



High levels, partitioning and fish consumption based water guidelines of perfluoroalkyl acids downstream of a former firefighting training facility in Canada



Satyendra P. Bhavsar^{a,b,*}, Craig Fowler^c, Sarah Day^c, Steve Petro^a, Nilima Gandhi^b, Sarah B. Gewurtz^b, Chunyan Hao^a, Xiaoming Zhao^a, Ken G. Drouillard^b, Dave Morse^a

^a Ontario Ministry of the Environment and Climate Change, 125 Resources Road, Toronto, ON M9P 3V6, Canada

^b Great Lakes Institute for Environmental Research, University of Windsor, 401 Sunset Avenue, Windsor, ON N9B 3P4, Canada

^c Ontario Ministry of the Environment and Climate Change, 119 King Street West, 9th Floor, Hamilton, ON L8P 4Y7, Canada

ARTICLE INFO

Article history:

Received 30 January 2016

Received in revised form 17 May 2016

Accepted 23 May 2016

Available online 11 June 2016

Keywords:

Perfluoroalkyl acids PFAAs

Perfluorooctane sulfonic acid PFOS

Firefighting

Guideline

Fish advisory

Worldwide

ABSTRACT

High levels of perfluoroalkyl acids (PFAAs), especially perfluorooctane sulfonic acid (PFOS), have been observed at locations in/around/downstream of the sites where PFOS-based firefighting foam was used repeatedly for a prolonged period. In this study, we conducted a detailed investigation of PFAA contamination in the Lake Niapenco area in Ontario, Canada, where among the highest ever reported levels of PFOS were recently measured in amphipods, fish and snapping turtle plasma. Levels and distribution of PFAAs in water, sediment and fish samples collected from the area varied widely. An upstream pond beside a former firefighting training area (FFTA) was confirmed as the source of PFAAs even 20 years after the last use of the foam at the FFTA. Recent PFOS concentration in water (~60 ng/L) at Lake Niapenco, about 14 km downstream of the pond, was still 3–7× higher than the background levels. For PFOS, Log K_D ranged 1.3–2.5 (mean ± SE: 1.7 ± 0.1), Log BAFs ranged 2.4–4.7 (3.4 ± 0.05), and Log BSAFs ranged 0.7–2.9 (1.7 ± 0.05). Some fish species-specific differences in BAF and BSAF were observed. At Log BAF of 4.7, fish PFOS levels at Lake Niapenco could reach 15,000 ng/g, 100× greater than a “do not eat” advisory benchmark, without exceeding the current drinking water guideline of 300 ng/L. A fish consumption based water guideline was estimated at 1–15 ng/L, which is likely applicable worldwide given that the Log BAFs observed in this study were comparable to those previously reported in the literature. It appears that PFAA in the downstream waters increased between 2011 and 2015; however, further monitoring is required to confirm this trend.

Crown Copyright © 2016 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Perfluoroalkyl acids (PFAAs) and their precursors have been used since the 1950s in diverse industrial and consumer products due to their unique hydrophobic and lipophobic properties (Lau et al., 2007). While their chemical and thermal stability make them ideal for many applications, they also make them highly persistent in the environment (Lau et al., 2007). Studies conducted since 2001 have described widespread presence of PFAAs in a variety of media even at remote locations, as well as a variety of adverse effects on health of wildlife and humans (Giesy and Kannan, 2001; Lau et al., 2007). In response to growing concern about the persistent, bioaccumulative and toxic (PBT) nature of perfluorooctane sulfonic acid (PFOS; the most studied PFAA) and its global presence, PFOS was voluntarily phased out by 3 M, the major

manufacturer, in 2002 (Lau et al., 2007). In 2009, PFOS, its salts and perfluorooctane sulfonyl fluoride were added to the Stockholm Convention on Persistent Organic Pollutants, a global treaty to protect human health and the environment from persistent organic pollutants (POPs) (UNEP, 2009).

One of the uses of PFOS was as an active ingredient in aqueous film-forming foam (AFFF) to fight large-scale fires involving hydrocarbons. Although a non-repetitive release of PFOS-based AFFF, such as accidental or single use discharge, can result in extremely high (10^3 – 10^6 ng/L) environmental levels of PFOS on a short term basis, the receiving water concentrations typically decline by more than three orders of magnitude within months (Awad et al., 2011; Kwadijk et al., 2014; Moody et al., 2002). However, elevated levels of PFOS can be found in the downstream water, sediment and fish even after a decade (Awad et al., 2011). At locations in/around/downstream of the sites where PFOS-based AFFF was used repeatedly and for a prolonged period, such as firefighting training areas (FTTAs), the persistent nature of the chemical group has resulted in continued high environmental levels long after. For example, PFOS concentrations as high as 10^3 – 10^6 ng/L range have

* Corresponding author at: Ontario Ministry of the Environment and Climate Change, 125 Resources Road, Toronto, ON M9P 3V6, Canada.

E-mail addresses: s.bhavsar@utoronto.ca, satyendra.bhavsar@ontario.ca (S.P. Bhavsar).

been measured in ground water around FFTAs at U.S. Air Force Bases years after known last use of AFFF (Moody et al., 2003; Schultz et al., 2004).

Recently, PFOS concentrations among the highest ever reported worldwide were measured in water, amphipods, fish and snapping turtle plasma collected from the Lake Niapenco area, a rural site in southern Ontario, Canada (de Solla et al., 2012; Gewurtz et al., 2014). As a result, restrictive fish consumption advisories were issued to protect the health of humans consuming fish (OMOEC, 2015). It was hypothesized that Hamilton International Airport had resulted in the high PFOS concentrations without knowledge of a known spill or use of AFFF at the airport (de Solla et al., 2012). Alternatively, a landfill site, which is located downstream of the Hamilton International Airport and was closed in 1980, could be a source of PFOS to the environment (Huset et al., 2011; Li et al., 2012). Given that a direct link between the elevated PFOS concentrations and the Hamilton International Airport was lacking, it was important to properly investigate the source and extent of contamination to aid in enhancing our understanding of this problem, which is global in nature (Das et al., 2015; Filipovic et al., 2015).

This study was initiated to examine if the previously hypothesized source (Hamilton International Airport) or any other sources could be systematically linked to the high levels of PFOS observed in the Lake Niapenco area. Water, surface sediment and sediment core samples were collected to locate the source(s), understand the activities contributing to the PFAA contamination problem, and delineate the extent of the contamination in the area. A short-term 4-year temporal trend was derived based on the sampling events conducted in 2011 and 2015. Using widely varying PFAA measurements, this study also reports field-based sediment/water distribution coefficients (K_D), bioaccumulation factors (BAF), and biota/sediment accumulation factors (BSAF), which are useful in understanding PFAA behavior in aquatic systems, applying environmental models and verifying laboratory derived values. Using the bioaccumulation factors, a fish consumption based guideline for PFOS in water was derived for the protection of human health.

2. Method

2.1. Study area

The study focused on the upper Welland River area in the Niagara Region of southern Ontario, Canada (Fig. 1). Lake Niapenco (also

known as Binbrook Reservoir), is located in the upper Welland River system and is where environmental concentrations of PFOS including in fish are among the highest ever reported worldwide (de Solla et al., 2012; Gewurtz et al., 2014). The Welland River flows from its headwaters south of the City of Hamilton, Ontario, drains an area of 880 km², and runs into the Niagara River near Niagara Falls, Ontario. The land around the upper Welland River and Lake Niapenco is largely agricultural and includes some residential. There are no waste water treatment plant discharges to the lake and there is virtually no industry nearby. As such, elevated PFAAs would not be expected in this area based on the land use (Gewurtz et al., 2013; Gewurtz et al., 2009).

2.2. Sample collection

Sediment samples were collected in 2010 from 7 locations in the study area (sites 1, 4, 5, 7, 8, 11, 13; Fig. 1). The results (discussed later) identified a drainage pond beside the firefighting training area (FFTA-Pond) on the Hamilton International Airport property as a potentially major source of the downstream PFAA contamination. In 2011, sediment samples from 9 more sites and water samples from all 16 sites (Fig. 1) were collected to investigate if any other source(s) is contributing to the contamination. The 16 sampling sites included locations upstream of the airport, FFTA-Pond, ditches/streams/river downstream of the FFTA and airport area, and Lake Niapenco (Fig. 1). Site 1 was the most upstream sampling location in the Welland River watershed and can be considered background. Site 2 was in the adjacent Twenty Mile Creek watershed. Site 14 was downstream of both the airport and closed landfill property. Field duplicate and blank samples were collected. Twelve of the 16 sites were revisited in July 2015, and water samples were collected in triplicates to examine mid-term (4 year) trends and environmental variability.

Water was collected as single grab samples in 500 mL poly-ethylene terephthalate (PET) bottles from just below the water surface at the center of the stream where possible and using a water sampling pole where required. Sample bottles were rinsed three times with sample water before collecting a sample. Sediment samples were a composite of three or more grab samples collected from the top 5–10 cm. Samples from the locations 11, 13 and 15 were collected using a sediment dredge Ponar, and other locations were sampled using a stainless steel mixing spoon. In addition to the defined 16 sites, surface sediment grab samples

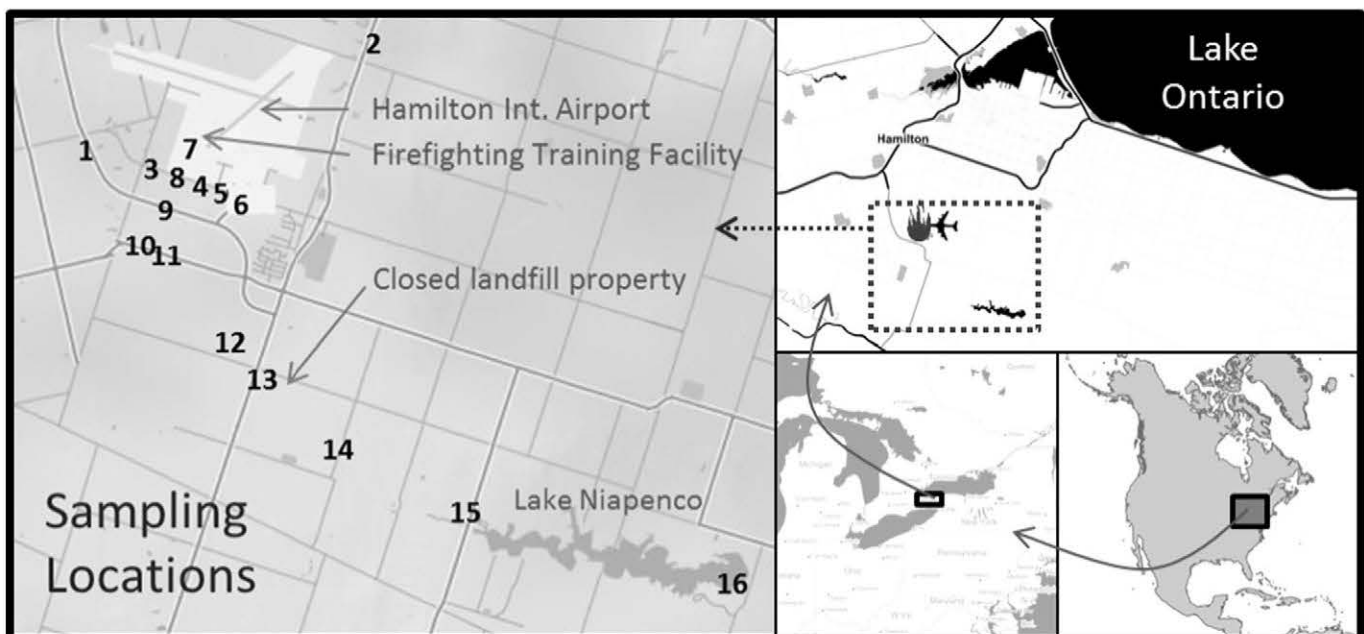


Fig. 1. Map of sampling locations around the firefighting training facility on the Hamilton International Airport (Ontario, Canada) property and Lake Niapenco area.

were also collected from two locations in Lake Niapenco, one closer to the middle and the other near the outlet. The samples were homogenized in a stainless steel pan and placed in 500 mL PET bottles. A duplicate sample was also collected.

In addition, 9 sediment cores were collected in 2011 from Lake Niapenco, a potential depository of washed off sediments from upstream locations including ditches exiting the airport. The cores were collected from different locations throughout the lake using a sediment corer, and were sliced at 1 cm intervals. Samples collected from the top 10 cm representing greater than half a century time span (discussed later) were analyzed for the PFAA content.

The water and sediment samples were stored in a cooler during transport to the OMOECC laboratory in Toronto, and were refrigerated at 5–6 °C until analysis.

2.3. Analytical details

2.3.1. PFAA analysis

The analytical method is described in detail in the supporting information and summarized here. The liquid chromatography-tandem mass spectrometric (LC-MS/MS) analyses of PFAAs were performed at the OMOECC laboratories in Toronto. Native and isotopically-labeled PFAA standards were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Water samples or sediment sample extracts were prepared to a solvent mixture of 50:50 methanol–water for instrument analysis performed on an Agilent 1100 series liquid chromatography system (Mississauga, ON, Canada) coupled to an SCIEX 4000QTRAP® mass spectrometer (Concord, ON, Canada). The analytes were separated on a 50 mm × 2.1 mm Genesis C18 column (Grace Discovery Science, Deerfield, IL, USA) using gradient elution. Mass spectrometric detection was achieved using multiple reaction monitoring (MRM) in negative electrospray ionization mode. Multi-isotope calibration was established to quantify the target analytes where isotopically-labeled $^{13}\text{C}_4$ -PFOS, $^{13}\text{C}_2$ -PFOA, $^{13}\text{C}_5$ -PFNA, $^{13}\text{C}_2$ -PFDA, and $^{13}\text{C}_2$ -PFDoA were used as internal standards for PFHxS/PFOS/PFDS/PFOA, PFHpA/PFOA/ $^{13}\text{C}_4$ -PFOA (surrogate), PFNA, PFDA/PFUa, and PFDoA/PFTeA, respectively.

2.3.2. Pb-210 dating

The Pb-210 method was used to determine the accumulation rate of sediments in Lake Niapenco and the age of sediment at depths in the sediment columns. Sediment samples collected at 1 cm interval for

two of the 9 sediment cores were analyzed for Pb-210. Both Slope Regression and Constant Rate of Supply (CRS) models were used to increase confidence in the findings.

3. Results

3.1. Water

The levels of PFAAs in water samples from the 16 locations varied by as much as four orders of magnitude, as presented in Figs. 2 and S1 and Table S2. Overall, PFAA levels were generally low upstream of the airport, were highest at the FFTA-Pond, and exponentially declined downstream of the pond. PFOS and PFHxS were two major PFAAs present with concentrations of 49,000 and 19,000 ng/L at the FFTA-Pond, respectively. Their levels declined by approximately 80%, 88% and >99% at the three (about 0.5, 1.1 and 1.7 km) downstream locations in the ditch draining the pond, respectively. The PFHxS levels (~50 ng/L) at 14 km downstream in Lake Niapenco, the first major depository basin downstream of the airport, were only slightly elevated compared to site 1 upstream of the airport (background). However, PFOS levels at Lake Niapenco (~60 ng/L) were still about 3–7× higher than the background levels.

The levels of PFDS, PFUnA and PFDoA were below the detection limits for all sites, except barely detected PFUnA at the FFTA-Pond. PFOSA was detected at only three locations: the FFTA-Pond and two just downstream sites in the ditch draining the pond (i.e., sites 7, 8, 9; within 1 km of the pond). Similar to PFOSA, PFHpA, PFNA and PFDA were elevated at the three sites (7–9), but then declined to the background levels observed at the most upstream site. PFOA was also high (4700 ng/L) at the pond and two just downstream sites (1100 and 630 ng/L, respectively), but declined to 12–13 ng/L at Lake Niapenco. These PFOA concentrations at Lake Niapenco (12–13 ng/L) were greater than the background, which was below detection levels (<5 ng/L).

In the tributaries along the southern boundary of the airport (sites 4, 5 and 6), water concentrations of PFAAs also decreased with distance from the FFTA-Pond and were near background levels at site 6. However, the sites 4, 5 and 6 were not connected to the ditch draining the FFTA-Pond. As such, elevated levels of PFOS, PFHxS, PFOA, and to certain extent, PFHpA and PFNA at site 4 (another ditch draining a different area of the airport) were unexpected.

The site 3 (tributary at Glanaster Road) captures runoff from the western boundary of the airport and had a PFOS concentration in

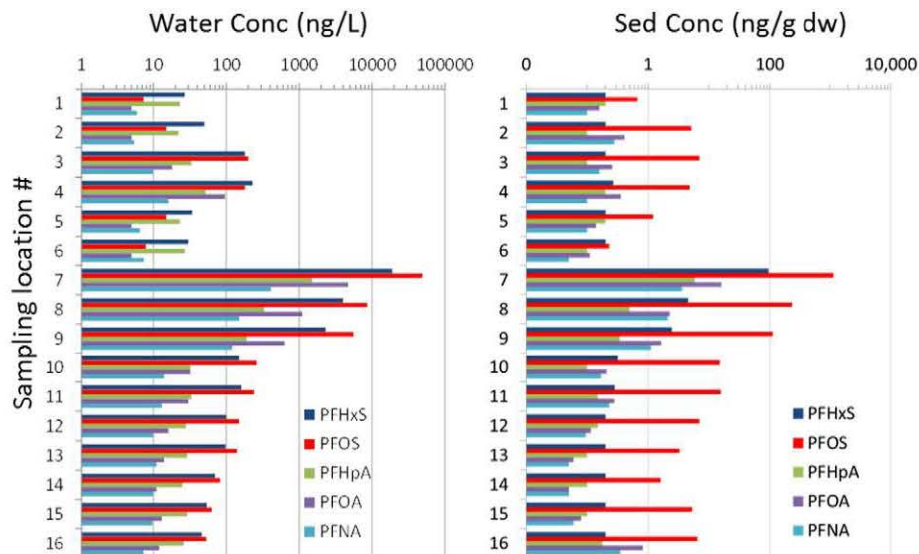


Fig. 2. Concentrations of major PFAAs (logarithmic scale) in water (ng/L) samples collected in 2011, and surface sediments collected in 2010/2011/2015 (ng/g dw; average; see Table S3 for sample details).

water of 200 ng/L, which is comparable to the concentrations about 1.7 km downstream of the FFTA-Pond in the ditch draining the pond. Concentrations are higher than background and indicate that surface water drainage from the western property boundary may be contributing PFOS from the FFTA, but at lower concentrations than the southern property boundary along the sites 8–10. The 2011 PFAA water concentrations at sampling site 2 (Upper James St), in the adjacent Twenty Mile Creek watershed, were comparable to the background levels.

3.2. Surface sediments

The sediment measurements followed the same spatial pattern observed for the water samples. The PFAA levels were highest at the FFTA-Pond and declined exponentially at the downstream sites (Table S3). Almost all of the PFAAs measured were above the detection limits at the FFTA-Pond; however, only PFOS was above the background levels at site 10, about 1.7 km downstream of the FFTA-Pond (Table S3).

The average concentrations of PFOS were 1150 ng/g dw at the FFTA-Pond, declined to about 15 ng/g dw at site 10, and then ranged from 2–7 ng/g dw in the vicinity of Lake Niapenco (sites 12–16) (Fig. 2, Table S3). PFOS concentrations in the two surface sediment samples collected from Lake Niapenco were 2.5 and 3.5 ng/g dw (Table S3). Overall, these PFOS levels at the downstream sites were still above the background levels of about 1 ng/g dw (site 1) (Fig. 2, Table S3). Analogous to the water measurements, levels of PFOS at sites 2, 3 and 4 were above background at 5.1, 6.9 and 4.8 ng/g dw, respectively (Fig. 2, Table S3).

3.3. Sediment cores

Similar to the sediment grab samples, PFOS was the predominant PFAA in all 1-cm slices of the 9 sediment cores and typically contributed 90–96% to the \sum PFAAs measured (Table S4). PFOA was the only other PFAA consistently detected in the sediment core subsamples and represented about 5–8% of \sum PFAAs (e.g., Table S5). There were also minor detections of PFNA (five cores near inlet), PFOSA (cores near middle and outlet) and PFUNA (two cores near outlet) (Table S5).

The concentrations of PFOS were marginally higher in sediment cores collected closer to the inlet of the lake (Fig. 3), which would be a

result of deposition of PFOS contaminated sediments drained from the FFTA-Pond. PFOS concentrations at different depths were generally similar but showed a slight increasing trend from the older to more recently deposited sediments (Fig. 3, Tables S4). Average PFOS concentrations ranged from 2.1 ng/g (6–7 cm) to 3.2 ng/g (4–5 cm) (Tables S4, S5). These PFOS levels were similar to the two surface grab samples (2.5–3.5 ng/g). Although the average PFOS concentration was highest for the 4–5 cm section, the value was largely influenced by a measurement of 8.9 ng/g dw at the sampling location close to the inlet of Lake Niapenco (Tables S4, S5).

The Pb-210 analysis of two sediment cores collected from the inlet and center of the Lake Niapenco showed an exponential drop in the Pb-210 activity as a function of depth in the cores. The surface activity was $\sim 9.35\times$ the estimated background Pb-210 level of about 1.27 DPM/g (lowest observed activity of the cores). The results from both Pb-210 statistical models were similar indicating average sedimentation rate of about 0.18 g/cm²/yr. The top 5 and 10 cm of the cores approximately represented 22–26 and 50–54 years, respectively (Fig. 3).

3.4. 2015 vs 2011 Water

The triplicate water samples collected in 2015 highlighted minimal PFOS variability at each sampling site (Coefficient of Variation 0–61%; Fig. 4, Table S6). All 12 of the 16 water sampling sites of 2011 that were revisited in 2015 showed similar spatial pattern of PFOS with the highest concentrations at the FFTA-Pond (110,000–140,000 ng/L; Fig. 4, Table S6). There was a 30% decrease at the most upstream, background site (# 1) and site 11 (Fig. 4). It appears that PFOS at the FFTA-Pond more than doubled (increase by about 160%) in four years (Fig. 4); however, the measured values could be within a high spatial variability that may exist at this pond. Increases in PFOS water concentrations at the other sites (except site 2) typically ranged from 20–90%, with about 30–40% increase at Lake Niapenco (Fig. 4). The highest increase of almost six fold (15 to 87 ng/L) was observed at site 2 (Fig. 4), which is in an adjacent watershed.

In contrast to PFOS, PFHxS showed declines between 2011 and 2015 at the upstream sites, an increase by about 50% at the FFTA-Pond, and mostly (20–100%) increases downstream in the vicinity of Lake

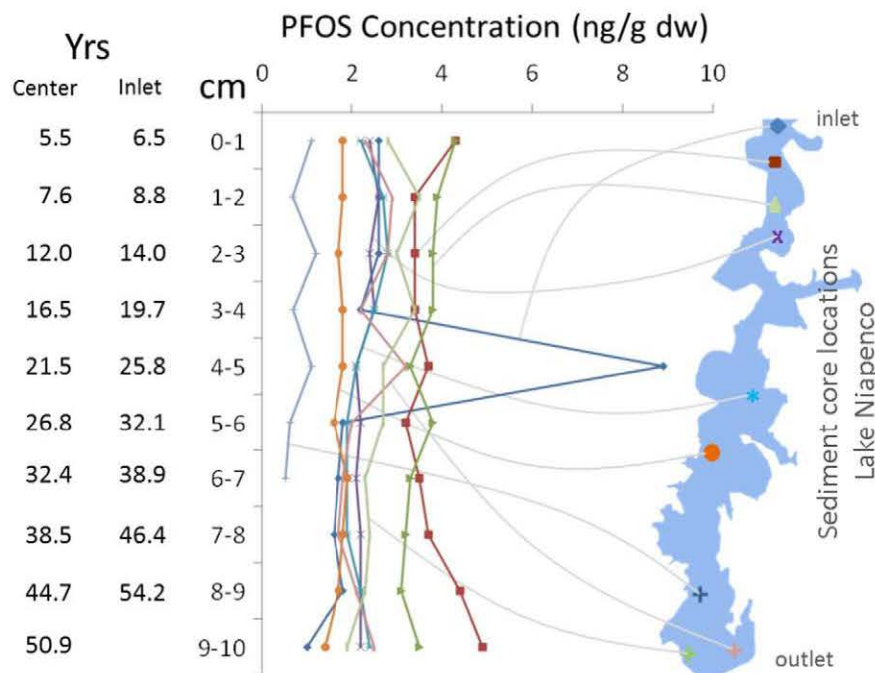


Fig. 3. Concentrations (ng/g dw) of PFOS and time period for various depths of the sediment cores collected from Lake Niapenco in 2011. Note: only two sediment cores collected from the center and inlet of the lake were dated.

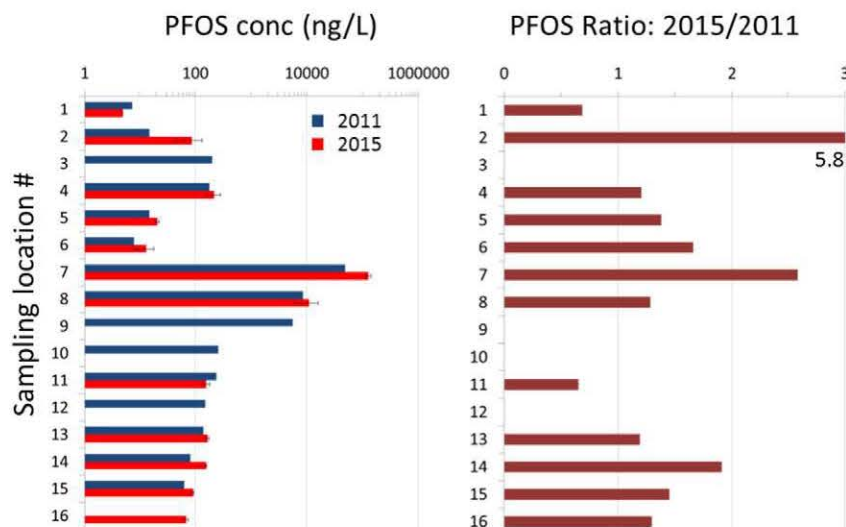


Fig. 4. Comparison of PFOS concentrations (ng/L; logarithmic scale) in water samples collected in 2011 and 2015. Whiskers present standard deviations for the 2015 samples.

Niapenco (except for the outlet of Lake Niapenco, where 2011 and 2015 measurement were similar – 46 and 43 ng/L, respectively) (Fig. S3a). Although the spatial patterns for PFOA in the 2011 and 2015 samples were slightly different from PFOS and PFHxS, mostly increases in the range of 40–220% were observed downstream of the FFTA-Pond, including increases of about 40–120% at Lake Niapenco (Fig. S3b). Similarly, increases (30–60%) in concentrations of PFHpA were also generally observed for the locations downstream of the FFTA-Pond (Fig. S3c). The comparison of the 2011 and 2015 water PFAA measurements should be viewed with caution due to differences in antecedent precipitation between the two sampling events as discussed later.

3.5. Environmental partitioning

Field-based sediment/water distribution coefficients (K_D , L/kg) were calculated as ratios of concentrations in sediment to water using measured values for the 16 sites (Table 1). Using the measured concentrations of three major PFAAs (i.e., PFOS, PFOA and PFHxS) in Lake Niapenco surface sediments and water from this study and a total of 100 samples of 10 sport fish species from our companion, parallel study already published (Gewurtz et al., 2014), field-derived bioaccumulation factors (BAF, C_{fish}/C_{water} , L/kg) and biota–sediment accumulation factors (BSAF, $C_{fish}/C_{sediment}$, kg/kg) were calculated (Table 1). Both BSAF and BAF are simple, two-box empirical models, and depend on ecosystem parameters (e.g., trophic level, diet of the organisms, and chemical distribution between the sediment and water) (e.g., citations in Bhavsar et al., 2010). Fish generally take up some portion of contaminants from both sediment and water. Although technically BSAFs and BAFs do not consider the contaminant burden of an organism that originates from pelagic and benthic exposures, respectively, both exposures are typically implicitly accounted for in the empirical relationships. As such, simple field-derived BSAFs and BAFs allow estimation of chemical residues in fish from a measured chemical concentration in the reference sediment and water, respectively, and vice versa.

Log K_D ranged 1.3–2.5 (mean \pm SE: 1.7 ± 0.1) for PFOS, 0.3–1.9 (1.0 ± 0.1) for PFOA, and 0.0–0.9 (0.4 ± 0.1) for PFHxS (Table 1). Overall Log BAFs ranged 2.4–4.7 (3.4 ± 0.05) for PFOS, 0.9–1.8 (1.1 ± 0.02) for PFOA, and 0.6–2.7 (0.9 ± 0.04) for PFHxS (Table 1). Overall Log BSAFs ranged 0.7–2.9 (1.7 ± 0.05) for PFOS, and –0.1–0.8 (0.0 ± 0.02) for PFOA (Table 1). Some fish species-specific differences in BAF and BSAF were observed (Table 1). As shown in Fig. S4, BAF and BSAF for PFOS were significantly greater for Common Carp, Largemouth Bass and Smallmouth Bass compared to Black Crappie, Brown Bullhead, Northern Pike, Pumpkinseed, White Crappie and Yellow Perch

($p < 0.05$; ANOVA; post-hoc Tukey Test), while Channel Catfish did not differ from any other species ($p > 0.05$; ANOVA; post-hoc Tukey Test).

4. Discussion

4.1. Source track down

A strong spatial pattern in PFAA levels in the water and sediment samples collected from the upper Welland River – Lake Niapenco area was observed. The levels were typically below the detection limits or low at the upstream sites, highest at the FFTA-Pond on the airport property, and declined exponentially at the downstream sites. PFOS was the predominant PFAAs measured and was elevated even at Lake Niapenco, 14 km downstream of the FFTA-Pond. A Principal Component Analysis (PCA) conducted using statistical software R also indicated site specific differences in the abundances of three major PFAAs observed (i.e., PFOS, PFOA and PFHxS) (Fig. S5). The PFAA contamination in the area was accidentally discovered by de Solla et al. (2012), who also reported a similar spatial trend as observed in this study. The water concentrations of PFOS reported by de Solla et al. (2012) for 2010 and measured in this study for 2011 generally agree well, and any differences can be attributed to inter-laboratory differences and/or environmental variability.

Compared to site 13, there was no increase in the PFAA levels at site 14, which was downstream of the closed landfill property. These results show that the closed landfill property has no measurable contribution to the PFAA contamination in the area. Depth profile of the PFAAs in the Lake Niapenco sediment cores showed highest PFOS concentration of about 9 ng/g dw at 4–5 cm depth near the inlet of Lake Niapenco (Fig. 3, Table S4). The age profile from the Pb-210 analysis for the core indicated accumulation of this sediment layer about 26 years before the collection of the sediment core in 2011 (Fig. 3). This peak PFOS concentration in the sediment core suggest a time period of the mid-1980s. However, PFOS can migrate down the sediment core through the pore water (Myers et al., 2012); as such, year of peak concentrations could be a little more recent (e.g., late-1980s to early-1990s). This observation matches well with the history of 15,000 L PFOS-based AFFF sprayed each year at the FFTA on the Hamilton Airport property between 1985 and 1994 (citations in Gewurtz et al., 2014). Accordingly, this study confirms that historical firefighting training involving PFOS-based AFFF is the source of the high levels of PFAAs, especially PFOS, found at the downstream sites, with the FFTA-Pond beside the FFTA acting as an on-going source to downstream waters. The FFTA was recently closed

Table 1
Sediment/water distribution coefficient (K_D), bioaccumulation factor (BAF), and biota-sediment accumulation factors (BSAF). n: number of samples; min: minimum; max: maximum; SD: standard deviation; SE: standard error of mean. Most surface sediment concentrations of PFHxS were below the detection limits; as such, K_D and Log BSAF values were not calculated.

	n	PFOS			PFOA			PFHxS		
		Min-max	Mean/median	SD/SE	Min-max	Mean/median	SD/SE	Min-max	Mean/median	SD/SE
Log K_D (L/kg)	16	1.3–2.5	1.7/1.6	0.3/0.1	0.3–1.9	1.0/0.8	0.5/0.1			
Log BAF (L/kg)										
All species	100	2.4–4.7	3.4/3.6	0.5/0.05	0.9–1.8	1.1/1.0	0.2/0.02	0.6–2.7	0.9/0.6	0.4/0.04
Black Crappie	13	2.6–3.7	3.2/3.2	0.4/0.1	0.9–1.8	1.4/1.3	0.3/0.1	0.6–1.5	0.9/0.6	0.4/0.1
Brown Bullhead	3	2.7–3.1	2.9/3.0	0.2/0.1	0.9–1.1	1.0/1.0	0.1/0.1	0.6–0.6	0.6/0.6	0.0/0.0
Channel Catfish	7	2.9–3.9	3.5/3.5	0.4/0.2	0.9–1.2	1.0/1.0	0.1/0.0	0.6–0.6	0.6/0.6	0.0/0.0
Common Carp	25	3.1–4.7	3.9/3.7	0.4/0.1	0.9–1.5	1.1/1.1	0.2/0.0	0.6–2.7	1.3/1.0	0.7/0.1
Largemouth Bass	16	3.5–3.9	3.7/3.7	0.1/0.0	0.9–1.0	0.9/0.9	0.0/0.0	0.6–1.1	0.7/0.6	0.2/0.0
Northern Pike	7	2.4–3.7	3.0/2.8	0.5/0.2	0.9–1.0	0.9/0.9	0.0/0.0	0.6–1.4	0.8/0.6	0.3/0.1
Pumpkinseed	4	2.6–2.9	2.8/2.8	0.2/0.1	0.9–1.3	1.0/1.0	0.2/0.1	0.6–0.6	0.6/0.6	0.0/0.0
Smallmouth Bass	6	3.6–4.1	3.8/3.8	0.2/0.1	0.9–1.0	0.9/0.9	0.0/0.0	0.6–0.6	0.6/0.6	0.0/0.0
White Crappie	13	2.6–3.7	3.0/2.9	0.4/0.1	0.9–1.6	1.1/1.0	0.2/0.0	0.6–1.6	0.9/0.7	0.3/0.1
Yellow Perch	6	2.6–3.4	2.9/2.8	0.3/0.1	0.9–1.1	0.9/0.9	0.1/0.0	0.6–0.8	0.6/0.6	0.1/0.0
Log BSAF (kg/kg)										
All species	100	0.7–2.9	1.7/1.8	0.5/0.05	(–0.1)–(0.8)	0.0/–0.1	0.22/0.02			
Black Crappie	13	0.9–2.0	1.5/1.5	0.4/0.1	(–0.15)–(0.76)	0.31/0.23	0.32/0.09			
Brown Bullhead	3	1.0–1.4	1.2/1.3	0.2/0.1	(–0.15)–(0.06)	–0.04/–0.03	0.10/0.06			
Channel Catfish	7	1.2–2.2	1.8/1.8	0.4/0.2	(–0.15)–(0.11)	–0.05/–0.07	0.10/0.04			
Common Carp	25	1.4–2.9	2.2/2.0	0.4/0.1	(–0.15)–(0.42)	0.05/0.03	0.19/0.04			
Largemouth Bass	16	1.8–2.2	2.0/2.0	0.1/0.0	(–0.15)–(–0.07)	–0.14/–0.15	0.02/0.00			
Northern Pike	7	0.7–2.0	1.3/1.1	0.5/0.2	(–0.15)–(–0.10)	–0.14/–0.15	0.02/0.01			
Pumpkinseed	4	0.8–1.2	1.1/1.1	0.2/0.1	(–0.15)–(0.20)	–0.04/–0.11	0.16/0.08			
Smallmouth Bass	6	1.9–2.4	2.1/2.0	0.2/0.1	(–0.15)–(–0.07)	–0.13/–0.15	0.03/0.01			
White Crappie	13	0.9–2.0	1.3/1.2	0.4/0.1	(–0.15)–(0.58)	0.01/–0.03	0.18/0.05			
Yellow Perch	6	0.9–1.7	1.2/1.1	0.3/0.1	(–0.15)–(0.00)	–0.12/–0.15	0.06/0.02			

after the downstream PFAA contamination was linked with the FFTA activities by this study.

Another ditch draining a different area of the airport (site 4) demonstrated elevated levels of PFOS, PFHxS, PFOA, and to a certain extent, PFHpA and PFNA, and appeared an anomaly at first. However, a recent report indicated historical existence of a training area at the south end of the airport, which was close to the sampling site 4 of this study and operated between 1965 and 1984 (Van Dongen M., 2012a). There is a possibility that PFOS-based AFFF was used at this historical FFTA between 1981 and 1984 (Van Dongen M., 2012a). Apparently, past uses of the AFFF at this old FFTA are resulting in water concentrations of about 200 ng/L of PFOS and PFHxS, and about 100 ng/L of PFOA at an adjacent location (site 4; Table S2) even after 30 years of their cessation and possibly restructuring of the area.

The identification of the FFTA-Pond on the airport property by this study as the source of the downstream PFAA contamination spurred Tradeport, the operator of the airport, to retain a consultant in 2011 to conduct an initial investigation on the extent of soil and subsurface PFOS and PFOA contamination at the FFTA. The study reported 210–26,000 ng/g PFOS and 11–350 ng/g PFOA in the 0–60 cm deep soil layers (exp Services Inc., 2011). The levels of PFOS and PFOA in the groundwater samples ranged <DL-560,000 ng/L and <DL-130,000 ng/L, respectively (DL, detection limit). The surface water sample collected by the consultant from the FFTA-Pond contained a PFOS water concentration of 45,000 ng/L (exp Services Inc., 2011), which is similar to the 49,000 ng/L measured in 2011 in this study (Fig. 2, Table S2).

The study initiated by Tradeport support our findings of the PFAA contamination in and around the FFTA. It is believed that the groundwater at the FFTA flows north (exp Services Inc., 2011), opposite to the surface water movement. We hypothesize that a portion of historically contaminated groundwater has recently surfaced, flows into a ditch at the western property boundary, and eventually migrates to the Welland River tributary at Glanaster Rd. (Site 3 of this study), where elevated levels of PFOS, PFHxS and PFOA were observed in the 2011 water samples (Fig. 2, Table S2). According to this hypothesis, we may observe increasing concentrations at site 3 and further downstream as more PFAA contaminated groundwater emerge in the surface water. Unfortunately, the tributary (site 3) was dry during our 2015 sampling campaign, which prevented us from examining the 4-year trend for this site.

4.2. Short-term (4 year) trend

A limited comparison of PFAA measurements for water samples collected in 2011 and 2015 indicated an increasing trend downstream of the FFTA-Pond. This observation was unexpected as the airport operator, Tradeport, blocked the ditches draining the contaminated training pad to prevent off site migration of the contaminants (Van Dongen M., 2012c). The OMOECC has made recommendations that the ditch draining the FFTA-Pond off the airport property needs to be blocked; however, it is not clear if this action has been completed at this time.

It should also be noted that the 2011 water sampling event was conducted in spring and was preceded by more precipitation than the 2015 water sampling event, which was conducted in summer (2011: prior 3 and 7 days – 9 and 54 mm, respectively; 2015: prior 3 and 7 days – 9 and 11 mm, respectively; EC, 2015a). It is possible that the greater precipitation prior to the 2011 sampling would have led to more dilution compared to the 2015 sampling. As such, the perceived increase in water concentrations between 2011 and 2015 needs to be further evaluated with another round of comprehensive sampling, preferably in spring with a similar amount of prior precipitation. Efforts should be especially focused at site 2, which is in the adjacent Twenty Mile Creek watershed and showed almost a six-fold increase between 2011 and 2015 (Fig. 4). The decreases in the concentrations of major long-chain PFAAs at the most upstream location (site 1; Figs. 4, S3) could be a reflection of reductions in PFAAs sources due to phase out by 3 M (Awad et al., 2011).

4.3. Comparison to guidelines

The PFOS water concentrations at the FFTA-Pond and two just downstream sites (# 7, 8 and 9) exceeded the drinking water guideline of 300 ng/L set by Health Canada, which is similar to the guidelines developed by the United States Environmental Protection Agency (USEPA) (200 ng/L), Health Protection Agency of the United Kingdom (300 ng/L), and Minnesota Department of Health (300 ng/L) (HC, 2015, MDH, 2015a; UKPH, 2013, USEPA, 2014). The PFOS water concentrations at these three sites also typically exceeded the Environment Canada's draft guideline of 6000 ng/L for the protection of aquatic life and the no effect level of 491 ng/L for fish (EC, 2015b, EC, 2006) (Fig. 2, Tables S2, S6). All the sites downstream of the FFTA-Pond including Lake Niapenco (sites 7–16) as well as sites downstream of the airport's western property boundary (site 4) and in the adjacent watershed (site 2) exceeded suggested PFOS guideline of 47 ng/L for the protection of avian wildlife (Giesy et al., 2010). However, the lower guideline is based on toxicity studies at low concentrations and possesses high uncertainties; as such, exceedance of the guideline indicates only a possibility of risk. The levels of PFOS detected in the two wells were below the drinking water guideline of 300 ng/L (Van Dongen M., 2012b).

Similar to PFOS, the levels of PFOA exceeded the drinking water guideline of 300 ng/L set by Health Canada and Minnesota Department of Health, and 400 ng/L set by USEPA only at the FFTA-Pond (site 7) and the ditch draining the pond out of the airport property (site 8) (Fig. 2, Tables S2, S6) (HC, 2015, MDH, 2015a, USEPA, 2014). PFHxS, which has longer serum half-lives than PFOS in most tested animals and in humans (Wang et al., 2013), was another major PFAA found in waters downstream of the FFTA-Pond (Fig. 2, Tables S2, S6). However, widely accepted guidelines for PFHxS are not available due to lack of sufficient toxicological data. Sediment samples showed above background concentrations of PFOS downstream of the FFTA-Pond (sites 2–4, 7–16) (Fig. 2, Table S3). To our knowledge, no widely accepted sediment quality guidelines are available for PFAAs.

4.4. Bioaccumulation factors

BAF and BSAF for PFOS for an individual fish species could vary by an order of magnitude even within a narrow size range (e.g., Figs. S4, S6) due to the lack of positive relationship between fish length and PFOS concentration for the species studied (except Common Carp) (Gewurtz et al., 2014). However, it appears that accumulation of PFOS in large bodied fish tends to be greater than smaller fish (Fig. S6), with Northern Pike as a notable exception. Overall, the Log K_p , Log BAFs and Log BSAF values and patterns observed in this study are in agreement with the reported values for not only other sport fish from Europe (Kwadijk et al., 2010; Kwadijk et al., 2014; Labadie and Chevreuil, 2011), but also for a forage fish from Etobicoke Creek, Ontario, Canada (Awad et al., 2011). Overall observations for PFOS in Lake Niapenco in this and two related studies (de Solla et al., 2012; Gewurtz et al., 2014) support previous findings of a higher bioconcentration from water at lower trophic levels and relatively small biomagnification at higher trophic levels (Martin et al., 2004; Stevens and Coryell, 2007).

4.5. Fish consumption based PFOS water guideline

PFOS concentrations in Lake Niapenco waters (53–91) were typically below the guidelines for drinking water and protection of aquatic biota including fish (Figs. 2, 4, S3b, Tables S2, S6). However, PFOS levels in the edible portion of Niapenco fish were among the highest reported worldwide, resulting in issuance of restrictive fish consumption advisories (Gewurtz et al., 2014; OMOECC, 2015). PFOS concentrations in many fish species (Largemouth Bass, Black Crappie, Smallmouth Bass, Rock Bass, Channel Catfish, White Crappie, and Northern Pike) from this area exceeded the 95th percentile concentration of values reported in the peer-reviewed literature (Gewurtz et al., 2014). Two Common

Carp from Lake Niapenco had PFOS concentrations of 2300–2400 ng/g ww, which was about 4× greater than the “do not eat” fish consumption advisory benchmark of 640 ng/g ww used by the Province of Ontario, Canada (Gewurtz et al., 2014).

Based on the current drinking water guideline of 300 ng/L (HC, 2015) and BAFs reported in this study (Table 1), PFOS concentrations in Lake Niapenco fish could theoretically reach as high as 15,000 ng/g without exceeding the drinking water guideline (at Log BAF = 4.7 L/kg). This fish concentration would be almost 100× greater than the “do not eat” advisory benchmark of 160 ng/g for the sensitive population of children and women of child-bearing age (OMOEC, 2015). Unfortunately, simple treatment such as boiling water and cooking fish are not effective in removing PFAAs (Bhavsar et al., 2014; MDH, 2015b). As such, a fish consumption based water quality guideline is needed to direct remediation efforts that would ensure adequate protection of human health.

The Ontario Ministry of the Environment and Climate Change (OMOEC) recommends PFOS concentrations of less than 80 and 40 ng/g in the edible portion of fish for consumption frequencies of 8 and 16 meals/month, respectively (OMOEC, 2015). These benchmarks are based on 70 kg average weight for an adult and a meal size of 227 g (8 oz or half a pound) (OMOEC, 2015). As per Log BAFs of 3.4 ± 0.05 (mean \pm SE; range: 2.4–4.7; Table 1), PFOS water concentrations of 15 ± 2.8 (2–300) ng/L and 8 ± 1 (<1–152) ng/L would result in 8 and 16 meals/month advisories, respectively, for most fish. Since the BAFs observed in this study are similar to many other reports as discussed above, these fish consumption based water guidelines for PFOS would likely be applicable worldwide. This statement is supported by similar fish consumption based water guidelines of <1–12 ng/L PFOS calculated by RIVM Dutch National Institute for Public Health and the Environment and Minnesota Pollution Control Agency (Moermond et al., 2010; Stevens and Coryell, 2007). The minor differences in the derived guidelines are attributed to differences in the parameters such as fish consumption rate, BAF and tolerable daily intake.

Notes

The authors declare no competing financial interest.

Acknowledgements

We thank Brian Thorburn and Alexis Knight of OMOEC.

Appendix A. Supplementary data

Supplementary data (detailed analytical method, and additional 6 tables and 6 figures) associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.envint.2016.05.023>.

References

- Awad, E., Zhang, X.M., Bhavsar, S.P., Petro, S., Crozier, P.W., Reiner, E.J., Fletcher, R., Tittlemier, S.A., Braekevelt, E., 2011. Long-term environmental fate of perfluorinated compounds after accidental release at Toronto Airport. *Environ. Sci. Technol.* 45, 8081–8089.
- Bhavsar, S.P., Gewurtz, S.B., Helm, P.A., Labencki, T.L., Marvin, C.H., Fletcher, R., Hayton, A., Reiner, E.J., Boyd, D., 2010. Estimating sediment quality thresholds to prevent restrictions on fish consumption: Application to polychlorinated biphenyls and dioxins-furans in the Canadian Great Lakes. *Integr. Environ. Assess. Manage.* 6, 641–652.
- Bhavsar, S.P., Zhang, X., Guo, R., Braekevelt, E., Petro, S., Gandhi, N., Reiner, E.J., Lee, H., Bronson, R., Tittlemier, S.A., 2014. Cooking fish is not effective in reducing exposure to perfluoroalkyl and polyfluoroalkyl substances. *Environ. Int.* 66, 107–114.
- Das, P., Megharaj, M., Naidu, R., 2015. Perfluorooctane sulfonate release pattern from soils of fire training areas in Australia and its bioaccumulation potential in the earthworm *Eisenia fetida*. *Environ. Sci. Pollut. Res.* 22, 8902–8910.
- de Solla, S.R., De Silva, A.O., Letcher, R.J., 2012. 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.* 39, 19–26.
- EC, 2006. Ecological screening assessment report on perfluorooctane sulfonate, its salts and its precursors that contain the C₈F₁₇SO₂ or C₈F₁₇SO₂N moiety. Environment Canada http://www.ec.gc.ca/lcpe-cepa/documents/substances/spfo-pfos/ecological_sar_pfos_eng.pdf (Accessed in November 2015).
- EC, 2015a. Climate data. Environment Canada <http://climate.weather.gc.ca> (Accessed in November 2015).
- EC, 2015b. Perfluorooctane Sulfonate in the Canadian Environment: Federal Environmental Quality Guidelines for PFOS. www.ec.gc.ca/toxiques-toxics/default.asp?lang=En&nav=7331A46C-1&offset=3&toc=show (Accessed in November 2015).
- exp Services Inc., 2011. Initial Subsurface Investigation – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA): Former Fire Training Facility, 9800 Airport Road, Hamilton, ON, Canada.
- Filipovic, M., Woldegiorgis, A., Norstrom, K., Bibi, M., Lindberg, M., Osteras, A.-H., 2015. Historical usage of aqueous film forming foam: a case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish. *Chemosphere* 129, 39–45.
- Gewurtz, S.B., Bhavsar, S.P., Crozier, P.W., Diamond, M.L., Helm, P.A., Marvin, C.H., Reiner, E.J., 2009. Perfluoroalkyl contaminants in window film: indoor/outdoor, urban/rural, and winter/summer contamination and assessment of carpet as a possible source. *Environ. Sci. Technol.* 43, 7317.
- Gewurtz, S.B., Backus, S.M., De Silva, A.O., Ahrens, L., Armellin, A., Evans, M., Fraser, S., Gledhill, M., Guerra, P., Harner, T., Helm, P.A., Hung, H., Khera, N., Kim, M.G., King, M., Lee, S.C., Letcher, R.J., Martin, P., Marvin, C., McGoldrick, D.J., Myers, A.L., Pelletier, M., Pomeroy, J., Reiner, E.J., Rondeau, M., Sauve, M.-C., Sekela, M., Shoeib, M., Smith, D.W., Smyth, S.A., Struger, J., Spry, D., Syrgiannis, J., Waltho, J., 2013. Perfluoroalkyl acids in the Canadian environment: multi-media assessment of current status and trends. *Environ. Int.* 59, 183–200.
- Gewurtz, S.B., Bhavsar, S.P., Petro, S., Mahon, C.G., Zhao, X., Morse, D., Reiner, E.J., Tittlemier, S.A., Braekevelt, E., Drouillard, K., 2014. High levels of perfluoroalkyl acids in sport fish species downstream of a firefighting training facility at Hamilton International Airport, Ontario, Canada. *Environ. Int.* 67, 1–11.
- Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* 35, 1339–1342.
- Giesy, J.P., Nalle, J.B., Khim, J.S., Jones, P.D., Newsted, J.L., 2010. Aquatic toxicology of perfluorinated chemicals. *Rev. Environ. Contam. Toxicol.* 202 (202), 1–52.
- HC, 2015. Canadian Drinking Water Guidelines. Health Canada <http://www.hc-sc.gc.ca/ewh-semt/water-eau/drink-potab/guide/index-eng.php> (Accessed in November 2015).
- Huset, C.A., Barlaz, M.A., Barofsky, D.F., Field, J.A., 2011. Quantitative determination of fluorochlorinated in municipal landfill leachates. *Chemosphere* 82, 1380–1386.
- Kwadijk, C.J.A.F., Korytar, P., Koelmans, A.A., 2010. Distribution of perfluorinated compounds in aquatic systems in the Netherlands. *Environ. Sci. Technol.* 44, 3746–3751.
- Kwadijk, C.J.A.F., Kotterman, M., Koelmans, A.A., 2014. Partitioning of perfluorooctanesulfonate and perfluorohexanesulfonate in the aquatic environment after an accidental release of aqueous film forming foam at Schiphol Amsterdam Airport. *Environ. Toxicol. Chem.* 33, 1761–1765.
- Labadie, P., Chevreuil, M., 2011. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Urge River (nearby Paris, France). *Environ. Pollut.* 159, 391–397.
- Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., Seed, J., 2007. Perfluoroalkyl acids: a review of monitoring and toxicological findings. *Toxicol. Sci.* 99, 366–394.
- Li, B., Danon-Schaffer, M.N., Li, L.Y., Ikononou, M.G., Grace, J.R., 2012. Occurrence of PFCS and PBDEs in landfill leachates from across Canada. *Water Air Soil Pollut.* 223, 3365–3372.
- Martin, J.W., Whittle, D.M., Muir, D.C.G., Mabury, S.A., 2004. Perfluoroalkyl contaminants in a food web from lake Ontario. *Environ. Sci. Technol.* 38, 5379–5385.
- MDH, 2015a. Overview of Perfluorochemicals and Health. Minnesota Department of Health <http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/health.html> (Accessed in November 2015).
- MDH, 2015b. Aqueous Film Forming Foams. Minnesota Department of Health <http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/aff.html> (Accessed in November 2015).
- Moermond, C.T.A., Verbruggen, E.M.J., Smit, C.E., 2010. Environmental Risk Limits for PFOS: A Proposal for Water Quality Standards in Accordance With the Water Framework Directive. RIVM, The Netherlands.
- Moody, C., Martin, J., Kwan, W., Muir, D., Mabury, S., 2002. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of firefighting foam into Etobicoke Creek. *Environ. Sci. Technol.* 36, 545–551.
- Moody, C.A., Hebert, G.N., Strauss, S.H., Field, J.A., 2003. Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. *J. Environ. Monit.* 5, 341–345.
- Myers, A.L., Crozier, P.W., Helm, P.A., Brimacombe, C., Furdul, V.J., Reiner, E.J., Burniston, D., Marvin, C.H., 2012. Fate, distribution, and contrasting temporal trends of perfluoroalkyl substances (PFASs) in Lake Ontario, Canada. *Environ. Int.* 44, 92–99.
- OMOEC, 2015. 2015–2016 Guide to Eating Ontario Fish. Ontario Ministry of the Environment and Climate Change, Toronto, Ontario, Canada.
- Schultz, M.M., Barofsky, D.F., Field, J.A., 2004. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. *Environ. Sci. Technol.* 38, 1828–1835.
- Stevens, J.B., Coryell, A., 2007. Surface Water Quality Criterion for Perfluorooctane Sulfonic Acid. STS Consultants Ltd. and Minnesota Pollution Control Agency.
- UKPH, 2013. PFOS and PFOA Incident Management. U.K. Public Health https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/338259/PFOS_and_PFOA_Incident_Management_phe_v2.pdf (Accessed in November 2015).
- UNEP, 2009. The nine new POPs. An Introduction to the Nine Chemicals Added to the Stockholm Convention by the Conference of the Parties at Its Fourth Meeting. Available online <http://chm.pops.int/Programmes/NewPOPs/Publications/tabid/695/language/en-US/Default.aspx> (Accessed in November 2015).

- USEPA, 2014. Drinking Water Health Advisories for PFOA and PFOS. <https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos> (Accessed in November 2015).
- Van Dongen, M., 2012a. Another PFOS polluted site at airport? *Hamilton Spectator*, Hamilton, ON, Canada <http://www.thespec.com/news-story/2254274-another-pfos-polluted-site-at-airport/> (Accessed in November 2015)
- Van Dongen, M., 2012b. Hamilton Airport's Water Pollution Leaves Region With a Dangerous Legacy. *Hamilton Spectator*, Hamilton, ON, Canada <http://www.thespec.com/news-story/2247400-hamilton-airport-s-water-pollution-leaves-region-with-a-dangerous-legacy/> (Accessed in November 2015).
- Van Dongen, M., 2012c. Hamilton Airport Pollution: Who will pay? *Hamilton Spectator*, Hamilton, ON, Canada [http://m.thespec.com/news-story/2200907-hamilton-airport-pollution-who-will-pay-](http://m.thespec.com/news-story/2200907-hamilton-airport-pollution-who-will-pay/) (Accessed in November 2015)
- Wang, Z., Cousins, I.T., Scheringer, M., Hungerbuehler, K., 2013. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFASs) and their potential precursors. *Environ. Int.* 60, 242–248.