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Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada

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ABSTRACT

Per- and poly-fluorinated compounds (PFCs), which include perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs) and various precursors, are used in a wide variety of industrial, commercial and domestic products. This includes aqueous film forming foam (AFFF), which is used by military and commercial airports as fire suppressants. In a preliminary assessment prior to this study, very high concentrations (>1 ppm wet weight) of the PFSA, perfluorooctane sulfonate (PFOS), were discovered in the plasma of snapping turtles (*Chelydra serpentina*) collected in 2008 from Lake Niapenco in southern Ontario, Canada. We presently report on a suite of C_6 to C_{15} PFCAs, C_4, C_6, C_8 and C_{10} PFSAs, several PFC precursors (e.g. perfluorooctane sulfonamide, PFOSA), and a cyclic perfluorinated acid used in aircraft hydraulic fluid, perfluoroethylcyclohexane sulfonate (PFECHS) in surface water from the Welland River and Lake Niapenco, downstream of the John C. Munro International Airport, Hamilton, Ontario, Canada. Amphipods, shrimp, and water were sampled from the Welland River and Lake Niapenco, as well as local references. The same suite of PFCs in turtle plasma from Lake Niapenco was compared to those from other southern Ontario sites. PFOS dominated the sum PFCs in all substrates (e.g., >99% in plasma of turtles downstream the Hamilton Airport, and 72.1 to 94.1% at all other sites). PFOS averaged 2223 (±247.1 SE) ng/g in turtle plasma from Lake Niapenco, and ranged from 9.0 to 171.4 elsewhere. Mean PFOS in amphipods and in water were 518.1 (±83.8) ng/g and 130.3 (±43.6) ng/L downstream of the airport, and 19.1 (±2.7) ng/g and 6.8 (±0.5) ng/L at reference sites, respectively. Concentrations of selected PFCs declined with distance downstream from the airport. Although there was no known spill event or publicly reported use of AFFF associated with a fire event at the Hamilton airport, the airport is a likely major source of PFC contamination in the Welland River.

1. Introduction

Per- and poly-fluorinated compounds (PFCs) are a broad class of substances and are used in a wide variety of industrial and consumer products such as fluorinated polymers, surfactants, insecticides, and aqueous fire-fighting foams, and have been manufactured for over 50 years (Moody and Field, 2000; and references therein; Skutlarek et al., 2006). PFCs categorized as perfluoroalkyl acids (PFAAs) generally have a high thermal and chemical stability, and are both hydrophobic and lipophobic (Moody and Field, 2000). Perfluorinated carboxylic acids (PFCAs) and sulfonic acids (PFSAs) are recalcitrant to environmental degradation as they are fully oxidized with high chemical stability, but under environmental pH conditions exist in their anionic conjugate base forms (Prevedouros et al., 2006). Several PFAAs, and in particular PFCAs and PFSAs (especially perfluorooctane sulfonate [PFOS]), have been shown to be globally distributed, and are persistent and bioaccumulative contaminants found in tissues of wildlife worldwide (Butt et al., 2010; Houde et al., 2006; Houde et al., 2011). PFAA burdens tend to be highest in proteinaceous tissues such as blood, liver, and kidneys (Gruber et al., 2007; Martin et al., 2004) rather than in lipid stores typical of legacy POPs.

Until recently, perfluorinated C_5 to C_{18} compounds were considered high production volume chemicals, as annual imports to North America exceeded approximately 500,000 kg (Rogers, 1999). For example, the manufacture of PFOS and its precursors, or collectively designated as “PreFOS”, was voluntarily phased out between 2000 and 2002 by 3M Co., which at the time was producing ~80% of the world's PFOS (Martin et al., 2010).

Recently, the use of PFAAs in aqueous film forming foam (AFFF) has been linked to substantial environmental contamination, following the handling, storage, usage. PFAAs were additives in AFFFs to

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act as low viscosity vapor sealants to inhibit combustion of jet fuel (Kishi and Arai, 2008; Moody and Field, 2000), and thus were used as fire retardants for fuel-based fires. The contamination of groundwater by PFCs has been associated with the use of AFFFs at fire-training sites at several military bases in the United States (Levine et al., 1997). More recently, a malfunction at the Lester B. Pearson International Airport (Toronto, Canada), released 22,000 L of AFFF into storm drains that empty into Etobicoke Creek (Moody et al., 2002). After over 150 days following the release, PFAA concentrations in surface waters ranged from non-detectable to 2260 μg/L (Moody et al., 2002), and PFOS comprised >99% of the PFCs measured in fish liver. Further, in 2005, 48,000 L of AFFF was applied to a fire at the Pearson airport, when Flight 358 overran the runway and started to burn adjacent to Etobicoke Creek (Oakes et al., 2010). There was some evidence of oxidative stress and enlarged livers in fish in Etobicoke Creek downstream of the event, 9 days following the release of AFFF.

In Feb 2010, snapping turtle (*Chelydra serpentina*) plasma collected in 2007 and 2008 was analyzed from three Ontario sites, including Lake Niapenco (Welland River) as the reference site. Unexpectedly, mean concentrations of PFCs, particularly PFOS, were much higher in Lake Niapenco compared to two industrial sites. We subsequently noted that the John C. Munro International Airport (Hamilton) was at the headwaters of the Welland River, which drains into Lake Niapenco. The high concentrations at Lake Niapenco were the impetus of the present study to investigate the source of PFC contamination, and to investigate the bioaccumulative behavior of PFCs in the watershed downstream. To test the hypothesis that the airport was not the source of PFCs, we further sampled turtles from Lake Niapenco, along with amphipods and surface water from a number of sites downstream of the airport, as well as a second creek that drains the airport, and local reference sites outside the Welland River watershed. We hypothesized that PFC concentrations in amphipods, turtles, and water; i) do not differ between the reference and airport influenced sites, ii) do not vary with distance from the airport, and iii) the PFC profile does not differ with distance or geographic location. We also report on levels of decafluoro(pentafluoroethyl)-cyclohexanesulfonate (PFECHS), which is a novel compound that thus far has been reported in fish and surface waters (De Silva et al., 2011).

2. Methods

2.1. Sampling sites

The headwater of the Welland River is adjacent to and on the property of the John C. Munro International Airport, Hamilton, Ontario, Canada (Fig. 1). Storage facilities, most buildings, and the fire fighting training area are on the south side of the airport, near the drainage towards the upper Welland River. Small ephemeral streams on the south side of the airport drain into the upper Welland River (Stations 1–5), which then drains into Lake Niapenco (Stations 6–8), and subsequently into the lower Welland River (Stations 9–11). Lake Niapenco is divided in two (east and west) by a weir, but the two sides are connected by a drainage pipe. Two reference sites outside the Welland River watershed were also sampled; Twenty Mile Creek (Stations 14, 15) drains the northern section airport, but is independent of the Welland River. Big Creek (Stations 12, 13), west of the airport, drains south into the Grand River. Two sites adjacent and south of Lake Niapenco (Stations 16, 17), which drains into the lower Welland River, but not downstream of the airport, were also sampled.

Snapping turtles were sampled throughout southern Ontario: at, Credit River (Mississauga), Island Lake Conservation Area (Orangeville), Humber River (Toronto), Cootes Paradise, Lake Niapenco, and Welland River (Hamilton) (Fig. S1). Amphipods and water were sampled from Lake Niapenco and the Welland River, and surrounding creeks (Fig. 1).

2.2. Sampling methods

Snapping turtles were caught in July 2008 and July and August 2010, using hoop nets baited with canned fish, which were left overnight and checked the following day. Whenever possible, the sex of males was positively identified by eliciting eversion of the penis; otherwise the sex of adults was identified by the relative size of the precloacal area (de Solla et al., 2001). Approximately 5 to 8 ml of blood was taken from the caudal vein using 10 ml sodium heparin coated vacutainers® and 22 gauge double-sided needles. The blood samples were stored on ice, centrifuged for 5 min, and the blood plasma transferred to cryovials and stored in a nitrogen (gaseous phase) cryogenic container. Once brought back to the laboratory, the samples were stored in a −80 °C freezer until analyzed for PFCs.

Amphipods were caught by swishing kicknets along the base of vegetation, Oct 2010. The amphipods were sieved and concentrated, then brought to a laboratory, where they were sorted the same day, or kept in a fridge until the next day. Amphipods were generally identified as either *Gammarus* or *Hyalella*. Other animals were sampled opportunistically; damselfly nymphs (suborder *Zygoptera*), freshwater shrimp (infraorder *Caridea*), two juvenile sunfish (*Centrarchidae spp.*) and a juvenile bullhead fish (*Ameiurus spp.*) were also caught. Animals were rinsed, and kept at −80 °C until analyzed. Generally, we collected at least 2 g (wet weight) of amphipods per sample (~70 animals).

Water samples were taken at approximately where amphipods were sampled, Oct 22, 2010, using 500 ml containers. Staff waded to roughly 2 to 5 ft from shore in chestwaders, and collected water samples from approximately 6″ below the surface, facing upstream to prevent disturbed sediment from entering the container. Water samples were allowed to settle and were kept in a fridge at 4 °C until analyzed for PFCs.

2.3. Chemicals and standards

The perfluorosulfonate standards [C_4 (PFBS), C_6 (PFHxS), C_8 (PFOS) and C_{10} (PFDS)], perfluorocarboxylic acid standards (C_6 to C_{14} chain lengths; PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA and PFTeA, respectively), 6:2, 8:2 and 10:2 FTUCAs, and 6:2, 8:2 and 10:2 FTOHs, and perfluorosulfonamides (PFOSA, NMeFOSA) (Table S1) and all internal and isotopically-labeled standards were obtained from Wellington Laboratories (Guelph, ON, Canada). The suite of twenty-two PFCs and fourteen isotopically labeled surrogates that were examined in this study are listed in Table S2. All solvents used were HPLC grade and purchased from Fisher Scientific (Ottawa, Canada). A neat standard of the potassium salt of perfluoro-4-ethylcyclohexanesulfonate (PFECHS, CAS# 335-24-0) was obtained from Wako Chemicals (Richmond, VA, USA).

2.4. Snapping turtle plasma sample analysis

The analysis of turtle plasma samples was performed in the Organic Contaminants Research Lab (OCRL) at the National Wildlife Research Centre, Ottawa, Ontario. Extraction and cleanup are described elsewhere (Chu and Letcher, 2008; Gebbink et al., 2009). For full analytical details see the Supplementary Information. Briefly, following extraction with 10 mM KOH acetonitrile/water and fractionation, the target compounds were separated by liquid chromatography tandem mass spectrometry (LC–MS/MS) using a Waters 2695 HPLC; details are in the Supplementary Information (Tables S1 and S2). Briefly, for neutral PFCs in fraction 1, atmospheric pressure photoionization (APPI) was used in negative mode, and for acidic PFCs in fraction 2 an electrospray ionization (ESI) source in negative mode was used. APPI and ESI analyses of fractions 1 and 2, respectively, were performed in multiple reaction monitoring mode (MRM). Quantification was performed using an internal standard approach. Analytes were quantified using the relative response factors of PFCs to ^{13}C-, ^{18}O- or ^{2}H-labeled surrogates via internal standard calibration curves.

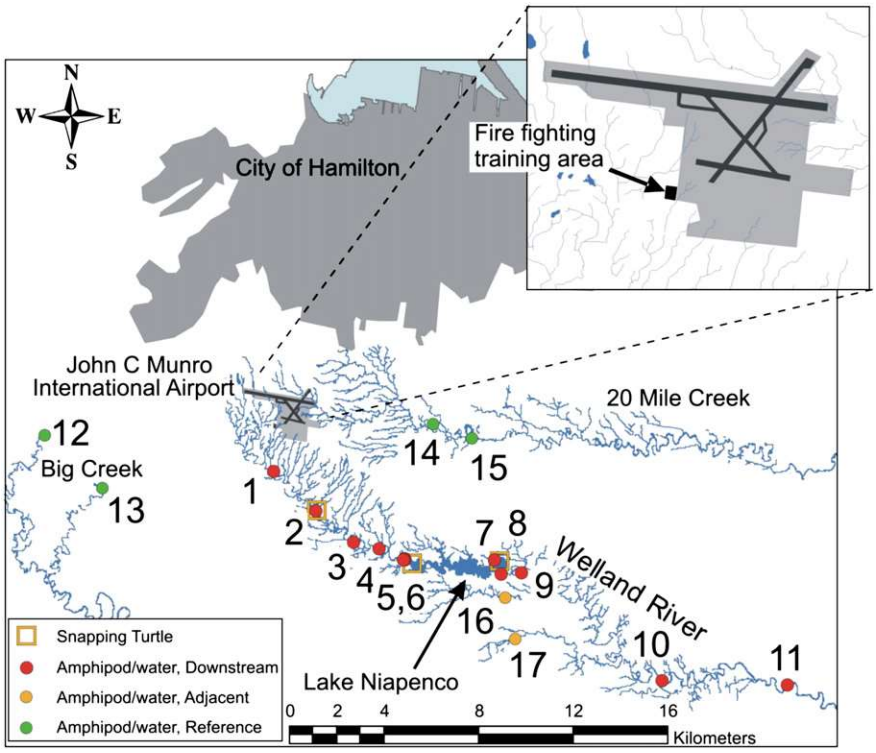

Fig. 1. John C Munro International Airport, Welland River, Lake Niapenco,, station numbers, and sampling locations for snapping turtles, amphipods and water. Reference sites are in 20 Mile Creek and Big Creek. Potentially contaminated sites are downstream of the airport in the Welland River. Sites adjacent to the Welland River but not downstream of the airport were also sampled. The inset map of the airport includes the location of the fire fighting training area, which drains into the Welland River.

To check for contamination, one blank sample was prepared with approximately every 10 plasma samples. All the PFCs analyzed in the blanks were either not detected or below the MDL except for PFBS and PFDA, which were below 1 ppb ww. The concentrations of target compounds in real samples were subtracted by the concentration in blank samples.

The method detection limits (MDLs) for quantification and limits of detection (LODs) for the target compounds are listed in Table S3. Analytes with signal to noise ratios less than 3 were reported as <LOD. The MDL was defined as the concentration yielding a signal to noise ratio of 10. The recoveries for internal standards were determined by the external standard method. There was minor contamination of PFBS and PFDA in blank samples (<1 ppb wet weight [ww]), which was subtracted from the concentrations in plasma samples. The mean percent recovery of five spiked quality control samples (bovine serum) was 103.9% (77.9%–170.5%). The mean percent recovery of internal standards was 68.2% (51.5%–88.2%). See Table S4 for more details of the percent recoveries in the bovine serum.

2.5. Amphipods, fish and shrimp sample analysis

Small-bodied organisms were homogenized as a pooled sample (2 to 3 shrimp per sample or ~2 g of amphipods per sample) or individually (fish) using a hand held homogenizer (Tissue-Tearor, Biospec Products). Extractions on 0.2 g of sample homogenate were conducted using a modified version of the method reported by Powley et al. (2005). Details of the extraction and QA/QC measures are presented in the Supporting Information. Briefly, and similar to the analysis and quantification of PFCs in snapping turtle plasma, a cocktail of isotopically-labeled PFC standards (Wellington Labs, Guelph, ON, Canada) was added to the homogenate and a liquid extraction was performed with methanol in two iterations, and taken to dryness with N_2. After reconstituting in 1 ml methanol, the extract was subjected to clean up using activated carbon. The final extract was reconstituted in 1 ml 50/50 methanol water for analysis by LC–MS/MS using scheduled MRM. Instrumentation consisted of an Agilent 1200 series liquid chromatograph coupled to a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems-MDS Sciex, Concord, ON, Canada).

2.6. Water sample analysis

Water samples were analyzed by combining 0.5 ml of water sample with 0.5 ml methanol (Omnisolv grade, VWR) and a full suite of isotopically-labeled surrogates (Wellington Labs, Guelph, ON, Canada). It was not necessary to extract the water samples due to the high levels of PFAAs. Analysis was conducted on 40 µl injections onto an LC–MS/MS system consisting of an Agilent 1100 series LC coupled to a Sciex 4000 QTRAP mass spectrometer (Applied Biosystems-MDS Sciex). Further details regarding instrumental parameters and QA/QC measures are available in the Supporting Information.

2.7. Data analysis

For observations below detection limits for PFCs in turtle plasma or amphipods, maximum likelihood estimation was generally used to calculate replacement values. “Naïve” substitution methods (e.g. using 1/2 MDL, zero, or a random number) generally give poor results (Helsel, 2006). Using Excel's (Microsoft Corp) iterative Solver function, for each compound observations below MDL were replaced with values that were fit along a quantile normal plot (log-transformed) of the population mean and variance, which had the maximum log-likelihood (Villanueva, 2005). Since each observation is unique, the assumption was made that the replacement values would be proportional to the total contamination. All PFCs were positively correlated with PFOS, therefore values <MDL were sorted such that the replacement values were proportional to PFOS concentrations. An exception was PFDS, for which the highest concentration was 0.98 ng/g, and 72.4% of the observations were below MDL; in this case values below MDL were treated as zero.

For the other taxa (e.g. fish and shrimp), there were too few observations to calculate replacement values. However, most values were either all above the MDL or all below the MDL for a given compound; the values <MDL were given a value of zero. For water samples, specific analytes were consistently above or below MDL for each analyte.

Concentrations were compared among sites using Analysis of Variance, with Fisher's PLSD *post hoc* test. If required, concentrations were log-transformed prior to analysis. Principal Component Analysis (PCA) was used to determine if the profiles of PFCs in water and in amphipods were independent of the influence of the airport. For both PFC concentrations in water and amphipods, the PFCs were reported untransformed, but expressed as a proportion of the sum PFCs, then centered around the means and scaled by the standard deviations prior to using PCA. The components were not rotated.

3. Results

3.1. Snapping turtles

Only PFCAs and PFSAs were detected in turtle plasma (PFHxS, PFNA, PFOS, PFDA, PFUnA, PFDS, PFDoA, PFTrDA, PFTeDA; Table 1). FTUCAs and FTOHs were generally below detection limits. There were 3 animals that had measurable concentrations of PFOSA (0.77 to 0.95 ng/g). PFOA was not detected in plasma from any turtle.

PFOS contributed 99.0% to 99.8% of sum PFC in plasma of turtles downstream the Hamilton Airport, but contributed 72.1% to 94.1% at all other sites (Table 1). Concentrations of PFOS in turtle plasma differed among sites ($F_{[5,40]}=67.22$, $P<0.0001$). Concentrations in samples from east and west Lake Niapenco, downstream of the Hamilton International Airport, were much higher than the four other sites (all $P<0.0001$) (Fig. 2a). Concentrations of PFOS were 40 times higher at Lake Niapenco compared to Cootes Paradise, Hamilton, and 122 times higher than Island Lake Conservation Area. Island Lake had lower concentrations compared to all sites (all $P\leq0.0001$).

3.2. Amphipods

Unlike for the turtle plasma, virtually every PFCA (PFPeA to PFTeA) and PFSA (PFBS, PFHxS, PFOS, and PFDS) was detected in amphipods, except PFDS (Table 2). PFECHS was 30.63 ng/g in amphipods immediately downstream of the airport (Station 1; 1.61 km), but declined to just above MDL (0.12 ng/g), 52.4 km downstream (Station 11). Mean concentrations of PFOS differed among sites ($F_{[4,24]}=34.36$, $P<0.0001$), and the reference sites (Stations 12–15) had lower concentrations than any other site (all $P\leq0.0011$), while the adjacent creeks (Stations 16, 17) had lower concentrations than the upper Welland River (Stations 1–5) and Lake Niapenco (Stations 6–8) (all $P<0.0064$; Fig. 2b). The upper and lower Welland River and Lake Niapenco did not differ (all $P\geq0.1494$).

The profile of PFCs also differed among sites. There were four components from the PCA, and the first two contributed 38.8% and 21.0% of the total variance. The first component had a large positive loading for PFOS, and negative loadings for the seven PFCs, many minor, of the sum PFCs (e.g. PFDA, PFNA, PFDoA, PFTeA, etc.; Fig. 3a). The second component had large positive loadings of PFHxA, PFHxS, and PFPeA (Fig. 3a). When a PCA was performed including the freshwater shrimp, amphipods, fish and larval damselflies, the pattern was almost identical. Thus, the location of the sampling was a more important determinant of the PFC profile than the species of animal sampled. PCA scores varied among sites for the 1st and 2nd components ($F_{[4,24]}=27.38$, $P<0.0001$; $F_{[4,24]}=3.33$, $P<0.0263$; Fig. 3). The sites downstream of the airport had relatively high PFOS concentrations and the sites in the upper Welland River also had relatively higher concentrations of PFHxA, PFHxS, and PFPeA.

When only the sites that were directly downstream of the airport were included (e.g. Lake Niapenco, upper and lower Welland River (Stations 1–11)), the 2nd and 3rd component varied with the natural logarithm-transformed distance from the airport (component 1: $r^2=0.35$, $F_{[1,15]}=8.0$, $P<0.0127$; component 2: $r^2=0.84$, $F_{[1,15]}=79.51$, $P<0.0001$). Thus, as the distance between the sampling station and the airport increased, the profile of PFCs in amphipods changed, with relative concentrations of PFPeA, PFHxA, PFHpA, and PFHxS in amphipods decreasing with distance from the airport. Using linear regression, concentrations of PFPeA, PFHxA, PFHpA PFHxS, PFECHS all declined with the log distance downstream from the airport ($r^2=0.67$ to 0.83, $P\leq0.0001$). Concentrations of most PFCs when samples in the Welland river were pooled (Stations 1–11) in sampling stations were elevated relative to the reference sites as far as 52 km downstream of the airport, which was the last sampling site (ANOVA; statistics not shown).

Although we had too few samples to do cross-species comparisons, we report PFCs in whole bodies of other taxonomic groups (collectively n = 10; Table 3). Many taxonomic groups were caught from one sampling station: Tyneside road (Station 5), which is approximately 50 m upstream of Lake Niapenco. At this station, one juvenile

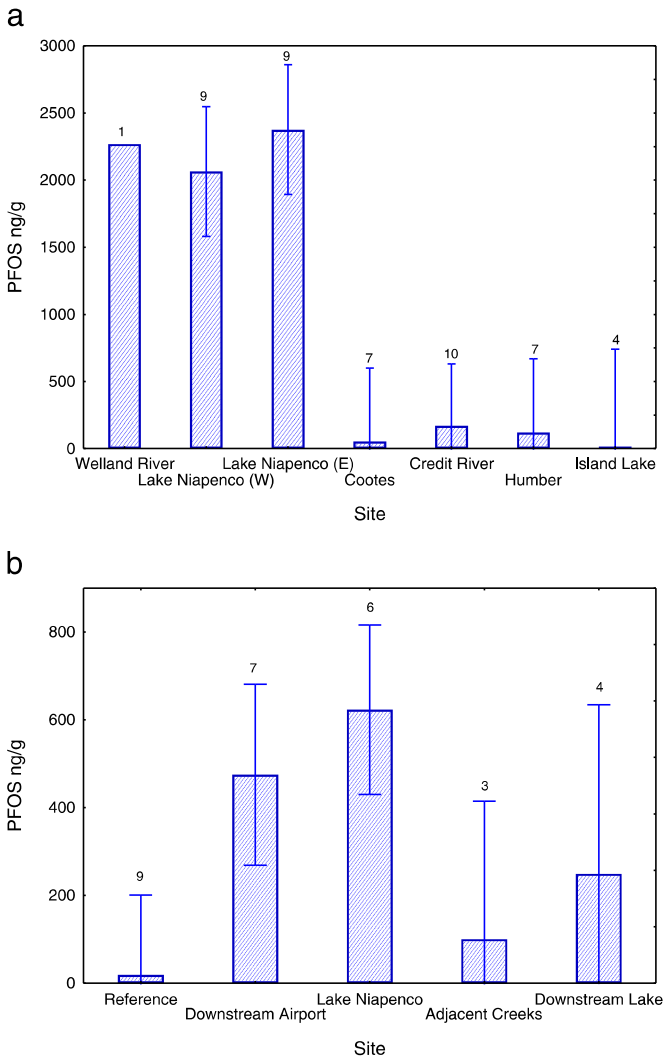

Fig. 2. Arithmetic mean (95% C.I.) concentrations of PFOS (ng/g ww) in (a) turtle plasma from downstream the Hamilton airport (Welland River, Lake Niapenco), compared to other sites without upstream influences from Airports, 2007–2010, and (b) in amphipods from reference sites, downstream airport, Lake Niapenco, streams adjacent to Lake Niapenco, and downstream of Lake Niapenco. Sample sizes are given above each bar.

Table 1
Arithmetic mean (standard deviation) concentrations of perfluorinated compounds (ng/g wet weight) in snapping turtle plasma from southern Ontario 2007–2010; Lake Niapenco and Welland River are downstream of the John C Munro International Airport, Hamilton, ON.

Site	n	PFHxS	PFOS	PFDS	PFNA	PFDA	PFUnA	PFDoA	PFTrA	PFTeA	Sum PFCs
Lake Niapenco (E)	9	2.3 (2)	2376.7 (1460.3)	0.3 (0.2)	0.6 (0.2)	4.3 (2.1)	3.6 (2.5)	0.1 (0.1)	0.7 (0.4)	<0.1	2388.5 (1463.3)
Lake Niapenco (W)	9	3.2 (1.7)	2065.2 (649.6)	0.2 (0.1)	0.1 (0.1)	2 (1)	1.6 (0.4)	<0.1	0.1 (0.2)	<0.1	2072.3 (650)
Upper Welland River	1	8.2	2269.4	0.3	0.3	3.4	1.8	<0.1	0.5	<0.1	2283.8
Credit River	10	0.2 (0.2)	171.4 (120)	4.2 (2.2)	0.3 (0.2)	2.7 (1.4)	2.6 (1.2)	2.4 (1.2)	1.4 (0.7)	0.6 (0.3)	185.8 (126.4)
Cootes Paradise	7	0.1 (0.1)	53 (17.1)	2.2 (0.7)	<0.1	4.5 (3.4)	0.8 (0.3)	0.3 (0.3)	<0.1	<0.1	60.9 (21)
Humber River	7	0.2 (0.2)	121.4 (90.1)	7.2 (5.5)	0.2 (0.2)	2.3 (0.9)	2 (0.7)	2 (0.5)	0.7 (0.2)	0.4 (0.2)	136.3 (96.3)
Island Lake	4	<0.1	15.1 (9)	0.4 (0.2)	<0.1	1.2 (0.7)	1.3 (0.7)	<0.1	<0.1	<0.1	18 (10.5)

Table 2
Arithmetic mean (standard deviation) concentrations of perfluorinated compounds in amphipods (ng/g ww) and water (ng/L) from sampling stations downstream of the Hamilton International Airport, Ontario in the Welland River. See Figure 1 for the location of the water or amphipod sampling areas (station numbers).

Station number	1	2	3	4	5	6	7,8	9	10	11	12, 13, 14, 15	16	17
Distance from Airport (km)	1.61	6.32	10.33	12.38	14.77	14.83	19.29	22.66	42.04	52.36	R	A1	A2
Amphipod													
n	2	1	1	1	2	6	2		1	1	9	2	1
PFPeA	19 (1.3)	9.7	0	0.1	7.4 (0.3)	2.1 (1)	1.5 (1)		0.1	0.2	0 (0)	0.1 (0)	0.1
PFHxA	5.4 (0.2)	4.6	0.1	0.5	2.2 (0.1)	1.1 (0.6)	1.6 (1)		0.6	0.5	0.1 (0.1)	0.2 (0)	0.3
PFHpA	25.1 (0.6)	12.3	0.6	1.8	10.3 (2.3)	4.8 (1.7)	4.1 (2.8)		2.4	1.6	1.6 (1)	2.3 (0.1)	0.9
PFOA	53.8 (3.3)	49.8	17.2	37.8	42.3 (3)	60.4 (24.5)	37.6 (28.2)		50.7	34.1	9 (4.5)	47.8 (18.4)	27.6
PFNA	44.8 (0.2)	44.6	7.3	15.3	65.5 (3)	48 (17.2)	59 (34.8)		12.2	7.9	7 (3.3)	15.6 (1.2)	7.5
PFDA	11.3 (0.8)	8.4	2.8	5.8	12.3 (1.7)	13 (4.1)	51.9 (31)		4.6	3.6	4 (2.3)	7.8 (1.2)	6.8
PFUnA	4.4 (0.1)	2	1.1	2.6	3.8 (1.2)	4.5 (1.4)	49 (31)		1.4	1.2	1.3 (0.6)	1.4 (0)	1.4
PFDoA	1.1 (0.2)	0.9	0.1	0.2	0.2 (0)	1 (0.3)	7.6 (5.7)		0.6	0.5	0.5 (0.3)	0.7 (0.1)	0.9
PFTrA	0.2 (0)	0.6	0.05	0.1	0.2 (0)	0.6 (0.6)	4.1 (2.4)		0.1	0.1	0.3 (0.3)	0.1 (0)	0.8
PFTeA	0.6 (0.1)	0.2	0.2	0.2	0.2 (0)	0.4 (0.2)	0.9 (0.4)		0.4	0.2	0.3 (0.3)	0.8 (0)	0.5
PFHxS	40.2 (4.8)	15.4	0.7	2.3	9.9 (0.9)	4.4 (2.2)	6.3 (3.4)		1.7	2.4	0.2 (0.2)	0.3 (0.1)	0.3
PFOS	643.5 (55.1)	376.8	49.2	169.8	721.4 (42.8)	455.4 (151.2)	1125.9 (636.8)		210.6	287.2	19.1 (8)	65.7 (0.4)	169.7
PFDS	0.5 (0.7)	≤0.25	0.6	0.7	≤0.25	0.2 (0.2)	≤0.25		≤0.25	≤0.25	0.1 (0.2)	0.3 (0.1)	≤0.25
PFECHS	30.6 (4.1)	12.1	2.9	5.3	8.2 (0.5)	2.9 (1.7)	2.5 (3.3)		0.1	0.1	0.3 (0.8)	0.05 (0.01)	0.08
PFOSA	2.6 (0.3)	1.2	0.5	0.9	1.5 (0.1)	2.4 (1.8)	16.2 (13.5)		11.7	17.2	0.4 (0.2)	1 (0.1)	2.9
Sum	883.1 (69.2)	538.7	83.5	243.3	885.5 (32.9)	601.3 (166.7)	1368.3 (795.3)		296.9	356.7	44.2 (15)	144.1 (15.7)	219.6
Water													
n	1	1	1	1	1	2	2	1	1	1	3	1	1
PFPeA	270	151	3.3	5.7	2.4	7.6 (0.8)	8.6 (0.6)	6.9	8.1	7	1.4 (0.5)	1.2	1.7
PFHxA	176.6	105.8	25	25.8	25.6	29.5 (3)	15.4 (7.1)	13.3	16.2	13.8	4.3 (0.8)	5.2	6.7
PFHpA	70.6	40	13.9	14.5	14.7	15.7 (0.6)	10.9 (0.1)	6.1	8.7	8.6	1.2 (0.3)	2.2	4.7
PFOA	62.4	31	7.4	7.7	15.9	8.8 (0.8)	10.9 (6.4)	17.3	29.8	22.4	5.3 (0.3)	17.2	38.8
PFNA	17.3	4	0.5	1.1	2.1	0.9 (0.8)	1.4 (0.4)	5.9	5	4.3	1.3 (0)	1.9	2.7
PFECHS	20.0	15.1	10.8	8.4	7.3	10.9 (1.5)	1.7 (1.1)	11.3	14.2	23.6	2.8 (2.7)	4.5	6.6
L-PFOS 99 m/z	392	126.4	38.4	44.4	60.8	49 (7.4)	63.5 (17.1)	76	65.4	61.4	6.1 (1.5)	9.7	29.4
L-PFOS 80 m/z	458.0	121.4	36.0	30.2	46.0	44.9 (5.2)	59.2 (16.1)	62.2	72	58.0	7.5 (3.2)	7.0	22.2
PFBS	28.6	18.3	9.6	9.4	7	9 (2.6)	5.9 (4.8)	9.9	10.1	2.8	10.2 (8.3)	18.1	2.7
Sum	1037.5	491.6	108.9	117	135.9	131.3 (4.1)	118.2 (34.2)	146.6	157.5	144	32.5 (13.9)	60	93.3

R: sampling stations from reference creeks.
A1 and A2: sampling stations immediately south to Lake Niapenco.

sunfish, two juvenile bullhead, damselflies, amphipods, and shrimp were all sampled. Generally, amphipods had a wider range of PFCs detectable in whole bodies, and they also had higher sum PFCs (Table 3).

3.3. Water

Short chain PFCAs, PFPeA, PFHxA, PFHpA, PFOA, and PFNA as well as the PFSAs, PFOS, and PFBS were measurable in water. Concentrations of PFPeA, PFHxA, PFHpA, PFNA PFOS, and PFBS all declined with the log distance downstream ($r^2 = 0.34$ to 0.82, $P \leq 0.0436$). Unlike in the amphipods, the concentrations of PFECHS did not decline with distance from the airport, but concentrations were lower ($F_{[4,12]} = 3.92$, $P < 0.0291$) in the reference sites (Stations 12–15) compared to the upper (Stations 1–5; $P < 0.0217$) or lower (Stations 9–11; $P < 0.0057$) Welland rivers. The mean concentrations of PFOS varied among sites ($F_{[4,12]} = 10.90$, $P < 0.0006$). Although the sum PFCs did not vary between the reference sites (Stations 12–15) and the sites adjacent to Lake Niapenco (Stations 16,17), sum PFCs were lower at the reference sites compared to the upper and lower Welland River, and Lake Niapenco (all $P < 0.0128$).

The profile of PFCs also differed among sites. The first two components from the PCA contributed 46.3% and 17.6% of the total variance. The first component had a large positive loading for PFBS, PFOA and PFNA, and large negative loadings for PFHpA and PFHxA (Fig. 3b). The second component had a large negative loading for PFOS (Fig. 3b). PCA scores varied among sites for both the 1st and 2nd components ($F_{[4,12]} = 158.1$, $P < 0.0001$; $F_{[4,12]} = 4.37$, $P < 0.0208$). The sites downstream of the airport had relatively high concentrations of PFOS, and the sites in the upper Welland River had relatively higher concentrations of PFHxA and PFPeA. Generally, the concentrations of PFPeA, PFHxA, PFHpA, PFNA and PFOS in water initially decreased rapidly with distance from the airport (Stations 1–3; ~10 km), then remained relatively stable between 10 and 52 km (Stations 3–11).

4. Discussion

Lake Niapenco is an artificial lake within Niagara Peninsula Conservation Authority property, adjacent to the town of Binbrook of about 1000 people, with no WWTP effluent discharge and virtually no local industry. As such, Lake Niapenco was expected to be representative of background PFC contamination in the absence of point sources, and thus was treated as a reference site in a study examining PFC burdens in snapping turtles that was initiated in 2007. The high concentrations of PFOS at Lake Niapenco compared to the two industrial sites were the impetus of the present study to track down the source of PFC contamination. Due to the high concentrations of PFOS in the turtle plasma from Lake Niapenco, the Ontario Ministry of the Environment (OMOE) reanalyzed previously sampled fish from Lake Niapenco for PFOS. The OMOE created fish consumption guidelines for PFOS, starting at 0.080 μg/g, with complete restriction advised for levels above 0.160 μg/g for sensitive populations and 0.640 μg/g for the general population (OMOE, 2011). There were partial or complete consumption restrictions for largemouth and smallmouth bass, black crappie, and common carp for both sensitive and general populations (OMOE, 2011).

In the present study, our data demonstrates that the Welland River, including Lake Niapenco, has been contaminated with PFOS and much lower concentrations of other PFAAs. Snapping turtles, amphipods, and water all showed elevated concentrations of PFAAs, although the patterns of PFAAs varied depending on the substrate. The evidence presented strongly implicates that the source of the contamination is the John C. Munro International Airport, since the site closest to the airport (Welland River, by White Church Road) was among the most contaminated by PFAAs and especially PFOS. Furthermore, the southern portion of the airport drains directly into the Welland River. Storage areas, fire-fighting training areas, and other facilities are close to the drainage areas that drain towards the creek (Fig. 1). Concentrations of PFCs, particularly PFOS, remained elevated in both water and amphipods in the Welland River for a minimum of 52 km downstream, and it is unknown how much further the contamination continues. Out of 38 rivers sampled from 2001–2008 across Canada, PFOS concentrations in water ranged from

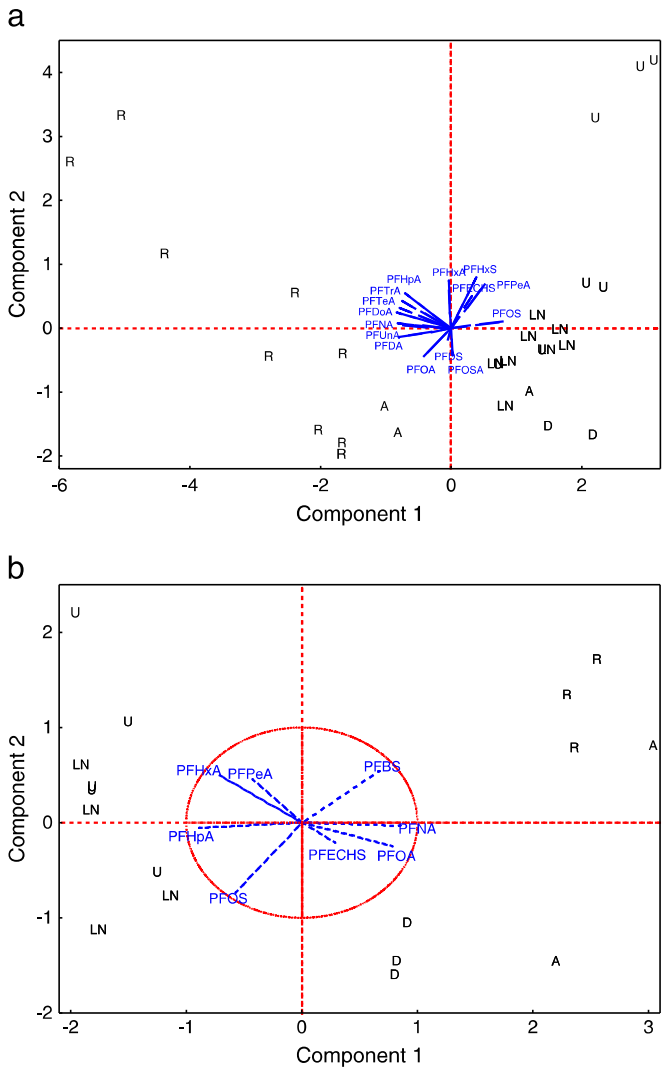

Fig. 3. a, b. Loadings and scores of first two principal components of perfluorinated compounds from reference sites and Welland River, 2010, in a) amphipods and b) water; R: reference site; U: upstream Lake Niapenco, LN: Lake Niapenco, D: downstream Lake Niapenco; A: adjacent to Lake Niapenco. Refer to Figure 1 for sampling locations.

between<MDL to 34.6 ng/L (Scott et al., 2009). The highest value reported in that study (34.6 ng/L) was from Sandusk Creek, which was downstream of a large tire fire that persisted for 17 days in Hagersville, ON; the next highest value was approximately 7.9 ng/L. By comparison, we found that concentrations downstream of the airport in the upper Welland River ranged from 38.4 to 392.0 ng/L.

Usage of AFFF in the defense industry, airports, and fire departments has previously been documented as a point release of PFCs (Moody et al., 2002, 2003; Oakes et al., 2010; Schultz et al., 2004) with some AFFF releases specifically correlated with PFOS contamination. Historically, PFOS was an active ingredient in AFFF (Moody and Field, 2000).

According to assessments performed by the Canadian federal government, PFOS was not manufactured in Canada but was imported as the raw chemical, in products, and in formulations. An estimated usage of PFOS in Canada from 1997 to 2000 was reported as 318 t with one of the applications being AFFF. While there is considerable evidence that PFOS-based AFFF usage occurred in Canada historically, its current use is not clear given manufacturer phase out and government restrictions. The leading global PFOS manufacturer at the time, 3M, announced a phase out of PFOS production by 2002 due to environmental concerns. Despite the phase out, it is possible that PFOS-based AFFF usage continued beyond 2002 in order to use up stocks. Furthermore, production of perfluorooctane sulfonyl fluoride [POSF] plus PFOS (and its salts) production continues in Europe and in China (<42 to 82 t in Europe and <50 t in China in 2003), although by 2006 China had increased its "PreFOS" production to 200 t (Martin et al., 2010). The Canadian federal government introduced PFOS regulations in June 2008, pursuant to the Canadian Environmental Protection Act, 1999. These regulations prohibit the manufacture, use, sale, and import of PFOS-containing products with certain exemptions. One of these exemptions permitted use of AFFF containing PFOS (but not for training or testing purposes) until 2013 if it was manufactured or imported before the regulation was established. A second exemption is that AFFF could be used at any time provided the PFOS concentration was at or below 0.5 ppm (Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations, Canada Gazette, Dec. 16 2006).

PFECHS also appeared to be associated with the airport. Howard and Muir (2010) identified PFECHS as a possible persistent and bioaccumulative substance that was in commerce based on its listing on both the Canadian Domestic Substance List and on the USEPA Toxic Substances Control Act Inventory Update Rule (TSCA-IUR) database from 1986 to 2006. Although there is no evidence to suggest that PFECHS was used in AFFF based on patent literature, it is currently used as an abrasion inhibitor in aircraft hydraulic fluids (U.S. EPA, 2010). It is not definitively known if PFECHS is used in other applications other than in hydraulic fluids. Recently, De Silva et al. (2011) measured PFECHS in top predator fish (<MDL to 3.7 ng g^{-1} wet weight in whole body homogenate) in the Great Lakes and surface waters (0.16 to 5.7 ng L^{-1}).

There has been no (known) monitoring of PFCs from the John C. Munro International Airport; however, other studies have indicated significant runoff into the Welland River. Annual monitoring from 1998 onward has indicated propylene glycol and stormwater management practices implemented by the airport have not been sufficient to prevent contamination into the upper Welland River (Niagara Peninsula Conservation Authority, 2009). Furthermore, in June 2007, Niagara Peninsula Conservation Authority staff observed a spill of unknown compounds into a tributary of the Welland River and reported it to the Ontario Ministry of the Environment Spills Action Centre. In 2005, the airport in Hamilton hosted a one day Aircraft Rescue Firefighting Course, October 1st, which included fire suppression training and hands-on-training involving a burning aircraft (Hamilton International, 2005). Although the specific source of the PFOS has not been determined in the present study, the airport has been source of event release or runoff into the watershed. Given the use of PFCs in AFFFs at airports, the present combined data suggests that the airport is a likely source of elevated PFC contamination in the upper Welland River. However, the presence of PFECHS is also suggestive of contamination originating from airport-related activities. PFECHS is not known to be incorporated in AFFF but has reported usage in aircraft hydraulic fluids. Therefore, AFFF emission is not the sole source of PFC contamination in Lake Niapenco. The airport may also be a source of some other PFCs, as many declined as the distance increased from the airport in either amphipods or water samples. However, we do not have known sources of these compounds, except as possible contaminants or impurities in AFFF. In any case, the concentrations of most other PFCs were much lower than PFOS, especially in amphipods.

Once in the environment, PFAAs will persist (Houde et al., 2011). Following contamination of groundwater by AFFF products, PFCAs were reported in groundwater at the Tyndall Air Force Base, FL, 7–11 years after the last application (Moody and Field, 2000). PFOS is not only highly stable to degradation under either aerobic or anaerobic conditions, but PFAAs are also end products of degradation of PFCs which possess an environmentally labile moiety. These PFCs include FTOHs, FTCAs, FTUCAs, fluorotelomer sulfonates, and perfluorooctane sulfonamides (Butt et al., 2010; Dinglasan et al., 2004; Rhoads et al., 2008).

Table 3
Arithmetic mean (where applicable) concentrations of perfluorinated compounds in water (ng/L) and biota (ng/g ww) from Tyneside Road (Station 5; Fig. 1), Welland River, immediately upstream of Lake Niapenco.

Compound	Water ng/L	Amphipod	Damselfly	Shrimp	Shrimp[a]	Sunfish	Bullhead	Turtle plasma
N (pools)	1	2	2	3	3	1	1	9[b]
PFPeA	2.40	7.42	<0.25	<0.25	<0.25	<0.25	<0.25	<0.1
PFHxA	25.60	2.22	<0.25	<0.25	<0.25	<0.25	<0.25	<0.1
PFHpA	14.74	10.35	0.33	0.3	<0.25	0.71	0.72	<0.1
PFOA	15.90	42.33	2.63	2.00	1.11	1.29	3.03	<0.1
PFNA	2.14	65.51	5.08	3.89	0.78	3.76	10.82	0.1
PFDA	<0.25	12.31	1.31	1.18	0.39	4.85	11.64	2.0
PFUnA	<0.25	3.77	0.35	0.50	0.07	1.33	5.26	1.6
PFDoA	<0.25	0.21	<0.25	<0.25	<0.25	<0.25	1.55	<0.1
PFTrA	<0.25	0.18	<0.25	<0.25	<0.25	<0.25	<0.25	0.1
PFTeA	<0.25	0.23	<0.25	<0.25	<0.25	<0.25	<0.25	<0.1
PFHxS	<0.25	9.92	1.65	2.58	1.06	1.16	3.09	3.2
PFOS	78.20	721.35	170.32	157.46	75.51	507.93	350.83	2065
L-PFOS 99 m/z	60.80							
PFDS	ND	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	0.1
PFECHS	7.30	8.19	0.47	ND		6.10	ND	
PFOSA	ND	1.52	0.64	2.53	4.75	1.44	1.27	
PFBS	7.02							
Sum	135.90	885.52	182.79	157.46	83.68	528.57	388.22	2072

Values listed as <MDL if values were below method detection limits, or as ND if not detected.
[a] Shrimp from other sites downstream of airport.
[b] Individual animals, not pools. Turtles from Lake Niapenco proper.

Kannan et al. (2005) estimated that the bioaccumulation factor (L/kg) of PFOS was approximately 1000 for amphipods (unspecified species) and 2400 for round gobies (*Neogobius melanostomus*). Given the concentrations of PFOS in water and amphipods at the present 17 sampling stations along the Welland River and adjacent watersheds, we estimated that the mean BAF was 6000 L/kg (range 1300–18,000). However, except for the Lake Niapenco site, which had a mean BAF of 13500, at all other sites the amphipods were in running water (Welland River). The BAF for turtle plasma ranged from 18,000 to 42,000; by comparison the BAF for PFOS of fish liver tissue downstream of the Pearson airport following the use of AFFF ranged between 6300 to 125,000 (Moody et al., 2002). The BAFs for turtle plasma are difficult to compare with the BAFs for whole body amphipods or liver in fish, as PFCs tend to be highest in proteinaceous tissues such as blood rather than in lipid stores. Similarly, the estimated mean BAF for PFECHS was 520 (range 4–1530) for amphipods. We found that the concentrations of PFOS were not correlated between amphipods and water among the 17 sampling stations ($r^2 = 0.15$, $F_{[1,10]} = 1.75$ $P < 0.2151$). Given the intermittent nature of streams relative to standing waters, due to varying water flows and water quality, it is likely that the exposure of amphipods (or other biota) varies not just spatially, but temporally as well.

In this study, amphipods had measurable concentrations of PFCs that were below detection limits for damselflies, shrimp, bullhead, sunfish, or turtles (e.g. PFPeA, PFHxA, PFDoA, PFTrA, and PFTeA) from the same location, with the exception of PFDS, which was found in turtle plasma but not in other biota or in water. Benthic species, such as amphipods, often have similar or higher concentrations of PFOS than nonbenthic feeding species that are at the same or higher trophic level (Martin et al., 2004). For example, the amphipod *Diporeia hoyi*, had PFOS concentrations two to six times higher than those of pelagic fish from the same lakes (Martin et al., 2004). Although the sample size is too small to make any strong conclusions, the present study is suggestive that amphipods had higher concentrations of PFCAs and PFSAs compared to fish, damselflies, and shrimp (Table 3).

Conversely, although snapping turtles had fewer PFCAs or PFSAs above detection limits compared to amphipods, concentrations of PFOS in plasma averaged 2377 at Lake Niapenco East (range 866–5392 ng/g ww). From other sites throughout southern Ontario, mean concentrations of PFOS in snapping turtle plasma ranged from 53–171 ng/g among sites with appreciable municipal and/or industrial influences, and was 15 ng/g at a control site. PFOS concentrations in plasma of male and female snapping turtles were 137 and 6.1 ng/g ww, respectively, from Lake St. Clair, Michigan (Kannan et al., 2005). Mean concentrations of PFOS in plasma juvenile Loggerhead (*Caretta caretta*) sea turtles ranged from 1.44–9.34 ng/g ww along the east coast of the US (O'Connell et al., 2010). Keller et al. (2005) reported mean concentrations of 11 and 39.4 ng/g ww in the plasma of adult loggerhead and Kemp's Ridley sea turtles (*Lepidochelys kempii*), respectively. We found that concentrations in PFAAs in snapping turtles from the Welland River were remarkably higher than those reported in reptiles elsewhere, and most wildlife in general, and represent substantial local contamination by PFCs in the watershed. Further monitoring of terminal PFAAs such as PFCAs and PFSAs in this watershed is recommended to ascertain whether the elevated levels are the result of a historic or continued release of contaminants.

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References

Butt CM, Berger U, Bossi R, Tomy GT. Levels and trends of poly- and perfluorinated compounds in the arctic environment. Sci Total Environ 2010;408:2936–65.
Chu SG, Letcher RJ. Analysis of fluorotelomer alcohols and perfluorinated sulfonamides in biotic samples by liquid chromatography–atmospheric pressure photoionization mass spectrometry. J Chromatogr A 2008;1215:92–9.
De Silva AO, Spencer C, Scott BF, Backus S, Muir DCG. Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate in the Great Lakes of North America. Environ Sci Technol 2011;45:8060–6.
de Solla SR, Portelli M, Spiro H, Brooks RJ. Penis displays of snapping turtles (*Chelydra serpentina*) in response to handling: defensive or displacement behaviour? Chel Conserv Biol 2001;4:187–9.
Dinglasan MJA, Ye Y, Edwards EA, Mabury SA. Fluorotelemer alcohol biodegradation yields poly- and perfluorinated acids. Environ Sci Technol 2004;38:2857–64.

Gebbink WA, Hebert CE, Letcher RJ. Perfluorinated carboxylates and sulfonates and precursor compounds in herring gull eggs from colonial sites spanning the Laurentian Great Lakes of North America. Environ Sci Technol 2009;43:7443–9.
Gruber L, Schlummer M, Ungewiss J, Wolz G, Moeller A, Weise N, et al. Tissue distribution of perfluorooctansulfonate (PFOS) and perfluorooctanoic acid (PFOA). Organohalogen Compd 2007;69:2889–91.
Hamilton International. Hamilton International firefighters hosts aircraft rescue firefighting course; 2005 http://hamiltonairport.brickworkscomm.com/newsletter.php?id=52.
Helsel DR. Fabricating data: how substituting values for nondetects can ruin results, and what can be done about it. Chemosphere 2006;65:2434–9.
Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DCG. Biological monitoring of polyfluoroalkyl substances: a review. Environ Sci Technol 2006;40:3463–73.
Houde M, De Silva AO, Muir DCG, Letcher RJ. Monitoring of perfluorinated compounds in aquatic biota: An updated review. Environ Sci Technol 2011;45:7962–73.
Howard PH, Muir DCG. Identifying new persistent and bioaccumulative organics among chemicals in commerce. Environ Sci Technol 2010;44:2277–85.
Kannan K, Tao L, Sinclair E, Pastva SD, Jude DJ, Giesy JP. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. Arch Environ Contam Toxicol 2005;48:559–66.
Keller JM, Kannan K, Taniyasu S, Yamashita N, Day RD, Arendt MD, et al. Perfluorinated compounds in the plasma of loggerhead and Kemp's ridley sea turtles from the southeastern coast of the United States. Environ Sci Technol 2005;39:9101–8.
Kishi T, Arai M. Study on the generation of perfluorooctane sulfonate from the aqueous film-forming foam. J Hazard Mater 2008;159:81–6.
Levine AD, Libelo EL, Bugna G, Shelley T, Mayfield H, Stauffer TB. Biogeochemical assessment of natural attenuation of JP-4-contaminated ground water in the presence of fluorinated surfactants. Sci Total Environ 1997;208:179–95.
Martin JW, Whittle DM, Muir DCG, Mabury SA. Perfluoroalkyl contaminants in a food web from Lake Ontario. Environ Sci Technol 2004;38:5379–85.
Martin JW, Asher BJ, Beesoon S, Benskin JP, Ross MS. PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? J Environ Monit 2010;12:1979–2004.
Moody CA, Field JA. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. Environ Sci Technol 2000;34:3864–70.
Moody CA, Martin JW, Kwan WC, Muir DCG, Mabury SA. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek. Environ Sci Technol 2002;36:545–51.
Moody CA, Hebert GN, Strauss SH, Field JA. 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 2003;5:341–5.
Niagara Peninsula Conservation Authority. Hamilton International Airport Biological Assessment of Water Quality 2008. Prepared for Damian Boucaud, Airport Operations Coordinator. Hamilton International Airport; 2009.
O'Connell SG, Arendt M, Segars A, Kimmel T, Braun-McNeill J, Avens L, et al. Temporal and spatial trends of perfluorinated compounds in juvenile Loggerhead Sea Turtles (*Caretta caretta*) along the East Coast of the United States. Environ Sci Technol 2010;44:5202–9.
Oakes KD, Benskin JP, Martin JW, Ings JS, Heinrichs JY, Dixon DG, et al. Biomonitoring of perfluorochemicals and toxicity to the downstream fish community of Etobicoke Creek following deployment of aqueous film-forming foam. Aquat Toxicol 2010;98:120–9.
Ontario Ministry of the Environment. Guide to eating Ontario sport fish 2010–2011. RevisedTwenty-sixth Edition. Toronto: Queen's Printer for Ontario; 2011. 285 pp.
Powley CR, George SW, Ryan TW, Buck RC. Matrix effect-free analytical methods for determination of perfluorinated carboxylic acids in environmental matrixes. Anal Chem 2005;77:6353–8.
Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. Sources, fate and transport of perfluorocarboxylates. Environ Sci Technol 2006;40:32–44.
Rhoads KR, Janssen E, Luthy RG, Criddle CS. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE) in activated sludge. Environ Sci Technol 2008;42:2873–8.
Rogers RS. Chem Eng News 1999;77:30. April 12.
Schultz MM, Barofsky DF, Field JA. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. Environ Sci Technol 2004;38:1828–35.
Scott BF, Spencer C, Lopex E, Muir DCG. Perfluorinated alkyl acid concentrations in Canadian Rivers and Creeks. Water Qual Res J Can 2009;44:263–77.
Skutlarek D, Exner M, Färber H. Perfluorinated surfactants in surface and drinking waters. Environ Sci Pollut Res 2006;13:299–307.
U.S. EPA. Recent advances in perfluoroalkyl acid (PFAA) research. Perfluoroalkyl acids (PFAA) days III workshop. North Carolina, USA, June 2010; 2010.
Villanueva P. MLE-based procedure for left-censored data excel spreadsheet. Washington, DC: Office of Pesticide Programs. U.S. Environmental Protection Agency; 2005.