Long-Term Environmental Fate of Perfluorinated Compounds after Accidental Release at Toronto Airport

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Ⓢ *Supporting Information*

ABSTRACT: Perfluorooctane sulfonate (PFOS; a perfluorinated compound or PFC), its salts, and perfluorooctane sulfonyl fluoride have recently been listed in Annex B of the Stockholm Convention due to their widespread presence, persistence, and toxicity. Because of the persistent nature of PFCs, it is generally presumed that the impact of direct discharges of these chemicals on a receiving environment would be long-lasting. However, long-term environmental fate studies based on field measurements are rare. We examined spatial and long-term (9 year) temporal trends of PFCs in water, sediment, fish, and fish liver collected in 2003, 2006, and 2009 from 10 locations spanning ~20 km in Etobicoke and Spring Creeks, where an accidental release of fire fighting foam containing PFOS from nearby Toronto International Airport occurred in 2000. Even a decade after the spill, sediment PFOS concentrations are still elevated in Spring Creek Pond which received the foam discharge; however, the major impact is relatively localized likely due to the stormwater management nature of the pond and the diluting effect of Etobicoke Creek. Fish and fish liver PFOS concentrations at a Spring Creek location downstream of Spring Creek Pond declined by about 70 and 85%, respectively, between 2003 and 2009. PFOS in water at locations further downstream in Etobicoke Creek have declined by >99.99% since the spill; however, the 2009 water and fish levels were ~2–10 times higher than upstream locations likely due to the long-term impact of the spill as well as urbanization. The decrease in the upstream PFOS concentrations likely reflects the reduction of PFOS sources due to phased out production by 3M and regulations on the use of PFOS in fire fighting foams. Field-based sediment/water distribution coefficients (K_D) and bioaccumulation factors (BAF) were calculated from environmental measurements. Log K_D values were 0.54–1.65 for perfluoroalkyl sulfonates (PFASs) and 1.00–1.85 for perfluorocarboxylates (PFCAs). Log BAF_{fish} ranged from 1.85 to 3.24 for PFASs and 0.88–3.47 for PFCAs, whereas log $BAF_{fish\ liver}$ ranged from 2.1–4.3 for PFASs and 1.0–5.0 for PFCAs.
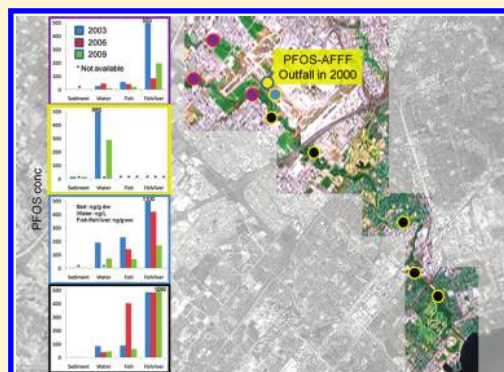
■ INTRODUCTION

Perfluorinated compounds (PFCs) such as perfluoroalkyl sulfonates (PFASs) and perfluorocarboxylates (PFCAs) have been produced in large quantities since the 1950s;[1,2] however, they have emerged as priority environmental contaminants only during the past decade. PFCs have low water and oil solubility, and unique surface properties, making them particularly useful as surfactants, in fabric and paper treatments, and in aqueous film-forming foam fire fighting agents (AFFF). A recent estimation for the historical global production of perfluorooctanesulfonate (PFOS), one of the most manufactured PFCs, was ~10 000 t.[2] The large number of carbon–fluorine bonds with full substitution of hydrogen by fluoride also make PFCs chemically stable and thus environmentally persistent.[3]

PFCs are ubiquitous in various environmental media worldwide,[4,5] including remote locations such as the Arctic[6] and the Tibetan Plateau.[7] They have been detected in various organisms at different

trophic levels including humans and have been identified as bioaccumulative.[3,8–11] PFCs have been recognized as endocrine disruptors, immuntoxicants, and potential carcinogens and have shown evidence of causing developmental delays and neonatal mortality in animal studies.[12] PFCs have also been associated with negative human health effects such as low birth weight and thyroid diseases.[13,14]

Due to the persistent, bioaccumulative, and toxic characteristics of PFCs, efforts have been made to limit their production and use. The major manufacturer of PFOS and PFOS-related
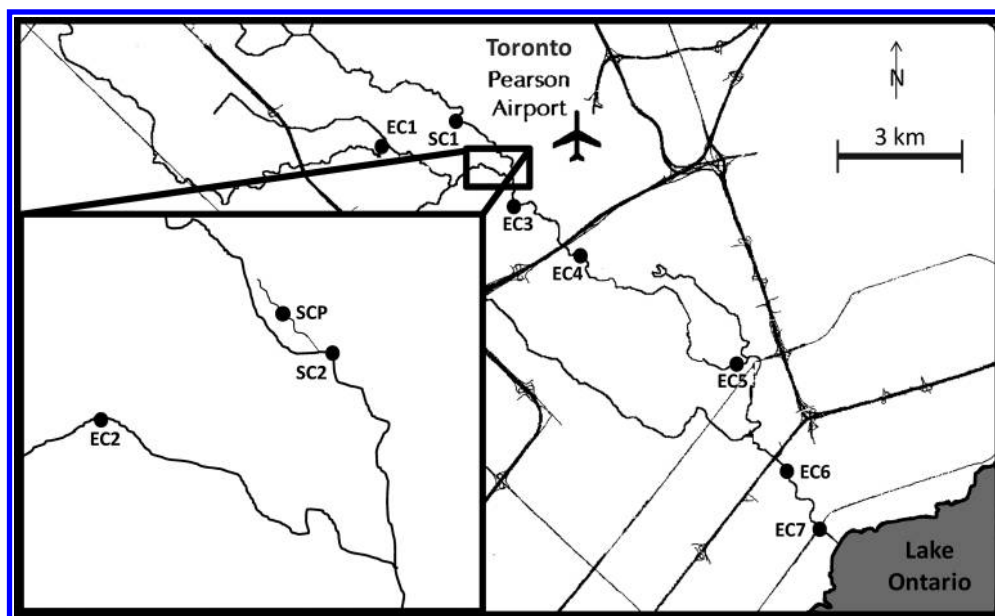
Figure 1. Map showing sampling locations along Etobicoke Creek (EC), Spring Creek (SC), and Spring Creek Pond (SCP).

products (3M Company) voluntarily phased out use of this compound in 2002, and PFOS-based AFFF has not since been imported into Canada. As per a regulation in 2008, existing AFFF stock containing PFOS are being removed and can be used until 2013 for emergency fires only, not for testing and practice.[15] In 2009, PFOS, its salts, and perfluorooctane sulfonyl fluoride were listed in Annex B of the Stockholm Convention on persistent organic pollutants[16] and added to Canada's virtual elimination list.[17] As a result of such regulations, the environmental and therefore human exposure pattern of PFCs have shifted from PFOS and PFOA to longer chain PFCAs.[18,19]

Aquatic systems are regarded as a major sink and the most important medium for PFC transport in the environment.[20,21] PFCs in the aquatic environment can directly contribute to human exposures via drinking water[22] and aquatic products such as fish and shellfish.[23] Emission pathways of PFCs to the aquatic environment include releases from manufacturing, wastewater treatment plants, and AFFF.[24−27] A few studies have reported temporal trends of PFCs in aquatic systems after discharges of AFFF.[27−30] However, these studies monitored PFC concentrations for only a few months, and based on the persistent nature of PFCs it is generally presumed that a release event could have a much longer lasting environmental impact. Furthermore, field-based information on multimedia PFC distribution is limited,[24] making it challenging to understand the behavior of these chemicals in the environment.

In this study, we examine spatial and long-term (9 year) temporal trends of PFCs in water, sediment, fish, and fish liver from Etobicoke and Spring Creeks after discharges of AFFF in 2000, 2002, and 2005 from nearby Toronto International Airport.[27,28] It has been demonstrated that a number of biochemical reactions occur in the liver cells of fish exposed to PFOS.[28,31] Thus, PFOS measurement in fish liver is important for toxicity evaluations via bioassays. The samples were collected in 2003, 2006, and 2009 from 3 locations upstream and 7 locations downstream of the 2000 spill outfall site. We calculated field-based sediment/water distribution coefficients (K_D) and bioaccumulation factors (BAF) from these multimedia measurements to better understand PFC behavior in aquatic systems.

■ MATERIALS AND METHODS

AFFF Spill History. On June 8, 2000, a fire alarm at an airline hanger at the L.B. Pearson Toronto International Airport malfunctioned, releasing 22,000 L of AFFF [trade name FC-206FC Light Water AFFF (inactive); produced by 3M] and 450,000 L of water from the sprinkler system into the storm sewers.[27] The AFFF passed through catch basins and storm sewers before being discharged into nearby Spring Creek (Figure 1). The total quantity of PFC released was estimated at 330−1650 kg.[27] In April 2002, a relatively minor AFFF spill occurred on the airport property (unknown amount; Randy McGill, Greater Toronto Airport Authority; Personal communication), which was contained in the nearby newly constructed Spring Creek Pond. This pond controls stormwater flow into Spring Creek, which merges into Etobicoke Creek (Figure 1). On August 2, 2005, 48,000 L of AFFF was applied to extinguish the fire caused by Air France flight 358 overrunning the runway. The majority of the AFFF applied was washed into Etobicoke Creek, downstream of Spring Creek, between EC3 and EC4 (locations described in Study Design below), by the dilution water and heavy precipitation. However, according to Oakes et al.,[28] the AFFF used in the 2005 incident did not contain PFOS, as it did in 2000 (and likely in 2002).

Study Design. Surface water, sediment, and forage fish (yearling whole body and young of the year liver) samples were collected from 10 locations (Figure 1) in the fall of 2003, 2006, and 2009 by staff from the Ontario Ministry of the Environment (OMOE), Ontario, Canada. One location (SCP) was in Spring Creek Pond within 100 m of the stormwater outfall that discharged AFFF spill runoff. Spring Creek Pond is <250 m long, acts as a stormwater management pond, and has a high and low flow outlet into the adjacent Spring Creek. In Spring Creek, two locations, one (SC1) ~2 km upstream and the other (SC2) within 100 m downstream of possible Spring Creek Pond overflow points, were sampled. Approximately 700 m from SC2, Spring Creek merges into Etobicoke Creek, which flows into Lake Ontario approximately 17 km downstream (Figure 1). In

Etobicoke Creek, sampling included two locations EC1 and EC2 about 5 km and 800 m upstream of the Spring/Etobicoke Creek confluence, respectively, and five locations, EC3, EC4, EC5, EC6, and EC7 approximately 1.7, 4.5, 10, 15, and 16.5 km downstream of the outfall, respectively.

Water and sediment sampling locations were relatively similar between years (within 14—41 m), with some exceptions (EC1 2003 vs 2006/2009: ~220 m; EC2 2009 vs 2003/2006: ~100 m; SC2 2006 vs 2003/2009: ~185 m; EC3 2006 vs 2003/2009: ~400 m; EC4 2009 vs 2003/2006: ~135 m; EC7 2006 vs 2003/2009: ~480 m). Fish samples were collected in the vicinity of the water/sediment stations when possible. In 2009, fish habitat was difficult to find at EC2, and the fish samples were collected approximately 100 m upstream of the water/sediment sample locations. Fish and fish liver samples were not collected from SCP due to the absence of fish; frequent drying of the creek likely prevented the establishment of fish populations. Due to limited fish size range availability, 2003 fish liver samples were not collected at EC4 and EC5. Samples were not collected from SCP, EC5, and EC6 in 2006 due to limitations of resources at that time.

Sampling Methods. Single grab water samples were collected in plastic bottles (1.5 L high-density polyethylene (HDPE) bottles in 2003 and 500 mL poly-ethylene terephthalate (PET) bottles in 2006 and 2009) from just below the water surface after rinsing the bottles three times with sample water. The sediment samples consisted of a composite of three grab samples representing the top 5 cm of fine silty sediment collected with a metal spoon and bowl. The samples were homogenized and placed in 500 mL PET jars. Fish were collected by seine net and consisted of young of the year common shiner (*Notropis cornutus*) 37—74 mm in length and yearling common shiner 80—155 mm in length.

The water and sediment samples were stored in a cooler, and the fish samples were kept on ice during transport to the OMOE laboratory in Toronto. At the laboratory, the total length of each fish was recorded, and the livers were extracted from the yearling common shiners. Liver samples from two to six fish were composited for each location and kept at −20 °C in food-grade plastic bags until analysis. Composite samples of five to ten young of the year common shiners (whole fish of similar size) were homogenized and refrozen at −20 °C in glass vials until analysis. Water and sediment samples were refrigerated at 5—6 °C until analysis.

Sample Preparation and Analysis. Complete details of sample preparation and analysis are provided in the Supporting Information (SI). Briefly, water samples were extracted using solid phase extraction (SPE) with a Waters Oasis HLB cartridge,[32] and sediment and biota samples were extracted by a modified Hanson procedure using tetra-*n*-butyl ammonium hydrogen sulfate (TBAS) and methyl *tert*-butyl ether (MTBE).[33] C13-labeled surrogates ($^{13}C_4$—PFOA) and internal standards ($^{13}C_2$—PFOA, $^{13}C_4$—PFOS, $^{13}C_5$—PFNA, $^{13}C_2$—PFDA, $^{13}C_2$—PFDoA) were added during sample processing for quantification and to monitor method performance (refer to SI Table S1 for acronym definitions). Blanks, duplicate, reference, and native analyte-spiked samples were analyzed with each batch of samples to monitor for contamination and analyte recovery. The fish livers from 2003 were processed and analyzed in a similar manner, except only 7H-dodecafluoroheptanoic acid (7H-DoFHpA) was used as an internal standard. Final methanol sample extracts were analyzed using liquid chromatography tandem mass spectrometry (LC-MS/MS) in negative electrospray ionization multiple reaction

monitoring (MRM) mode. The $m/z = M^-$ to $[M\text{-}44]^-$ transition was monitored for the carboxylic acids, and the $m/z = M^-$ to $[99]^-$ transition was monitored for the sulfonates. This transition is less sensitive than the alternate $m/z = M^-$ to $[80]^-$ transition but is free from interferences from cholic acids.[34] The method is accredited to ISO 17025 standards. The water method participated in the final validation to the ISO method 25101 and participates in performance evaluation studies through QUASI-MEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe). The biota sediment method participates in regular performance evaluation studies through the NCP (Northern Contaminants Program) quality assurance program. Sediment samples collected in 2009 were also analyzed for total organic carbon by coulometry using the OMOE method ORGC3012.[35]

■ RESULTS AND DISCUSSION

Spatial and Temporal Trends. We focus on the spatial and temporal trends of PFOS (Figure 2, SI Tables S2—S5), which is the predominant PFC in all four media and the main PFC component of the 22,000 L AFFF accidentally released at Toronto International Airport in 2000. The results for water, sediment, and fish liver should be viewed with caution due to the low sample sizes.

Water. PFOS was detected in all water samples and was the predominant PFC compound. Spatial and temporal variations of PFOS water concentrations are shown in Figure 2a. The highest PFOS concentrations were detected at SCP, which is closest to the stormwater outfall that carried spilled AFFF from the airport. The 2003 and 2009 levels were 690 and 290 ng/L, respectively (we lacked 2006 measurements for this location). The concentrations at SCP were ~25—40 times higher than the upstream concentrations (average of EC1 and SC1). EC2 is also upstream of the spill site, and PFOS levels in water were similar to the other further upstream locations EC1 and SC1 in 2003 and 2009. However, the 2006 EC2 levels were relatively elevated and initially attributed to a possible source from a fire training facility on the airport property just upstream of EC2. Further investigations revealed that the fire training facility uses "training foam" (i.e., non-PFOS-based AFFF), has a catchment tank with impermeable liner, and filters and reuses the water. It is possible that an industrial drain that discharges into Etobicoke Creek upstream of EC2 might have influenced the 2006 concentrations. We have received unconfirmed information about a possible cleanup/upgrade to the drain, which could have contributed to the lower concentrations in 2009.

The PFOS concentrations at SC2 (250 m downstream of SCP in the adjacent Spring Creek into which Spring Creek Pond overflows) were considerably (>70%) lower than SCP in both 2003 and 2009. At EC3, ~1.5 km downstream of SCP and <1 km downstream of the Spring/Etobicoke Creeks confluence, PFOS concentrations decreased by ~90% and ~75% in 2003 and 2009, respectively, compared to the levels at SCP. The decrease could be attributed to dilution as Spring Creek merges into Etobicoke Creek. PFOS concentrations at SC2, EC3, and EC4 in 2006 were lower than those observed at the same locations in 2009, which may be due to dilution from elevated precipitation (49 mm rainfall) during the week before the 2006 sampling, as compared to 2.2 mm for SC2/EC3 and 23 mm for EC4 in 2009.[36] For SC2, the lower 2006 levels could also be attributed to the different 2006 sampling station (~185 m upstream of 2003 and 2009
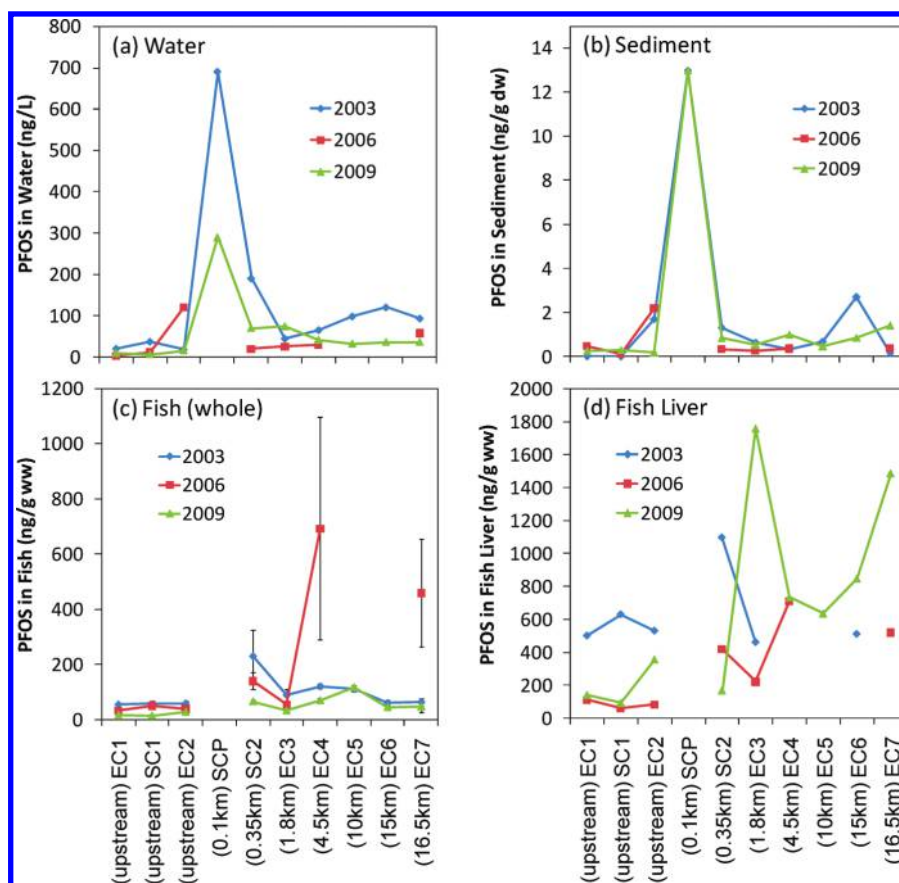
Figure 2. Spatial and temporal trends of PFOS in (a) water, (b) sediment, (c) whole fish, and (d) fish liver sampled in 2003, 2006, and 2009 from locations in Etobicoke Creek (EC) and Spring Creek (SC), upstream and downstream of the AFFF spill outfall in Spring Creek Pond (SCP). The fish concentrations are the median of 4−6 fish composites each containing 5−10 fish caught at each location, and the error bars represent one standard deviation of the measurements.

stations), which is parallel to Spring Creek Pond (compared to the other stations being downstream of the pond) and expected to be only partially impacted by the spill.

PFOS concentration in water collected further downstream of the spill outfall site (corresponding to just downstream of EC4 in this study) was ∼10[6] ng/L one day after the accident and decreased to ∼300 ng/L five months later.[27] PFOS concentration in water further decreased to 65−120 ng/L in 2003 and 29−41 ng/L in 2009, representing >99.9% decline since the spill (Figure 2a). The 2003 and 2009 concentrations are similar to reported values of 15−121 ng/L in 2003 Lake Ontario water.[37]

For all three sampling years, the PFOS water concentrations further downstream (average of EC6 and EC7) were still 5−10-fold greater than the upstream concentrations (average of EC1 and SC1). For EC3 to EC7, where Etobicoke Creek passes through a heavily urbanized area, an increasing trend in PFOS water concentrations was observed for 2003 and 2006. This trend is in agreement with other studies showing urban areas as a possible source of PFCs including PFOS.[4,38] However, to our knowledge, there is no wastewater discharge to Etobicoke Creek. In contrast, we found PFOS concentrations in 2009 slightly lower in the water sampled downstream. This observation likely reflects the phasing out of PFOS-containing products used in the urban area.

The 2009 PFOS concentration (290 ng/L) at SCP near the spill outfall was almost an order of magnitude greater than the

highest value of 34.6 ng/L reported from a study of 38 rivers across Canada.[39] The concentrations at locations just downstream (70 ng/L at SC3 and 74 ng/L at EC3) were almost twice as high, whereas the levels at locations further downstream EC4 to EC7 were comparable (32−41 ng/L). In contrast, the 2009 PFOS water concentrations at the upstream locations (6 ng/L at SC1 and 9.5 ng/L at EC1) were 3−6 times lower than 34.6 ng/L. These results suggest that the long-term impact of the AFFF spill on water quality at the downstream locations is evident. All 2009 PFOS concentrations in water were below the Estimated No-Effects Value (ENEV) of 491 ng/L used by Environment Canada[40] for a pelagic organism chronic end point. The 2009 water concentration at SCP (290 ng/L) near the spill outfall was 1.7 times lower than the ENEV, and the concentrations at the upstream and downstream locations were 31−82 and 7−15 times lower than the ENEV, respectively. Furthermore, the creek water is not a source of drinking water, and hence human exposure through that route is expected to be minimal.

Sediment. Similar to the water samples, elevated PFOS concentrations in the sediments were observed at SCP (Figure 2b). Whereas the PFOS concentration in water in 2003 was about twice as high as that of 2009, the two sediment concentrations were equal (13 ng/g dry weight). This could partly be attributed to different sampling stations at this location (∼100 m downstream of the outfall in 2003 compared to ∼10 m in 2009). This

sediment concentration is at least 1.5 times higher than PFOS concentrations in sediment from rivers, lakes, canals, and inland seas reported by other studies;[20,24,41−43] however, the SCP results were more than an order of magnitude lower than the levels found in Yangtze River Estuary, China.[44] It is possible that PFOS reached saturation in the SCP sediment due to greater affinity for water than for particles. It is noteworthy that the sediment PFOS levels at SC2 in Spring Creek, just 250 m downstream of SCP in Spring Creek Pond, decreased by >90% compared to ∼70% decline in the water between 2003 and 2009. This is likely a result of limited input from Spring Creek Pond due to its stormwater management nature and suggests a relatively localized impact of the AFFF spill on the PFOS sediment levels.

PFOS concentrations in sediment at site SC2 in 2006 were lower than 2003 and 2009 partly due to the different sampling location as mentioned for water above. As in the water samples, the downstream (average of EC6 and EC7) sediment PFOS levels (1.1 ng/g dw) were ∼5 times higher than the upstream levels (average of EC1 and SC1) and reflect impacts from the AFFF spill as well as urbanization. The observed covariation of PFOS concentrations in the sediment and water may be due to rapid equilibration between these phases. Laboratory kinetics experiments suggest PFOS can reach empirical equilibrium between water and sediment in ∼100 h.[45] Relatively higher PFOS concentrations in sediment collected in 2003 and 2006 (∼2 ng/g) at the upstream location EC2 could be a result of impacts from an industrial drain as mentioned above.

Fish. PFOS concentrations in fish (Figure 2c) for each location are based on the median values of 4−6 fish composites, each containing five to ten fish. In the absence of fish and fish liver samples from SCP, where the highest water and sediment PFOS concentrations were measured, fish collected from site SC2 best reflect impacts from the spill. At SC2, median fish PFOS concentrations decreased from 230 ng/g wet weight (ww) in 2003 to 140 ng/g ww in 2006 to 65 ng/g ww in 2009, which is a 70% decline between 2003 and 2009. In contrast to the water and sediment PFOS temporal trends at SC2, a continuous decrease in PFOS from 2003 to 2009 was observed in fish at this location. The water and sediment concentrations sampled at a single time point are more likely to be affected by factors such as dilution and high temporal/spatial heterogeneity and variability. The forage fish we sampled likely represented the surrounding habitat area and reflected integrated contaminant levels at the sampling locations.

Interestingly, although water and sediment PFOS levels at EC2 were elevated compared to the further upstream locations for at least one time point, likely due to impact from the industrial drain, levels of PFOS in fish from EC2 were generally similar to the upstream locations (EC1 and SC1) for all time points considered (Figure 1c).

The forage fish samples collected in 2009 from five locations in Etobicoke Creek downstream of the spill outfall had PFOS concentrations ranging from 32−117 ng/g ww. These concentrations are much higher (2−8 times) than the values measured for the two most upstream locations (17 and 14 ng/g ww) and are comparable to that of mature lake trout from Lake Ontario,[46] despite the fact that the fish in this study were only ∼5 cm long and less than 1-year old.

Concentrations of PFOS in 2006 fish samples from EC4 and EC7 were extremely high for unknown reasons. Although it has been suggested that the use of AFFF just upstream of EC4 during the 2005 Air France fire incident at the airport was likely not

PFOS-based,[28] the AFFF release may have influenced 2006 PFOS levels in downstream fish. Excluding these two time/location points, PFOS concentrations in fish along Etobicoke Creek generally decreased over time, and the downstream levels were higher than the upstream. This is consistent with the PFOS concentrations in water and may reflect the long-term impact of the AFFF spill on the aquatic system and/or potential sources from the more urbanized areas downstream.

Although the major impact of the spill was relatively contained in Spring Creek Pond, the effect of the spill was evident even 15 km downstream of the spill outfall and almost a decade after the spill occurred. Since urban sources could have influenced this upstream/downstream comparison, an assessment of PFC content in forage fish from other Greater Toronto Area creeks/rivers is recommended to identify the true impact of the spill on downstream Etobicoke Creek fish. Since the population of sport fish in Etobicoke Creek is poor, human exposure to PFOS through the consumption of sport fish is expected to be minimal.

Fish Liver. PFOS concentrations in fish liver analyzed in this study were generally higher than in the corresponding fish, which is similar to the findings of other studies.[43,47] The average PFOS concentration in fish livers collected upstream of the spill site in 2000 (approximately corresponding to SC1 in this study) was 9200 ng/g ww.[27] The PFOS concentration decreased over the subsequent years of this study (Figure 2d), reaching 500 ng/g ww in 2003 and 58 and 92 ng/g ww in 2006 and 2009. This trend also corresponds very well with the reported concentration of ∼300 ng/g ww PFOS in fish livers collected upstream of the spill site in 2005 by Oakes et al.[28] PFOS in fish livers collected from the two upstream locations EC1 and SC1 declined by approximately the same magnitude over the years, although EC2 showed high variability (Figure 2d). A declining PFOS trend, albeit at lower rates, was also observed for whole fish at all three upstream locations EC1, SC1, and EC2 with declines of 53−76% between 2003 and 2009 (Figure 2c). Locations upstream of the spill site are not believed to be affected by the AFFF spill. The decrease in PFOS concentration in fish and fish liver likely reflects the reduction of PFOS sources due to national and international efforts to limit PFOS production and use.

PFOS concentrations in the fish livers collected within the airport territory 21 days after the spill in 2000 were 2000−72900 ng/g ww.[27] A comparison of these measurements with the PFOS in fish livers collected in this study from SC2, just downstream of the AFFF spill site, shows a declining trend with concentrations of 1100, 420, and 170 ng/g ww in 2003, 2006, and 2009, respectively. This is a reduction of 92−99% during the decade following the spill and ∼85% between 2003 and 2009. PFOS concentrations in fish livers from the downstream locations were elevated compared to the upstream locations. Further, greater temporal and spatial variations in the downstream PFOS fish liver concentrations were observed compared to the fish liver from the upstream locations and other (water, sediment, whole fish) samples from the same downstream locations. It appears that factors other than direct sources affect PFOS concentration in fish liver, as suggested by a large RSD of 97% reported for PFOS in fish livers collected from the same location.[27]

PFC Profiles. Examining the relative abundance of individual PFC compounds has been shown to be useful to investigate sources, environmental transport, and bioaccumulation of PFCs.[20,38,48−50] The composition profiles of PFCs in water, sediment, fish and fish liver along Etobicoke Creek in 2003, 2006, and 2009 are presented in SI Figure S1.

Water. The PFC profiles in water were similar in 2003 and 2009 and were relatively higher in PFOS than in 2006 when lower PFOS concentrations were observed. PFHxS and PFOS concentrations were highly correlated with each other ($r = 0.93$, $p = 0.0254$), indicating common sources (SI Figure S2). The sources could originate from urban areas as a higher relative abundance of PFHxS and PFOS is found downstream than upstream, which is consistent with studies showing urban areas as sources of PFCs to rivers.[51] PFOS and PFOA were the predominant PFCs in all the water samples, accounting for 58−88% of the total PFCs. Of the 28 water samples, 19 samples had higher PFOS concentrations than PFOA. Of the nine samples in which PFOA was dominant, six were from the upstream locations. PFOS has been measured at higher levels than PFOA in water samples from the Great Lakes,[52] estuarine and coastal areas in Korea,[48] the Orge River in France,[43] and the Pearl River in China,[53] whereas PFOA was the predominant PFC in waters from rivers in Japan[38] and the Yangtze River in China.[53] Elevated PFOS/PFOA ratios are suggestive of unique localized sources of PFCs.[48] The PFOS/PFOA ratios of 22 and 10.1 at SCP in 2003 and 2009, respectively, confirm a unique source in the form of AFFF spilled in 2000 in that area.

Sediment. The PFC profiles in the sediments were different for the three sampling years and can be attributed to low detection frequency for many PFCs. PFOS and PFOA were the most frequently detected. The relative abundance of PFOS compared to PFOA was higher in sediment than in water, which reflects the difference in sediment-water distribution coefficient between the two compounds.[24] It is interesting to note that in the 2009 sediment samples, PFDS and long-chain PFCAs such as PFDoA and PFTeA were detected most and that PFDoA and PFTeA were in greater abundance than PFOS and PFOA at the upstream locations. However, this was not consistently observed for the 2003 and 2006 sediments, for which PFOS was in greater abundance. This likely reflects changes in PFC sources after 2006.

Fish and Fish Liver. The composition profile of PFCs in fish was different from that in water. The short-chain PFASs and PFCAs such as PFHxS, PFHpA, and PFOA were not detected or were at a very low abundance in fish compared to water. This reflects different bioaccumulation potentials of the various PFCs. The fish PFC profile for SC2, which was the closest fish sampling location downstream of the AFFF spill outfall, was dominated by PFOS. This relative PFOS abundance (62−80% of total PFCs) was higher than the upstream locations EC1 (34−49%), EC2 (45−58%), and SC1 (27−59%) and immediate downstream location EC3 (52−58%). This further indicates that a legacy PFOS source still exists at the 2000 spill outfall. For locations upstream and further downstream of the spill outfall, the differences in 2003 and 2009 fish PFC profiles (notably higher abundance of PFDS in 2003 in contrast to PFDoA and PFTeA in 2009) likely reflect a source pattern shift from PFASs to PFCAs with changes in PFC production over the past decade.

Generally, the PFC profile in fish livers was similar to that of whole fish. PFOS was the most abundant compound and the relative abundance increased downstream. The PFC profile in 2003 fish livers was different from the corresponding whole fish likely because PFDS and PFOSA were not examined in the 2003 livers.

The importation of PFOS-containing AFFF to Canada ceased in 2002, and a regulation in 2008 restricted the use of existing stocks to emergency use only.[15] In 2005, another incident involving fire on Air France flight 358 at the Toronto airport resulted in the application of 48,000 L of AFFF. High PFOS concentrations found in fish livers collected from the airport property 21 days after the accidental spill in 2000[27] were not observed in fish liver samples collected at the application site or further downstream 9 days after the 2005 incident.[28] This finding, together with the Material Safety Data Sheet for the 2005 AFFF, indicates that the composition of the AFFF was different from the one used in 2000.[28] This is consistent with the study in which a few AFFF samples manufactured after 2002 were analyzed using LC-MS/MS, and very low or no concentration of the known fluorinated compounds were found.[54] However, ^{19}F-NMR of these AFFF samples suggested compounds similar in structure to PFOS were present. These compounds may degrade to PFOS[38] and could act as a secondary source of PFOS found in Etobicoke Creek.

Field-Based Sediment/Water Distribution Coefficients and Bioaccumulation Factors. Field-based sediment/water distribution coefficients (K_D, L/kg) and bioaccumulation factors (BAF, L/kg) have been successfully used to verify laboratory-determined parameters and as inputs to environmental models.[24,43] K_D is the ratio of a chemical's concentration in sediment (ng/g dw) to its concentration in water (ng/L). The organic carbon/water distribution coefficient ($K_{OC} = K_D/f_{OC}$) was also calculated for the 2009 sediment samples. Fish and fish liver BAFs were calculated as the ratio of the concentration (ng/g ww) in fish and fish liver to the concentration in water (ng/L). No clear temporal and spatial trends in PFOS K_D, K_{OC}, or BAF were observed, including at the location closest to the spill site. We therefore report mean, standard error of the mean (SE), range, and number of values for each compound in Table 1.

Log K_D values derived from this study were 0.54−1.65 for PFASs and 1.00−1.85 for PFCAs. Most of these values were about an order of magnitude lower than those reported for locations in The Netherlands and France,[24,43] with the exception of the PFHpA, which was slightly higher.[43] K_D is sensitive to many environmental factors such as pH and salinity of water and the organic fraction of sediment.[43,45] Normalizing K_D to f_{OC} for the 2009 sediment reduced the RSD among the sampling locations from 11−40% to 5−20% for individual compounds. However, in contrast to the study by Kwadijk et al.,[24] weak or no correlations between K_D and f_{OC} were observed for linear-PFOS (SI Table S6). This may be caused by the contribution of an inorganic fraction such as mineral surface to the sorption of PFCs onto sediment.[55] Log K_{OC} for PFOS derived from this study (2.10 ± 0.07; Table 1) was about one log-unit lower than Log K_{OC} reported in other field-based studies;[24,43] however, it was closer to the log K_{OC} of 2.57 ± 0.13 derived in a laboratory experiment.[45]

Bioaccumulation of PFCs is usually quantified using wet weight based concentrations of PFCs in organisms due to the lack of knowledge of the binding sites.[56] Normalizing for lipid content, commonly done for neutral persistent organic pollutants, is generally considered to be inappropriate because PFCs are thought to be associated with proteins.[56] Log BAF$_{fish}$ ranged from 1.85−3.24 for PFASs and 0.88−3.47 for PFCAs, whereas Log BAF$_{fish\ liver}$ ranged from 2.1−4.3 for PFASs and 1.0−5.0 for PFCAs. BAF$_{fish\ liver}$ were generally higher than BAF$_{fish}$, which is consistent with other research.[43] Enrichment of PFCs in fish liver has been attributed to specific protein families.[43] However, the exact mechanism of PFC bioaccumulation and binding sites within organisms remains unclear. The differences in BAF$_{fish}$ and BAF$_{fish\ liver}$ between this and other studies[24,43] were generally less

Table 1. Sediment/Water Distribution Coefficient (K_D), Organic Carbon/Water Distribution Coefficient (K_{OC}), and Bioaccumulation Factor (BAF) Based on Fish and Fish Liver[a]

compound	Log K_D (L/kg)	Log K_{OC} (L/kg)[b]	Log BAF_{fish} (L/kg)	Log $BAF_{fish\ liver}$ (L/kg)
PFHxS	0.54 ± 0.20	0.97	1.85 ± 0.29	1.87 ± 0.09
	(0.21−0.91; n = 3)	(n = 1)	(1.02−3.03; n = 7)	(0.86−2.30; n = 15)
PFOS	1.22 ± 0.08	2.10 ± 0.07	3.30 ± 0.09	4.10 ± 0.09
	(0.24−2.18; n = 26)	(1.68−2.42; n = 10)	(2.51−4.38; n = 25)	(2.82−4.62; n = 22)
PFOSA	1.65 ± 0.10	2.56 ± 0.06	3.24 ± 0.07	3.74 ± 0.10
	(1.08−2.20; n = 11)	(2.38−2.71; n = 6)	(2.78−4.02; n = 25)	(2.67−4.19; n = 16)
PFHpA	1.00 ± 0.04	-[c]	2.16 ± 0.19	1.74 ± 0.15
	(0.96−1.03; n = 2)		(1.72−2.63; n = 4)	(0.49−3.46; n = 16)
PFOA	0.65 ± 0.07	1.47 ± 0.09	0.88 ± 0.09	1.39 ± 0.07
	(0.16−1.44; n = 21)	(0.88−1.85; n = 10)	(0.40−1.18; n = 10)	(0.89−2.03; n = 18)
PFNA	1.43 ± 0.06	2.06	2.05 ± 0.05	2.63 ± 0.07
	(1.32−1.52; n = 3)	(n = 1)	(1.58−2.41; n = 24)	(1.88−3.49; n = 21)
PFDA	1.75 ± 0.06	2.37 ± 0.14	3.37 ± 0.06	3.74 ± 0.17
	(1.36−2.00; n = 9)	(1.83−2.59; n = 5)	(2.85−3.92; n = 23)	(0.84−4.32; n = 20)
PFUnA	1.85	2.32	3.47	3.53
	(n = 1)	(n = 1)	(n = 1)	(n = 1)

[a] Expressed as mean ± SE (range; sample number). [b] K_{OC} is based on the water and sediment data of 2009. [c] Not calculated because PFHpA was not detected in water sampled in 2009.

than 0.5 log units even though the fish species examined were different.

In summary, this study investigated the fate of PFCs, especially PFOS, in the Etobicoke Creek watershed after a PFOS-containing AFFF was released from the Toronto International Airport in 2000. According to the PFC measurements in water, sediment, whole fish, and fish liver, elevated PFOS concentrations were observed close to the spill outfall almost a decade after the spill. However, a spatial survey shows that the major impact is relatively localized, as high PFOS concentrations were observed only at Spring Creek Pond. PFOS levels in fish livers from Spring Creek Pond were 92−99% lower in 2009 compared to those from the airport property 21 days after the spill. The levels were much lower at an Etobicoke Creek location just downstream of the outfall. Although PFOS water concentrations at locations further downstream in Etobicoke Creek have declined appreciably since the spill, the 2009 water and fish levels were ~2−10 times higher than upstream locations likely due to long-term impact of the spill as well as urbanization. Log K_D values derived from this study were 0.54−1.65 for PFASs and 1.00−1.85 for PFCAs. Log BAF_{fish} ranged from 1.85−3.24 for PFASs and 0.88−3.47 for PFCAs, whereas Log $BAF_{fish\ liver}$ ranged from 2.1−4.3 for PFASs and 1.0−5.0 for PFCAs.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Sample preparation and analysis, MDLs for the PFCs analyzed, PFC concentrations, correlation analysis of Log K_D with f_{OC}, analytical QA/QC data, composition of PFCs, and correlation between PFHxS and PFOS concentrations in water. This material is available free of charge via the Internet at http://pubs.acs.org.

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