL. Ahrens L. Kallenborn. 2019. Elucidation of contamination sources for poly- and perfluoroalkyl substances (PFASs) on Svalbard (Norwegian Arctic). *Env. Sci. Poll Res.* 26:7356-63.
37. Waiser MJ. Humphris D. Tumber V. Holm J. 2011. Effluent-Dominated Streams. Part 2: Presence and Possible Effects of Pharmaceuticals and Personal Care Products in Wascana Creek, Saskatchewan, Canada. *Env. Toxicol. Chem.* 30(2): 508-19.
38. Wang Y. Shi Y. Cai Y. 2019. Spatial distribution, seasonal variation and risks of legacy and emerging per- and polyfluoroalkyl substances in urban surface water in Beijing, China. *Sci. Tot. Env.* 673: 177-83.
39. Xu C. Liu Z. Song X. Ding X. Dind D. 2021. Legacy and emerging per- and polyfluoroalkyl substances (PFASs) in multi-media around a landfill in China: Implications for the usage of PFASs alternatives. *Sci. tot. Env.* 751.

Figures

Figure 1

PFASs sampling locations within each ocean area watersheds of Canada

Figure 2

a-f. Boxplots of the most frequently detected main PFASs measured in the Canadian surface waters from 2013-2020. 2a; PFBA, 2b; PFPeA, 2c; PFOS, 2d: PFOA, 2e; PFHpA and 2f; PFHxA.

Figure 3

a-f. Boxplots of the main PFASs measured in the Canadian surface waters as a function of the type of land use type (mixed-use, urban and MWWTP-associated).

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