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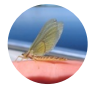

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Perfluoroalkyl Contaminants in Lake Ontario Lake Trout: Detailed Examination of Current Status and Long-Term Trends

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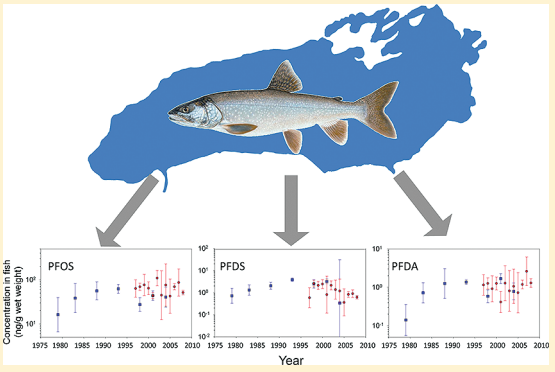
Supporting Information

ABSTRACT: Perfluoroalkyl contaminants (PFCs) were determined in Lake Ontario Lake Trout sampled annually between 1997 and 2008 in order to assess how current trends are responding to recent regulatory bans and voluntary phase-outs. We also combined our measurements with those of a previous study to provide an updated assessment of long-term trends. Concentrations of PFCs generally increased from the late 1970s until the mid-1980s to mid-1990s, after which concentrations either remained unchanged (perfluorooctane sulfonate (PFOS) and perfluorocarboxylates) or declined (perfluorodecanesulfonate (PFDS)). The temporal trends were assessed using three models, quadratic, exponential rise to maximum, and two-segment linear piecewise function, and then evaluated for best fit using Akaike Information Criteria. For PFOS and perfluorocarboxylates, the exponential rise to maximum function had the best fit. This is particularly interesting for PFOS as it suggests that although concentrations in Lake Ontario Lake Trout may have stopped increasing in response to voluntary phase-outs in 2000−2002, declines have yet to be observed. This may be due to continuing input of PFOS from products still in use and/or slow degradation of larger precursor molecules. A power analysis of PFOS suggested that 15 years of data with a within-year sample size of 10 is required to obtain sufficient power (80%) to detect a 5% decreasing trend. However, the length of the monitoring program had a greater influence on the ability to detect a trend compared to within-year sample size. This provides evidence that additional sampling years are required to detect a response to bans and phase-outs, given the variability in the fish data. The lack of observed declines of perfluorocarboxylate residues in fish may be expected as regulations for these compounds were only recently enacted. In contrast to the other compounds, the quadratic model had the best fit for PFDS. The results of this study emphasize the importance of long-term monitoring for assessing the effectiveness of bans and phase-outs on PFCs in the environment.



INTRODUCTION

For the past decade, perfluoroalkyl contaminants (PFCs) have attracted scientific and regulatory scrutiny due to their widespread environmental occurrence[1−3] and toxicity.[4,5] PFCs comprise a large group of chemicals that have been used in repellents for paper and packaging, carpets, and fabrics, as well as in aqueous film forming foam (AFFF) for fighting fuel fires.[6,7] The most commonly monitored and regulated PFCs include perfluoroalkyl sulfonates (especially perfluorooctane sulfonate, PFOS) and perfluorocarboxylates (particularly perfluorooctanoate, PFOA). However, most current monitoring programs also include the longer-chain perfluorocarboxylates (C_9−C_{15}) because they are more bioaccumulative and are frequently detected at higher concentrations in biota compared with PFOA.[2,3]

The history of PFC production is not well established due to proprietary issues, industry responses to regulations, and changing product lines.[8] Nonetheless, it is known that the 3M Company, which was the major manufacturer of perfluorooctane sulfonyl fluoride (PFOSF, used to make PFOS and its precursors), started production in 1949.[7,8] PFOSF was voluntarily phased-out by 3M between 2000 and 2002.[9] In contrast to PFOSF, production of PFOA and its known precursors continues. However, major manufacturers have voluntarily agreed to reduce emissions by 99% in 2015 (http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html). Regulation of the longer-chained perfluoroalkyl sulfonates and perfluorocarboxylates and their precursors is also now in progress in Canada[10] and the US (http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pfcs.html). However, despite these regulatory efforts, there continues to be fresh sources into the environment. For example, PFOSF-based production continues in China[11,12] and use exceptions exist in

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several countries.[13,14] In addition, PFCs are released from PFC-containing products still in use and through wastewater treatment plants and landfills.[7,15,16]

Monitoring data is critical for determining if PFC levels in the environment are responding to regulatory action.[3] Most temporal trend studies for PFCs quantify the probability of making a type I error, which is defined as rejection of a true null hypothesis and calculated by the statistical test selected.[17] Type II error and statistical power (defined as the probability that a monitoring program will detect a trend in sample measurements when the trend is occurring, despite the variability in the data) are less frequently evaluated.[17,18] However, power analysis can provide critical information on the number of years of data that are required before a significant trend of a given magnitude will likely be detected.[18] Power analysis can also be used to identify a within-year sample size that would optimize trend detection.[19] Many recent PFC monitoring programs have relied on short-term time trend data, whereby samples are not collected annually,[2,3,20] which reduces statistical power compared with annually collected data.[3,18]

Lake Ontario is an ideal system to study the recent time trends of PFCs because it contains elevated levels of many contaminants, including PFCs.[3,21] Lake Trout (*Salvelinus namaycush*) is among the most frequently used biomonitor for assessing contaminant trends in Lake Ontario as well as the other Great Lakes.[17] Martin et al.[22] previously evaluated the temporal trends of PFOS in Lake Ontario Lake Trout collected every three years between 1980 and 2001. A log−linear model applied to the entire data set showed that PFOS concentrations increased on average by 5.7% per year. However, on closer examination of the data, it was evident that the increase was not linear over the time period examined. PFOS concentrations increased between 1980 and 1989, decreased slightly between 1989 and 1995, and subsequently increased until 2001. Furdui et al.[20] measured perfluoroalkyl sulfonates and perfluorocarboxylates in Lake Ontario Lake Trout every 4 or 5 years between 1979 and 2004. They found that concentrations increased until the late 1980s/early 1990s. However, after this time, temporal patterns were difficult to distinguish because PFC concentrations were not measured every year. The temporal trends of PFCs were also recently determined in Herring Gull (*Larus argentatus*) eggs collected in 1990 and annually from 1997 to 2010 from the Great Lakes.[23] In Lake Ontario Herring Gull eggs, there was a marginally significant increasing trend for PFOS ($p = 0.06$) but no significant trend ($p > 0.05$) between 2000 and 2010. Perfluorocarboxylates also generally increased ($p < 0.05$) during the time period.

The objective of this study was to provide a detailed examination of PFC concentrations in Lake Ontario Lake Trout collected annually between 1997 and 2008. We also combined our data with those of Furdui et al.[20] in order to assess long-term trends. The influence of possible covariates (i.e., fish lipid, length, weight, age, growth, sex, and stable isotopes of nitrogen (δ^{15}N) and carbon (δ^{13}C)) on the trends were evaluated. Finally, we used power analyses to determine the optimal number of years and within-year sample size needed to detect future trends of PFOS in Lake Ontario Lake Trout, given the variability associated with the data. To our knowledge, this study is among the first to evaluate required sample size (both between- and within-year) for optimizing detection of regulatory actions/production phase-outs of PFOS in a biological monitoring program.

METHODS

Sample Collection. Lake Trout samples were collected annually between 1997 and 2008 (n = 7, 8, 6, 8, 3, 9, 7, 6, 6, 12, 5, and 10 individuals per year, respectively) from the western basin of Lake Ontario as part of Environment Canada's National Fish Contaminants Monitoring and Surveillance Program. The specific sites included Niagara-On-The-Lake (43.333°, −79.083°), Port Credit (43.500°, −79.583°), and Port Hope - Cobourg (43.917°, −78.167°) (Figure S-1). The fish from the three sites were combined to provide data representative of overall concentrations in western Lake Ontario. However, we also evaluated site-specific differences in 2006 (the only year where sample size was greater than 3 for each location) to determine the possible influence of spatial variation on overall results. Fish were caught using bottom set gill nets in late summer or early fall (August to October). Collection, storage, and processing methods are described elsewhere.[24,25] Following processing, samples were stored in Canada's National Aquatic Biological Specimen Bank at −80 °C until being selected for inclusion in this current retrospective investigation.

Chemical Analysis of PFCs. PFCs were analyzed according to De Silva et al.[26] using a methanolic extraction followed by cleanup using activated carbon SPE. Recovery standards consisting of 40 μL of isotopically labeled surrogate PFCs (Table S-1, Supporting Information) were added to the samples prior to extraction. Once extracted, the samples were reconstituted in 1 mL of 50:50 methanol:HPLC grade water and analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS) using an Agilent 1200 LC coupled to an AB Sciex 2000 mass spectrometer. Wet weight concentrations were determined using calibration curves based on relative response between native and isotopically labeled surrogate standards (Table S-1). For perfluorotridecanoate (PFTrA) and perfluorotetradecanoate (PFTeA), calibration curves were based on relative response of the analyte to $^{13}C_{1,2}$-perfluorododecanoate (PFDoA).

Spike and recovery tests (Table S-2) were conducted by spiking known concentrations of standards into samples (n = 7) that were left for 12 h prior to extraction. In general, recoveries were >80% with the exception of PFTrA which had a mean recovery of 70%. Routine method blanks were assessed by extracting blanks using surrogate standards and all reagents to determine method detection limits (MDL), defined as the concentration yielding the mean blank response plus 3 times the standard deviation (SD) of the blank response. PFOA and perfluorononanoate (PFNA) were the only analytes detected in method blanks with corresponding MDLs of 0.21 ng/g and 0.35 ng/g expressed on a per wet weight basis, respectively. PFNA concentrations in fish were above the MDL in all samples. In contrast, PFOA was typically not detected in fish extracts or was present at concentrations below the MDL. However, this may be expected because PFOA is not appreciably bioaccumulative in fish.[27] For all other analytes, MDL was defined by instrument detection limits corresponding to 0.10 ng/g based on the lowest calibration standard yielding a response with 10 times the signal-to-noise. Nondetect values were substituted with one-half of the analyte specific MDL. Based on good recoveries and low blanks, concentrations reported herein were not corrected for recoveries, blank signal, or matrix effects, consistent with previous studies from our

laboratory.[26] PFOA was the only exception, and therefore fish concentrations for this chemical are not reported in this paper.

Stable Isotope Analysis. Stable isotopes (δ^{15}N and δ^{13}C) were determined on subsets of individual whole fish samples at the Environmental Isotope Lab, University of Waterloo (Waterloo, ON, Canada) as described previously.[28] Prior to analysis, samples (~1.0−1.5 mg) were dried at 60 °C for ~48 h and then ground to a fine power using a ball mill (MM 400, Retsch, Haan, Germany). Samples were run on an Isochrom continuous-flow, stable-isotope mass spectrometer (GVInstruments/Micromass, Manchester, UK) coupled to a Carlo Erba Elemental Analyzer (CHNS-O EA 1108, Milan, Italy). Standard materials used were Peedee Belemnite formation for carbon and atmospheric air for nitrogen.

Fish were not pre-extracted to remove lipids prior to the stable isotope analysis, and lipid has the potential to influence δ^{13}C results.[29,30] Post et al.[29] recommended the following equation for correcting δ^{13}C for lipid content

$$\delta^{13}C_{\text{lipid normalized}} = \delta^{13}C_{\text{untreated}} - 3.32 + 0.99 \times \text{C:N} \quad (1)$$

where $\delta^{13}C_{\text{lipid normalized}}$ is an estimate of δ^{13}C that is normalized for the effects of lipid concentration, and C:N was determined from the %C and %N content of each sample. However, as the use of this equation has recently been questioned,[30] we present results for both $\delta^{13}C_{\text{lipid normalized}}$ and $\delta^{13}C_{\text{untreated}}$.

Data Treatment and Statistical Analysis. Prior to analysis, data were log-transformed to meet assumptions of normality and homogeneity of variance. Compounds detected in more than 80% of the samples (i.e., all PFCs except for perfluoroheptane sulfonate (PFHpS), PFOA, and PFTeA) were statistically evaluated. Our data set shared three common years, namely 1998, 2001, and 2004, with previous studies on PFCs in Lake Ontario Lake Trout.[20,21] For each of these three years, significant differences between studies were tested using the nonparametric Kruskal−Wallis test because the assumptions of normality (Shapiro-Wilk test) and homogeneity of variance (Levene's test) were not met in all cases even after log-transformation. When the assumptions of parametric tests were met, we also applied ANOVA, and the results were consistent with the nonparametric test. As presented below, this analysis showed that although there were significant differences present between the two data sets for some of the years/compounds, the overall trends were comparable between studies. Therefore, we combined our measurements with Furdui et al.[20,21] data from 1979, 1983, 1988, and 1993 for further temporal trend assessment. PFTrA was an obvious exception, as discussed below, and perfluorohexane sulfonate (PFHxS) was not evaluated by Furdui et al.[20,21] Therefore, PFTrA and PFHxS were excluded from the time trend modeling discussed below.

The biological variables used as covariates (i.e., fish lipid, length, weight, age, growth (evaluated as length at age and weight at age), δ^{15}N, and δ^{13}C) are summarized in Table S-3. The relationships between each PFC compound and covariate were analyzed for all years together and each year separately using a log−linear regression ($\log C_{CV} = \log(a) + b^{*}CV$), as done previously,[28,31] where CV represents a given covariate, C_{CV} is the concentration at covariate value CV, and a and b are constants representing the intercept and slope of the relationship. Significant differences in PFC concentrations between sexes were evaluated using the Kruskal−Wallis tests because assumptions of parametric tests were not consistently met.

Temporal trends of individual PFCs were evaluated using three models

$$\text{Quadratic: } C_t = a + bt + ct^2 \quad (2)$$

$$\text{Exponential rise to maximum: } C_t = a + b(1 - \exp^{-ct}) \quad (3)$$

$$\text{Two-segment linear piecewise: } f = \begin{cases} \dfrac{a(T - t) + b(t - t_{\min})}{T - t_{\min}}, & t_{\min} \le t \le T \\ \dfrac{b(t_{\max} - t) + c(t - T)}{t_{\max} - T}, & T \le t \le t_{\max} \end{cases} \quad (4)$$

where C_t is concentration at time t (year from start of the available record), and a, b, and c are estimated parameters. In the two-segment piecewise model, T is the breakpoint year (estimated by the model), $t_{\min}$ is the first year of the data set (1979), and $t_{\max}$ is the last year of the data set (2008). Percent annual change for this model was estimated from the slopes of a log−linear regression applied separately to data before and after the breakpoint year, as done previously.[32] The models were applied to annual geometric mean data as is a common practice in many contaminant trend studies.[17] For each analyte, the best fitting model was identified using Akaike Information Criteria (AIC).[33] AIC (corrected for small sample size) was calculated for each equation as follows: $\text{AIC} = n\log(\sigma^2) + 2K + (2K(K + 1)/(n - K - 1))$where n is sample size, σ^2 is the residual sum of squares/n, and K is the total number of estimated parameters in the model including σ^2 ($K = 4$ for the quadratic and exponential rise to maximum models and $K = 5$ for the piecewise model). The best fitting model had the lowest AIC. Akaike weights (w_i) were determined as $w_i = \exp(-\Delta\text{AIC}_i/2)/\Sigma_{i=1}^{M}\exp(-\Delta\text{AIC}_i/2)$, where M is the number of models. The w_i values indicate the probability that a given model is the best among all models evaluated in this study.

A power analysis was conducted to determine if the sampling regime utilized here was optimal to detect decreases in PFOS concentrations. Following Fryer and Nicholson,[19] power can be calculated from a noncentral F-distribution on 1 and T-2 degrees of freedom, with the noncentrality parameter (δ) determined as follows

$$\delta = \left\{\log\left(1 + \frac{q}{100}\right)\right\}^2 \left\{\frac{(T - 1)T(T + 1)}{12\psi^2}\right\} \quad (5)$$

where q is the minimum annual percent change that can be detected, T is the number of sampling years, and ψ^2 is the total residual variance of the model. ψ^2 can be determined as[19]

$$\psi^2 = \sigma^2{}_{\text{y}} + \frac{\sigma^2{}_{\text{w}}}{R} \quad (6)$$

where $\sigma^2{}_{\text{y}}$ and $\sigma^2{}_{\text{w}}$ are the random between-year and within-year variances of the model, respectively, and R is the within-year sample size. $\sigma^2{}_{\text{y}}$ and $\sigma^2{}_{\text{w}}$ were estimated using a linear mixed model that was fit using the restricted maximum likelihood method. Power can then be calculated as

$$power = 1 - FDist(F_{1-\alpha}, 1, T - 2, \delta) \quad (7)$$

where $F_{1-\alpha}$ is the $100(1-\alpha)^{\text{th}}$ percentile of a central F-distribution on 1 and $T - 2$ degrees of freedom, and α is the type I error rate. In this study, we used eqs 5−7 to determine

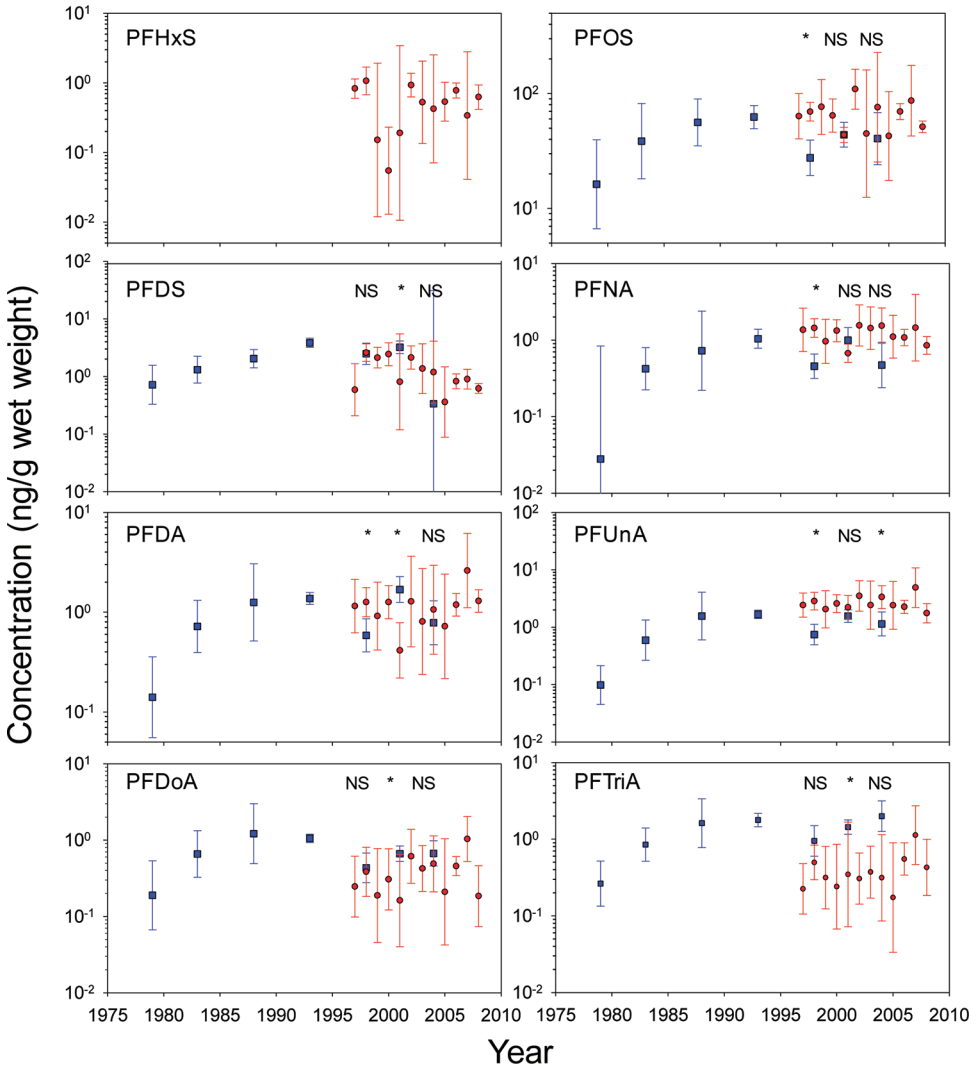

Figure 1. Temporal trends of PFC concentrations (geometric mean ±95% confidence interval) in Lake Ontario Lake Trout. Red circles represent data from this present study (1997−2008) and blue squares represent data from Furdui et al.[20,21] "NS" and "*" indicate no significant differences and significant differences, respectively, between our data and Furdui et al. data in 1998, 2001, and 2004.

the minimum percent change (q) that could be detected for an 80% power level and 5% type I error rate (α) as a function of T and R. PFOS data collected as part of this study only (1997 to 2008) were used to calculate σ^2_y and σ^2_w. These data were collected annually, which allows for a better estimation of σ^2_y. We assumed that random within- and between-year variance components of future time trends would be comparable to the 1997 to 2008 time range. In addition, it was assumed that future decreases in PFOS concentrations would follow a log−linear trend and that a power of 80% was adequate, consistent with previous power analyses.[18]

Statistica 9.0 (StatSoft, Tulsa, OK, USA) was used for comparison of our data with those of Furdui et al.,[20,21] the analysis of covariates, and the power analysis. SigmaPlot 11.0 (Systat Software Inc.) was used for the temporal trend model assessment. A type I error rate of $\alpha = 0.05$ was used in all statistical analyses.

RESULTS AND DISCUSSION

Overall Temporal Trends and Patterns. The temporal trends (1997−2008) of PFCs detected in greater than 80% of samples (all PFCs except for PFHpS, PFOA, and PFTeA) are shown in Figure 1 and Table S-4. Data from Furdui et al.[20,21] (1979−2004) are also shown in Figure 1 for comparison. The difference in geometric mean PFC concentrations between the two studies ranged from 1- to 4-fold; however, such differences in PFCs are expected given that the fish from the two studies were analyzed in different laboratories.[20] Furthermore, the differences between studies were not significant ($p > 0.05$) for more than half of the years/PFCs evaluated and the trends between the two studies were similar (Figure 1). PFTrA was an obvious exception, as concentrations reported by Furdui et al.[20,21] were consistently higher than our study (although only significantly higher in 2001) and increased from 1998 to 2004 (whereas our data showed no relationship with time, log−linear regression on 1997−2008 data, $p > 0.05$).

It is noteworthy that data from both Martin et al.[22] and Furdui et al.[20,21] suggested a dip in PFOS and perfluorocarboxylate concentrations in the mid-1990s, followed again by increases. Martin et al.[22] attributed this dip to shifts in food web processes perhaps as a result of the zebra mussel invasion. Examination of stable isotopes of nitrogen and carbon does not appear to support this hypothesis. The trophic position of Lake Ontario Lake Trout, as measured by δ^{15}N, remained relatively

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Table 1. Comparison of Three Models Used To Evaluate the PFC Concentration versus Year Relationship in Lake Ontario Lake Trout Using Akaike's Information Criterion (AIC) Corrected for Small Sample Size[e]

chemical	model	p-value	r^2	RSS[a]	K[b]	AIC[c]	w_i[d]
PFOS	piecewise	0.005	0.65	0.19	5	−14.87	0.05
	exponential rise to max	***0.001***	***0.67***	***0.18***	***4***	***-19.65***	***0.58***
	quadratic	0.002	0.62	0.21	4	−18.63	0.35
PFNA	piecewise	<0.0001	0.87	0.17	5	−15.43	0.08
	exponential rise to max	***<0.0001***	***0.94***	***0.16***	***4***	***-20.34***	***0.90***
	quadratic	<0.0001	0.84	0.45	4	−13.25	0.03
PFDA	piecewise	0.005	0.65	0.41	5	−9.47	0.09
	exponential rise to max	***0.001***	***0.65***	***0.41***	***4***	***-13.77***	***0.76***
	quadratic	0.025	0.43	0.66	4	−10.48	0.15
PFUnA	piecewise	<0.0001	0.93	0.17	5	−15.49	0.08
	exponential rise to max	***<0.0001***	***0.93***	***0.17***	***4***	***-20.08***	***0.78***
	quadratic	<0.0001	0.88	0.27	4	−16.69	0.14
PFDoA	piecewise	0.317	0.25	0.97	5	−3.47	0.03
	exponential rise to max	***0.568***	***0.08***	***1.18***	***4***	***-10.10***	***0.85***
	quadratic	0.729	0.05	1.23	4	−6.20	0.12
PFDS	piecewise	0.060	0.45	0.67	5	−6.04	0.11
	exponential rise to max	did not converge	-	-	4	-	-
	quadratic	***0.026***	***0.43***	***0.69***	***4***	***-10.17***	***0.89***

[a]RSS is residual sum of squares. [b]K is the number of estimated parameters in the model including σ^2. [c]AIC (corrected for small sample size) is calculated as AIC = $n\log(\sigma^2) + 2K + (2K(K+1)(n-K-1))$ where n is the sample size, σ^2 is the residual sum of squares/n, and K is the total number of estimated parameters in the model including σ^2. [d]Akaike weights (w_i) are calculated as follows: $w_i = \exp(-\Delta\mathrm{AIC}_i/2)/\Sigma_{i=1}^{M}\exp(-\Delta\mathrm{AIC}_i/2)$, where M is the number of models. [e]The best model for each compound is italicized and in bold font.

constant during this time period, whereas δ^{13}C (a measure of the source of carbon in the food web) decreased consistently from 1979 to 2004.[20,34] However, as discussed by Furdui et al.,[35] the stable isotope data should be interpreted with caution because a change in prey to a species having similar stable isotope values could still result in differences in PFC concentration. Furthermore, fluctuations in δ^{15}N and δ^{13}C in Lake Trout do not necessarily imply changes to diet as they could also be reflective of variations at the base of the food web.[36] With respect to the perfluorocarboxylates, Furdui et al.[20] performed an isomer-specific analysis that indicated a change to the major manufacturer in the mid-1990s (from 3M Company which synthesizes PFCs using electrochemical fluorination to other manufacturers that use telomerization) may be responsible for the dip in concentrations. In our data set, this dip in the mid-1990s was not evident (Figure 1). However, neither Martin et al.[22] nor Furdui et al.[20,21] evaluated annual measures. Annual measures (this study) revealed considerable interannual variation in PFC concentrations (Figure 1). This suggests that the dip observed by Furdui et al.[20,21] and Martin et al.[22] may have been partially an artifact of not measuring concentrations annually.

PFOS was the dominant PFC compound in Lake Ontario Lake Trout, consisting of 75 to 90% of total PFCs in all years (Figure S-2). Although PFOS is also the dominant PFC in fish from other waterbodies, the contaminant profile of PFCs in fish varies considerably, likely due to location-specific differences in sources.[3] The elevated proportion of PFOS concentrations in fish may be a result of the relatively high PFOSF production between 1970 and 2002[7,37] and the fact that PFOS is more bioaccumulative than PFOA, the most common residual and terminal product resulting from the fluorotelomer production method.[37]

Tables S-5 to S-7 show the results of the log−linear regression analyses testing for the influence of covariates for three representative PFC compounds (PFOS, PFDS, and perfluoroundecanoate (PFUnA)). The results of identical analyses for other PFCs were similar and thus not shown. There were no consistent significant relationships ($p > 0.05$) between PFC compounds and covariates fish lipid, length, weight, age, growth (measured as both length at age and weight at age), δ^{15}N, and δ^{13}C when assessing the data by combining all years and within years. In addition, there were no consistent significant differences in PFC concentrations between sexes ($p > 0.05$). This provides evidence that these variables do not influence the time trends of PFC concentrations in Lake Ontario Lake Trout, unlike legacy contaminants such as PCBs and mercury.[17] There were no significant differences in PFC concentrations in Lake Trout between the three collection sites in 2006 (Kruskal−Wallis, $p > 0.05$), which suggests that combining data from the three stations to represent overall western Lake Ontario fish contamination was reasonable in this study. However, because the sample size for each location in this study was generally less than 4, the power to detect differences was low. It should also be noted that the Lake Trout from Furdui et al.[20,21] were collected from the eastern basin of Lake Ontario by Main Duck Island (44.083°, −76.667), and it is possible that spatial differences could be responsible for differences observed between the two studies. However, Lake Ontario is generally well mixed; its circulation pattern is described as consisting of a major counter-clockwise gyre moving eastward from the mouth of the Niagara River along the south shore of the lake and then westward along the north shore.[38,39] Further, as Lake Trout is a top predatory fish, it has a relatively large home range[40] and thus its PFC burden likely integrates across large spatial areas, as found previously for PCBs and organochlorine pesticides.[41] The fact that Lake Trout were collected over three months each year could also be contributing to within-year variability. Additional studies to examine potential spatial and seasonal differences in PFC concentrations in Lake Ontario Lake Trout are recommended.

Table 2. Breakpoint Years Estimated by the Two-Segment Piecewise Regression Applied to PFC versus Time Data in Lake Ontario Lake Trout[a,c]

				before change point		after change point	
compound	breakpoint year	SE	p-value	% annual change	p-value	% annual change	p-value
PFOS	1989	3	<0.01	5.87	0.18	−0.18	0.83
PFNA	1988	2	<0.001	NA[b]	NA[b]	−0.03	0.30
PFDA	1984	2	<0.01	NA[b]	NA[b]	0.06	0.95
PFUnA	1985	1	<0.001	NA[b]	NA[b]	1.23	0.06
PFDoA	1984	3	0.056	NA[b]	NA[b]	−2.03	0.18
PFDS	1992	4	<0.01	5.00	0.10	−4.43	<0.01

[a]The log−linear regression was only conducted where there were three or more sampling years. [b]NA = not applicable. [c]The % annual change both before and after the change point, as estimated from the slope of log-linear regression applied separately before and after the breakpoint year, is also displayed.

Temporal Trend Modeling. Estimates of model parameters for the three models applied in this study are presented in Table S-8. For the perfluorocarboxylates (i.e., PFNA, perfluorodecanoate (PFDA), PFUnA, and PFDoA) and PFOS, the exponential rise to a maximum concentration model had the best performance (Table 1). This is particularly interesting for PFOS, which was voluntarily phased-out of production between 2000 and 2002 by the 3M Company. The results of this study suggest that although PFOS concentrations in Lake Ontario Lake Trout may have stopped increasing in response to this voluntary phase-out, concentration declines have yet to be observed. Gebbink et al.[23] found comparable results in Herring Gull eggs from Lake Ontario, where there was a marginally significant (p = 0.06) increasing trend in PFOS concentrations between 1990 and 2010 and no significant trend (p > 0.05) between 2000 and 2010. This stabilization, rather than decline, of PFOS concentrations in Lake Trout is likely the result of continued inputs to Lake Ontario. There continue to be specific use exemptions for PFOS, its salts, and precursors in both Canada and the U.S.[14,42] For example, some use of PFOS-based AFFF is permitted until 2013 in Canada, and the use PFOS and PFOS-like substances as an additive in hydraulic fluids is exempt from restrictions in the U.S. The importance of these sources were highlighted in a recent study that found evidence of PFOS and other PFC emissions originating from AFFF and aircraft hydraulic fluids at an airport.[16] In addition, wastewater treatment plant effluent is likely a major source of PFOS that originates from PFOSF-based products that are still in use.[43−45] At other locations where the primary source of PFOS is through recent emissions, levels in the environment are also slow to respond to regulatory actions.[2,3,11] In contrast, in more remote locations where the major source of PFOS is through atmospheric transport of precursor compounds, declines of PFOS concentrations were observed shortly after production phase-outs were in place.[3,11,46] These observations support the modeling work of Armitage et al.[11] who found that a rapid decrease of PFOS concentrations in biota following the 2000−2002 phase-outs was only possible if the major exposure route in the food web was uptake and metabolism of volatile precursor compounds to PFOS *in vivo*. The lack of recent concentration decline for PFOS could also be occurring because more time is needed for the trend to become apparent at a significance level of α = 0.05, as discussed below. In support of this latter hypothesis, examination of PFOS data between 2002 and 2008 in Figure 1 suggests that concentrations are beginning to decrease; however, the decrease was not statistically significant assuming a log−linear regression (p = 0.62, r^2 = 0.05). Concentrations of perfluorocarboxylates in Lake Trout have also not declined in response to phase-outs. However, unlike for PFOS, regulatory actions for perfluorocarboxylates are recent and still in discussion (http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pfcs.html),[10] which could explain the lack of declines.

PFDS was the only chemical where the quadratic model had the best fit (Table 1). PFDS increased from 1979 to 1993 in Lake Ontario Lake Trout and then declined until 2008. Similarly, Gebbink et al.[23] found that concentrations of PFDS decreased in Great Lakes Herring Gull eggs between 1990 and 2010. A source of PFDS appears to be PFOS-based AFFF,[47] although little is known about the use of PFDS or its precursors.[48]

The two-segment linear piecewise equation did not have the best model performance for any of the PFC chemicals analyzed (Table 1). This model assumes that concentrations followed a log−linear regression both before and after the break-point, when perhaps higher-order equations would have been more suitable for some of the compounds (Figure 1). Nonetheless, the two-segment linear piecewise equation is useful for identifying the year in which PFC concentrations began stabilizing (PFOS and perfluorocarboxylates) or decreasing (PFDS). The breakpoint year (±SE) estimated by the model ranged from 1984 ± 3 (for PFDoA) to 1992 ± 4 (for PFDS) (Table 2 and Figure S-3). The apparent half-life of PFDS, calculated from the year of the estimated breakpoint (1992) to 2008, was 16 years, which was comparable to half-lives of organochlorines in Lake Trout from the Great Lakes from the 1980s to 2000.[49] The half-lives for the other PFCs were not calculated because the relationship between concentration and time was not significantly different from zero (p > 0.05) after their respective breakpoint years (Table 2). Unfortunately, with the exception of PFOS, little is known about the production patterns of PFCs. For PFOS, the results of the two-segment linear piecewise regression indicate that concentrations began stabilizing in 1989 (Table 2 and Figure S-3). This corresponds to the temporal patterns of PFOS observed in Swedish Peregrine Falcon eggs (*Falco peregrinus*), where concentrations stabilized in ∼1984.[50] In liver tissue of Gray Seals (*Halichoerus grypus*) from the Baltic Sea, PFOS concentrations also stabilized, but later, in 1997.[51] These trends mirror PFOSF production volumes, which also began leveling out in the 1980s or early 1990s, although the exact year depends on the assumptions used in the calculations.[6,7,52] It is important to note that the PFOS trends in Lake Ontario Lake Trout (which remained relatively constant between 1984 to 2008) deviated from the observed drop in production volumes post-2000, no

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matter which assumptions were used in the production estimates.[7]

Model performance, as measured in this study using AIC, is based on the data currently available. Although the exponential rise to maximum model had the best fit for all PFCs evaluated except for PFDS, if PFC concentrations decline in the future, the quadratic or two-segment linear piecewise models would likely have a better performance.

Power Analysis. The results of a power analysis for predicting the length of time and within-year sample size needed to detect a decreasing trend of PFOS in Lake Ontario Lake Trout are shown in Figures 2, S-4, and S-5. This analysis

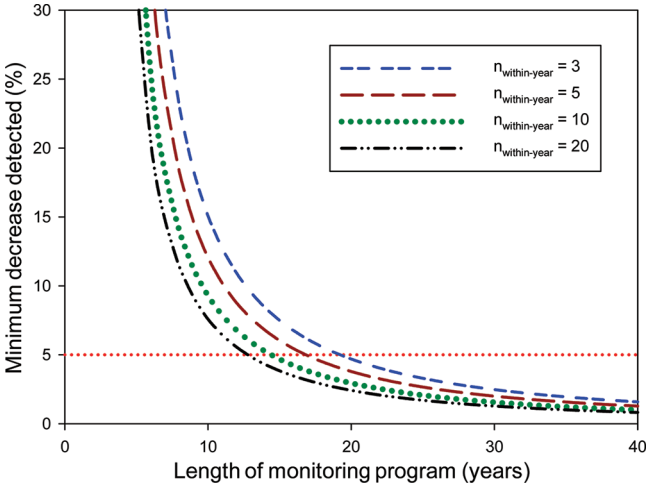

Figure 2. Results of a power analysis to assess optimal number of years and within-year sample sizes needed to detect decreasing trends of PFOS in Lake Ontario Lake Trout. The minimal percent annual decrease in PFOS concentrations that can be detected with an 80% power and 5% significance level is shown as a function of the length of the monitoring program (year) for within-year sample sizes ($n_{within-year}$) of 3, 5, 10, and 20. The red dotted line indicates a percent annual decrease of 5%.

assumes that future decreases in PFOS concentrations would follow a log−linear trend although other change patterns may become more relevant over time. However, as it is difficult to predict the nature of future trend patterns, it is convenient to evaluate power based on the log−linear model as it is the most simple and common monitoring objective for detecting environmental changes.[19]

Typically, contaminant monitoring programs aim to detect a minimum annual change of 5% at a 5% significance level and 80% power.[18] For PFOS in Lake Ontario Lake Trout, our results predict that it would take 13, 15, 17, and 19 years to detect a 5% annual decrease in concentrations with an 80% power and 5% significance level with within-year sample sizes of 20, 10, 5, and 3, respectively. The actual average annual percent decline that has been observed for PFOS varies between studies. For example, Ahrens et al.[53] determined that PFOS decreased by 2.5% per year between 1997 and 2009 in Tawny Owl (*Stix aluco*) eggs from Norway, Gebbink et al.[23] found decreases of approximately 4% per year in Herring Gulls eggs from Lakes Superior and Huron from 1990 to 2010, Ahrens et al.[54] reported that levels decreased at 12% per year between 1999 and 2008 in Harbor Seals (*Phoca vitulina*) from the German Bight, and Sundstrom et al.[55] found that PFOS in human milk samples from Stockholm, Sweden decreased 13% per year between 2001 and 2008. We also note that PCBs in Lake Ontario Lake Trout declined at a rate of ∼3 to 8% per year since production was banned in North America in the late 1970s.[49,56] In order to detect the low 2.5% annual change in PFOS concentrations observed by Ahrens et al.[53] in Lake Ontario Lake Trout, our results predict that it would take 19, 22, 26, and 29 years for within-year sample sizes of 20, 10, 5, and 3, respectively. However, it would likely take a shorter time to detect the larger annual change of 13% observed by Sundstrom et al.[55] (8, 9, 10, and 11 years for within-year sample sizes of 20, 10, 5, and 3, respectively). This analysis provides evidence that even if PFOS concentrations in the Lake Trout had started declining following the 2002 phase-out, there has not yet been sufficient time to achieve sufficient power for detecting the typical magnitude of percent decreases reported in the literature, given the variability in the data. These results emphasize the importance of long-term annual monitoring of PFCs (and other contaminants) in the environment if a biological monitoring program is to adequately assess the effectiveness of regulatory actions aimed at reducing environmental concentrations of harmful substances.

The number of years of sampling had a greater influence on the percent annual change of PFOS that could be detected, compared to within-year sample size (Figure S-4). For example, by 2015, which is 15 years from the start of the 2000−2002 PFOS phase-out, the power analysis predicts that the minimum annual change that would be detected with a 5% significance level and 80% power would be 5%, assuming our current average within-year sample size of 7. This is an approximate 70% decrease from the current (i.e., 8-years from the phase-out) detectable change of 17%. In comparison, if we had increased our within-year sample size to 15 every year from the start of the phase-out, we would presently be able to detect a 13% change, which is only 20% less than the current value. As such, given limited resources, it is better to increase the length of the monitoring program compared to within-year sample size. It should also be noted that the benefit of increasing within-year sample size was greatest for small within-year sample sizes of less than 10 but leveled off at larger sample sizes (Figure S-5). Although it would be beneficial to increase within-year sample size to 10, the benefits achieved in terms of increased power to detect change are much less than would be achieved by collecting annually for a longer time period post the PFOS phase-out.

■ ASSOCIATED CONTENT

Supporting Information

Additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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