

**Measurement of Gas-Phase Perfluoroalkyl Carboxylic Acids (PFCAs) Using
Nylon Passive Air Samplers**

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Abstract

Perfluoroalkyl carboxylic acids (PFCAs) are persistent anthropogenic compounds widely detected in environmental media. Few studies have measured ultrashort-chain PFCAs in air, despite their higher abundance compared to longer chains. Nylon passive air samplers (PAS) provide a cost-effective, low-labour technique to measure ultrashort- and short-chain gas-phase PFCAs. Method quality control and quality assurance parameters were optimized, including the calibration of perfluorobutanoic acid (PFBA), thereby improving confidence in reported mixing ratios. In a novel intercomparison with sorbent-impregnated polyurethane-foam (SIP) PAS at a wastewater treatment plant, good agreement between measurements was observed, with ultrashort-chain PFCAs dominating emissions. Nylon PAS were deployed in multiple Toronto locations, revealing Pearson International Airport to be a potential point source of perfluoropropanoic acid (PFPrA). Large-scale regional sampling along the St. Lawrence River, Quebec showed positive correlations between PFBA concentration and population size. These measurements have provided valuable insights into the sources and spatial distribution of PFCAs.

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Table of Contents

Abstract.....	ii
Acknowledgements	iii
List of Figures.....	vii
List of Tables.....	xi
List of Symbols and Abbreviations.....	xvi
Chapter 1. Introduction to perfluoroalkyl carboxylic acids in the atmosphere.....	1
1.1 Atmospheric transport and fate of pollutants	2
1.2 Background on poly- and perfluoroalkyl substances (PFAS)	4
1.3 Perfluoroalkyl carboxylic acids.....	6
1.3.1 Nomenclature, background, and physical properties	6
1.3.2 Sources and fate of PFCAs in the atmosphere	7
1.4 Sampling techniques for determination of PFCAs	10
1.4.1 Passive air sampling: theory and advantages	11
1.5 Separation theory: liquid chromatography	19
1.5.1 Ion chromatography theory and coupling to mass spectrometer	21
1.5.2 High performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS)	25
1.6 Quality assurance and quality control strategies for analytical measurements	26
1.7 Objectives.....	28
1.8 References	30
Chapter 2. Method development and validation of nylon passive air samplers for measurement of gas-phase PFCAs	39
2.1 Introduction	41
2.1.1 Perfluoroalkyl carboxylic acids (PFCAs)	41
2.1.2 Sampling techniques for the measurement of atmospheric PFCAs.....	42
2.1.3 Objectives.....	43
2.2 Methods.....	44
2.2.1 Materials and Chemicals.....	44
2.2.2 Preparation, deployment, and extraction of nylon PAS	47
2.2.3 Instrumental Analysis of PFCAs.....	48
2.2.4 Expanded quality assurance and quality control from field observations	51
2.2.5 Chamber calibration of nylon passive air samplers for PFBA _(g)	54
2.2.6 Duration of PAS deployment and sampling bias	57
2.2.7 Intercomparison between nylon and SIP PAS at a WWTP	57
2.2.8 Data Analysis	58

2.3 Results and Discussion.....	62
2.3.1 Resolving ¹³ C ₂ -TFA and TFA Interferences.....	62
2.3.2 Improving the quantitation of PFPrA.....	67
2.3.3 Extraction efficiency of C ₂ –C ₆ PFCAs from nylon filters.....	74
2.3.4 Inspection of overlying PP filters.....	77
2.3.5 Calibration of PFBA and revisiting TFA using atmospheric chamber.....	80
2.3.6 Duration of PAS deployment and potential sampling bias	84
2.3.7 Passive air sampling at a wastewater treatment plant: intercomparison between nylon PAS and SIP PAS and observed temporal trends	87
2.4 Conclusion	100
2.5 References	103

Chapter 3. Nylon passive air sampler measurement of gas-phase C₂–C₆ PFCAs in the Greater Toronto Area 110

3.1 Introduction.....	111
3.1.1 Sources and formation of PFCAs in the atmosphere	111
3.1.2 Airports as point sources of PFAS	112
3.1.3 Indoor environments as point sources of PFAS	113
3.1.4 Need for atmospheric measurements of ultrashort- and short-chain PFCAs.....	114
3.1.5 Objectives.....	115
3.2 Methods.....	116
3.2.1 Materials and Chemicals.....	116
3.2.2 Preparation, deployment, and analysis of nylon passive air samplers	116
3.2.3 Sampling Locations.....	118
3.3 Results and Discussion.....	121
3.3.1 Determination of C ₂ –C ₄ PFCA levels in Toronto during the 2024 SWAPIT campaign	121
3.3.2 Distribution of C ₂ –C ₅ PFCAs at Pearson International Airport and surrounding area	124
3.3.3 Measurement of C ₂ –C ₆ PFCAs at four indoor locations	130
3.4 Conclusion	134
3.5 References	136

Chapter 4. Nylon passive air sampling network for atmospheric measurements of C₂–C₆ PFCAs along the St. Lawrence River and Estuary, Quebec 143

4.1 Introduction.....	144
4.1.1 Sources, behaviour, and distribution of perfluoroalkyl carboxylic acids	144
4.1.2 Utility of passive air samplers for large monitoring networks.....	145
4.1.3 Objectives.....	146
4.2 Methods.....	147

4.2.1	Materials and Chemicals.....	147
4.2.2	Preparation, deployment, and analysis of nylon passive air samplers	147
4.2.3	Sampling Locations.....	148
4.3	Results and Discussion.....	151
4.3.1	Absolute PFCA concentrations and comparisons with past Canadian measurements	151
4.3.2	Spatial distribution of C2–C5 PFCAs along St. Lawrence River and Estuary	153
4.3.3	Correlation to population size	158
4.4	Conclusion	161
4.5	References	163
Chapter 5. Conclusions and future directions.....		166
5.1	Conclusions	167
5.2	Future directions.....	169
Appendix A: Supporting information for Chapter 2		171
S2.1	Supporting figures and tables for the methods section	171
S2.2	Standard Operating Procedure for Pimoroni Enviro+ Sensor	178
S2.3	Supporting equations, figures and tables for the results and discussion section	179
S2.3.1	Supporting information for Section 2.3.2.....	179
S2.3.2	Supporting information for Section 2.3.3.....	181
S2.3.3	Supporting information for Section 2.3.5.....	183
S2.3.4	Supporting information for Section 2.3.6.....	183
S2.3.5	Supporting information for Section 2.3.7.....	184
Appendix B: Supporting information for Chapter 3		186
S3.1	Supporting equations and tables for the results and discussion section.....	186
Appendix C: Supporting information for Chapter 4.....		189
S4.1	Supporting equations and tables for the results and discussion section.....	189

List of Figures

Figure 1.1 One-box model for a species X in the atmosphere, modified from Jacob (1999). F_{in} and F_{out} represent the flow of X into and out of the box, respectively. Emissions (E) and chemical production (P) are sources of X, and deposition (D) and chemical loss (L) are sinks of X.	3
Figure 1.2 General structure of a perfluoroalkyl carboxylic acid.	6
Figure 1.3 Simplified diagram of PFAS precursor atmospheric transformation pathways leading to PFCA and PFSA formation, modified from Young and Mabury (2010). Commercially produced compounds are shaded in gray.	8
Figure 1.4 Design of SIP PAS, modified from Wania & Shuthirasingham (2020).	14
Figure 1.5 (a) Passive air sampler components (simplified) with blue arrow showing direction of air flow, modified from Vanhauwaert et al (2025). (b) The uptake rate of PFCAs _(g) is determined by their rate of diffusion (k_D) through the PP filter and their rate of adsorption (k_{ads}) to the nylon filter and may be impacted by the solubilization (k_H) or reactive uptake (k_R) of gas-phase acids to the PP filters when water or particulate matter have accumulated, with blue arrows representing air flow. (c) Proposed reactive uptake mechanism whereby atmospheric acids, including PFCAs ($F_{(2n+1)}C_nCOOH$ where $n \geq 1$), sorb to the nylon filters through an acid-base reaction.	18
Figure 1.6 Schematic of an IC-CD-MS (IC-MS) system. Arrows display the flow of the mobile phase.	23
 Figure 2.1 Passive air sampler components and assembly order. After assembly, the filter pack is affixed inside the weatherproof cap. Reproduced from Vanhauwaert et al. (2025) with permission from the Royal Society of Chemistry.	46
Figure 2.2 Schematic of enclosed atmospheric chamber setup. Purple arrows indicate direction of air flow. A permeation tube filled with native PFBA is placed in the permeation oven and a known amount of gas-phase PFBA is emitted into the chamber. Adapted from Vanhauwaert et al. (2025) with permission from the Royal Society of Chemistry.	55
Figure 2.3 Nylon PAS ($n = 3$) and SIP disk ($n = 2$) sampling locations at the Wastewater Treatment Plant. Both types of passive samplers were deployed at a reference site (R), near a primary clarifier (PC), and between aeration tanks (AT).	57
Figure 2.4 Chromatograms of TFA (red, m/z 113) and $^{13}C_2$ -TFA (blue, m/z 115) (solid lines) in an extracted PAS deployed at Pearson International Airport, with dashed lines depicting TFA and $^{13}C_2$ -TFA in a 250 ng/L standard. Panel (a) shows separation using the concentrator column (750 μ L injection) and a short mobile phase gradient at 28 °C, with a peak for m/z 115 at 10.8 min overlapping with a shouldering peak at 10.35 min, and (b) shows separation using a 250 μ L loop injection and a long gradient at 25°C.	63
Figure 2.5 Chromatograms displaying TFA (red, m/z 113) and $^{13}C_2$ -TFA (blue, m/z 115) (solid lines) in an indoor PAS sample extract, with $^{13}C_2$ -TFA in a solvent blank overlayed (dashed lines), using three different analysis and separation methods: (a) Concentrator column with short separation gradient, (b) loop with long separation gradient, and (c) concentrator column with long separation gradient. Panels (b) and (c) show two separate peaks in the $^{13}C_2$ -TFA channel – the first belonging to $^{13}C_2$ -TFA and the second being an unknown isobaric interferent.	65

Figure 2.6 PFPrA mixing ratios (ppqv) measured at two SWAPIT sampling sites, High Park (n = 3) and Evergreen Brickworks (n = 3). PFPrA concentrations were quantified using the $^{13}\text{C}_1$ -PFPrA IS (green), $^{13}\text{C}_1$ -TFA IS (blue), and the $^{13}\text{C}_4$ -PFBA IS (purple). Error bars represent the standard deviation of triplicate measurements. 68

Figure 2.7 Chromatogram illustrating the separation of PFCAs (using our short gradient elution method for the concentrator column) in a PAS sample deployed at Evergreen Brickworks during the SWAPIT campaign (Jan. 29 – Mar. 11, 2024). The black trace is conductivity from the conductivity detector and the coloured traces are the PFCA mass abundances from the mass spectrometer, with the time delay of ~0.11 s between the two detectors corrected for. PFPeA and PFHxA were not detected in the sample so the mass abundances from the 100 ng/L and 50 ng/L standards were used for PFPeA and PFHxA, respectively. 69

Figure 2.8 Chromatograms depicting the separation of PFCAs and major anions sulfate (SO_4^{2-}) and nitrate (NO_3^-) in a PAS sample deployed at Pearson International Airport utilizing (a) the concentrator column with a short gradient and (b) the loop with a long gradient. C4–C6 PFCAs were not included in (b) as they are generally present at levels too low to quantify using the loop. 71

Figure 2.9 Chamber calibration for PFBA using the least-squares linear regression. The error in the regression slope represents one standard deviation. Dotted lines represent the bands of the linear regression at a 95% confidence interval. The mean measurement of triplicate PAS has an associated standard deviation represented with the error bars. The annular denuder measurement determines the mass of PFBA collected and is determined from the volume of air sampled and the PAS exposure time. 80

Figure 2.10 Linear uptake rate for TFA. The error in the regression slope represents one standard deviation. Dotted lines represent the confidence bands of the linear regression at a 95% confidence interval. The mean measurement of triplicate PAS has an associated standard deviation represented with the error bars. The annular denuder measurement determines the mass of PFBA collected and is determined from the volume of air sampled and the PAS exposure time. The TFA mass extracted from the nylon filters was corrected for TFA's 83% extraction efficiency. 83

Figure 2.11 C2–C5 PFCAs atmospheric concentrations (ppqv) measured at Pearson International Airport. PFHxA was not detected in samples and was omitted from this comparison. Sums of time-averaged PFCA concentrations measured in PAS deployed from November 3, 2023 to January 19, 2024 (n = 2) and PAS deployed January 19 to March 8, 2024 (n = 3), are shown in blue, with the Nov. – Jan. contribution depicted with diagonal lines; error bars represent the time-weighted propagated error for the sum of PFCA concentrations measured. PFCA measurements from PAS deployed November 3, 2023 to March 8, 2024 (n = 3) are shown in green; error bars represent standard deviation between triplicate measurements. The average temperature during the entire sampling period was $1.5 \pm 4.7^\circ\text{C}$ 86

Figure 2.12 Comparison of C2–C4 PFCA measurements using nylon and SIP PAS from the three process sites within a WWTP. Horizontal error bars represent the relative error between duplicate SIP PAS measurements collected over two months. Vertical error bars represent the time-weighted propagated error for the sum of nylon PAS concentrations from the entire month. The dashed line represents equal concentrations measured by the two samplers; the points situated above and below the line represent higher and lower analyte concentrations, respectively, measured by the nylon PAS compared with SIP PAS. 91

Figure 3.1 Sampling locations in Greater Toronto Area as part of the Study of Winter Air Pollution in Toronto (SWAPIT) campaign. Nylon PAS (n = 3) were deployed at High Park, Evergreen Brickworks, and University of Toronto Scarborough Campus (UTSC) from January to March 2024. Map was generated using OpenStreetMap data, available under the Open Database License (<https://www.openstreetmap.org/copyright>)..... 119

Figure 3.2 Map of possible airplane landing routes (blue lines) upon approach to runway 23 at Pearson International Airport (Nav Canada, 2021). Nylon PAS were deployed at the airport (YYZ) and at three surrounding sites (red circles) to make a transect along plane landing paths. At Site 1 (York University) plane altitude above sea level is approximately 900 m (3000 ft), at Site 2 planes are at an altitude of approximately 1500 – 1800 m (5000 – 6000 ft); A third site was chosen as a reference site, away from the plane landing paths. Yellow triangles represent planned sampling sites where PAS were lost. 120

Figure 3.3 Comparison of average nylon PAS C2–C4 PFCA measurements (ppqv) at three SWAPIT sites with previous Toronto winter measurements using ^anylon PAS at York University and a park (Vanhauwaert et al., 2025), ^bCIMS (Young et al., 2024) and to ^{c,d}annular denuder measurements from Beijing, China ^c(Wu et al., 2014), ^d(B. Zhang et al., 2018). In current work, nylon PAS (n = 3) were deployed Jan. – Mar. 2024 at three Toronto locations: High Park (HP), Evergreen Brickworks (EB), and University of Toronto Scarborough Campus (UTSC), with error bars indicating one standard deviation of the mean. *PFCA abundance depicted in refs. b and c are median values, with error bars representing minimum and maximum measurements. For ref. b the TFA maximum (979 ppqv) is not shown on the graph. 122

Figure 3.4 Atmospheric mixing ratios (ppqv) of C2–C5 PFCAs at Pearson International Airport, with a logarithmic (log₁₀) vertical axis. Nylon PAS were deployed November to January (n = 2), January to March (n = 3) and March to May (n = 5). Error bars represent the relative error between duplicate measurements or one standard deviation of replicate measurements. For clarity, TFA and PFPrA mixing ratios measured from March to May are displayed. 125

Figure 3.5 Nylon PAS measurements of C2–C5 PFCAs at Pearson International Airport and three sites in the surrounding area. All measurements were normalized to the same total sampling duration. The airport measurements displayed are the weighted sums of November to January, January to March and March to May measurements. Error bars represent one standard deviation of triplicate measurements for Sites 1, 2, and the reference, while the error bars for the airport measurements represent the propagated error for the weighted sums. 127

Figure 3.6 Nylon PAS (n = 3) measurements of C2–C6 PFCAs in air at four indoor locations from January to April 2025. Error bars represent one standard deviation of triplicate measurements. Lab 1 represents a lab with a fume hood, where high concentrations of PFAS are routinely used, while Lab 2 represents a lab where low concentrations of PFAS are periodically used. Office 1 is a shared office in a university building, and Office 2 is an office in a private residence. 131

Figure 4.1 Nylon PAS sampling locations along St. Lawrence River, Quebec, where site numbers correspond to those in Oh et al. (2024). Nylon PAS (n = 3) were deployed for approximately four months, from June to October 2024. Map inset provides a detailed view of sampling sites in Quebec City. Maps were generated using OpenStreetMap data, available under the Open Database License (<https://www.openstreetmap.org/copyright>)..... 149

Figure 4.2 Concentration profiles of C2–C5 PFCAs at 14 sampling sites along the St. Lawrence River and Estuary in Quebec. Values displayed at each site are average mixing ratios (ppqv) of triplicate nylon PAS (n = 3), or duplicate nylon PAS (n = 2; S6, S16). Error bars represent the propagated error for Σ C2–C5 PFCAs. With the exception of sites within Quebec City (S37–S40), sampling sites are organized by geographical location from west to east. 151

Figure 4.3 Mixing ratios of C2–C5 PFCAs (ppqv) measured using nylon PAS at 14 sites along the St. Lawrence River, Quebec from June to October 2024, with a logarithmic ($\log_{10}$) vertical axis. Error bars represent relative error between duplicate PAS or standard deviation of triplicate PAS measurements. With the exception of sites within Quebec City (S37–S40), sampling sites are organized by geographical location from west to east. 153

Figure 4.4 Box plot showing distribution of C2–C5 PFCA abundances measured by nylon PAS (n = 40) from June to October 2024 at 14 sites along the St. Lawrence River and Estuary in Quebec, Canada. The boxes represent the interquartile range (IQR), with the bottom and top boundaries of each box showing the 25th and 75th percentiles of data distribution, horizontal black lines representing the median, and black crosses representing the mean. Whiskers show the inner lower ($Q1 - 1.5 \times IQR$) and upper fences ($Q3 + 1.5 \times IQR$). Data outside the inner fences but inside the outer fences ($Q1 - 3 \times IQR$ and $Q3 + 3 \times IQR$) are outliers, denoted with circles; data outside the outer fences are far outliers, denoted with diamonds. 157

Figure 4.5 Correlation maps for PFCA atmospheric mixing ratios with population size. All correlations are based on average nylon PAS measurements determined from duplicate or triplicate samplers at each sampling site (n = 14). Sites exhibiting outlier TFA and PFPrA abundances, S40 and S16, were omitted in top line for comparison. Colour refers to Pearson's r for the linear relationship, point size refers to Pearson's r absolute linear relationship. When excluding outliers, the correlations between population size with TFA and Σ PFCAs concentrations are significant, as is the correlation between population size and PFBA concentration when all sites are considered. 159

Figure S2.1 From left to right: steps for the deployment of PAS. From right to left: steps for the collection of PAS (Carmichael, 2022). 174

Figure S2.2 Chromatograms depicting the abundance of PFPrA (pink, m/z 163) and $^{13}\text{C}_1$ -PFPrA (black, m/z 164) signals (solid lines) in a PAS sample (QC39-1) deployed in Quebec City (Jun. 20 – Oct. 16, 2024). Overlaid dashed lines represent PFPrA (pink) and $^{13}\text{C}_1$ -PFPrA (black) in a 500 ppt standard. (a) shows separation using the concentrator column (750 μL injection) and a short gradient, (b) shows separation using the loop (250 μL) and a long gradient. 181

Figure S4.1 Histograms depicting distribution of C2–C5 abundances in PAS extracts (n = 40). 191

List of Tables

Table 2.1 Operating parameters for IC-MS analysis using the concentrator column and loop with long or short gradients. Mobile phase A: Milli-Q water; and mobile phase B: 100 mM NaOH in Milli-Q water.....	49
Table 2.2 Mobile phase gradient for UPLC-MS/MS analysis of PFCAs and PFSA.	50
Table 2.3 Predicted and measured uptake rates of PFCAs, where those for C3–C6 were determined using Fuller’s law, based on the measured uptake rate for TFA from delivery of control gas quantities, as determined using an atmospheric chamber.....	59
Table 2.4 %Recoveries of 20 ng of C3–C6 PFCAs spiked in method blanks extracted with solvents of varying NaOH concentrations (n = 3). The notation RT describes the extraction solvent and samples which were at room temperature.....	74
Table 2.5 % Recoveries of 4 ng TFA, 1 ng PFPrA, 0.5 ng C4–C6 PFCAs spiked in method blanks extracted with solvents of varying NaOH concentrations (n = 3). The notation RT describes the extraction solvent and samples which were stored at room temperature. TFA and PFPrA recoveries were not blank corrected, while C4–C6 were blank corrected.	75
Table 2.6 %Recoveries of 20 ng C2–C6 PFCAs (high) and 4 ng TFA, 1 ng PFPrA, and 0.5 ng PFBA, PFPeA, and PFHxA (low) from PP filters using 3 mM NaOH extraction solvent at 4°C.77	
Table 2.7 Average C2–C5 PFCA quantities (ng) measured in nylon and respective PP filters from PAS deployed at Pearson International Airport. Relatively high levels in PP filters compared to their respective nylon filters are shown in bold	78
Table 2.8 Atmospheric concentrations (pg/m ³) of C2–C6 PFCAs measured at three sites within the WWTP using nylon PAS (n = 3) and SIP PAS (n = 2). Nylon PAS were deployed for one to two weeks for a combined sampling duration of one month, values displayed are sums of time weighted averages of C2–C6 PFCAs levels. SIP PAS values displayed are averages of duplicate samplers deployed May 25 – July 27, 2023. Relative errors (%) for SIP PAS and relative standard deviations (%) for nylon PAS are provided.	88
Table 2.9 Enrichment ratios at two WWTP sampling sites: the primary clarifier and between aeration tanks to those at the reference site, for nylon and SIP PAS.	89
Table 2.10 Comparison between average C4–C13 PFCAs and C8 PFSA (PFOS) atmospheric concentrations (pg/m ³) measured at three sites (primary clarifier, aeration tank, and a reference site) within a WWTP in 2009 (n = 2) and 2023 (n = 2), using SIP PAS, with relative errors (%) provided for each duplicate measurement. For each site, concentrations higher by a factor of 3 or more with respect to past or future measurements are displayed in bold font.	98
Table 3.1 PAS replicates (n), deployment dates, and sampling durations at sites in the GTA as part of SWAPIT, at Pearson International Airport, and at four indoor sites.	118

Table 4.1 Deployment details for nylon PAS at 14 sites along the St. Lawrence River, Quebec from June to October 2024.	150
--	-----

Table S2.1 List of PFCA and PFSA analytes and their acronyms and molecular weights (MW). Precursor and product ions for UPLC-MS/MS detection, allocation of the surrogate standards (SS) and internal standards (IS), and instrument limits of detection (iLOD) and quantitation (iLOQ).	171
--	-----

Table S2.2 PAS deployment dates and sampling times: at Pearson International Airport, three Toronto sites as part of SWAPIT, and indoors in a chemistry laboratory.	174
---	-----

Table S2.3 UPLC-MS/MS operating parameters for analysis of C4–C18 PFCAs and PFSAs.	175
--	-----

Table S2.4 UPLC-MS/MS operating parameters for analysis of ultrashort-chain (C1–C3) PFCAs and PFSAs	176
--	-----

Table S2.5 Calculated equivalent air volumes (V_{air}) for PFCAs and PFSAs on SIP disks. Calculated values were used to estimate the equivalent air volumes for nine PFSAs (TFMS, PFETs, PFPrS, PFPeS, PFHpS, PFNS, PFUnDS, PFDoDS, PFTrDS) and three PFCAs (TFA, PFPrA, PFHpA).	177
---	-----

Table S2.6 Recoveries (%) of surrogate standards spiked prior to extraction in method blanks (MB), field blanks (FB), and samples at WWTP sites, where PC is primary clarifier, AT is between aeration tanks, and R is upwind reference site. Spiking mass was 10 times lower than usual (50 pg instead of 500 pg). For all surrogate standards with an average recovery below 50%, an external recovery using the average recovery value was applied to the native PFAS in all samples.	177
--	-----

Table S2.7 Results of F-tests and two sample t-tests assuming equal variance performed on PAS extracts from samples deployed at High Park and Evergreen Brickworks during SWAPIT. PFPrA concentrations determined using the $^{13}\text{C}_1$ -PFPrA IS compared to the $^{13}\text{C}_1$ -TFA IS and $^{13}\text{C}_4$ -PFBA IS. An F value lower than the F critical value means the variances are equal. For the t-test a value of 4 was used for the degrees of freedom, and the T critical value was 2.78. A P value below 0.05 (shown in bold) indicates a statistically significant difference between values.	179
---	-----

Table S2.8 Peak areas of $^{13}\text{C}_1$ -TFA, $^{13}\text{C}_1$ -PFPrA, and $^{13}\text{C}_4$ -PFBA internal standards in aqueous C2–C6 PFCA standards and extracts of PAS (n = 3) deployed at Evergreen Brickworks.	179
---	-----

Table S2.9 TFA and PFPrA average concentrations (pg/m^3) measured in PAS deployed at Pearson International Airport, analyzed using two separate techniques: the concentrator column and short gradient compared with the loop and long gradient. $^{13}\text{C}_2$ -TFA displayed a co-eluting isobaric interference when analyzed with the short gradient.	180
---	-----

Table S2.10 Peak areas of $^{13}\text{C}_2\text{-TFA}$ and $^{13}\text{C}_1\text{-PFPrA}$ IS in a 500 ppt C2–C6 PFCA standard, PAS extracts deployed in Quebec City (QC S39-1) and at Pearson International Airport (YYZ-5 and YYZ-13). Two separate aliquots of each sample and standard were analyzed, each spiked with either $^{13}\text{C}_2\text{-TFA}$ or $^{13}\text{C}_1\text{-PFPrA}$ prior to IC-MS analysis utilizing the loop and long gradient method. 180

Table S2.11 % Recoveries of 4 ng TFA, 1 ng PFPrA, 0.5 ng C4–C6 PFCAs spiked in method blanks extracted with solvents of varying NaOH concentrations ($n = 3$). The notation RT describes the extraction solvent and samples which were stored at room temperature. All recoveries were blank subtracted. 182

Table S2.12 Method limits of detection (mLOD) and quantitation (mLOQ), and instrument limits of detection (iLOD) and quantitation (iLOQ) obtained during the low concentration extraction efficiency experiment. iLODs and iLOQs obtained during the high concentration extraction efficiency experiment are provided for reference. The 3 mM NaOH extraction solvent was used for all trials. 182

Table S2.13 Statistical comparison of C2–C6 PFCA recoveries from spiked method blanks ($n = 3$) extracted using 3 mM NaOH at 4 °C and room temperature. The high concentration spike consisted of 20 ng C3–C6 PFCAs and the low concentration spike was 4 ng TFA, 1 ng PFPrA, 0.5 ng C4–C6 PFCAs. A value of 4 was used for degrees of freedom in calculations. The t critical value at 95% confidence is 2.78. 182

Table S2.14 Statistical comparison of measured and predicted $\text{PFBA}_{(\text{g})}$ linear uptake rates $\text{PFBA}_{(\text{g})} (\text{ng m}^{-3}) \text{ t(h)} / [\text{PFBA}_{(\text{filter})} (\text{ng})]$ onto nylon PAS. A Welch t-test at a 95% confidence interval was performed between the measured PFBA uptake rate determined from our chamber calibration (without^a and with^b correction for plausible 82% recovery), and the predicted PFBA uptake rate which was calculated using the measured $\text{TFA}_{(\text{g})}$ uptake rate of $113 \pm 12 \text{ TFA}_{(\text{g})} (\text{ng m}^{-3}) \text{ t(h)} / [\text{TFA}_{(\text{filter})} (\text{ng})]$ to and Fuller's Law.....183

Table S2.15 Statistical comparison of the measured $\text{TFA}_{(\text{g})}$ linear uptake rate onto nylon PAS determined from our chamber calibration, $146 \pm 12 \text{ TFA}_{(\text{g})} (\text{ng m}^{-3}) \text{ t(h)} / [\text{TFA}_{(\text{filter})} (\text{ng})]$ to previously measured and predicted uptake rates. A Welch t-test at a 95% confidence interval was performed between our measured $\text{TFA}_{(\text{g})}$ uptake rate, our group's prior $\text{TFA}_{(\text{g})}$ measured uptake rate and the predicted rate which was based on previous $\text{HNO}_{3(\text{g})}$ calibrations. Both measured uptake rates were corrected for the 83% extraction efficiency of TFA. In the calculation of the predicted uptake rate, the extraction efficiency of NO_3^- was not determined or corrected for....183

Table S2.16 Statistical comparison of C2–C5 PFCAs measured at Pearson International Airport using PAS during a 6-month deployment ($n = 3$) compared with the weighted average of two shorter deployments ($n = 5$). A value of 6 was used for degrees of freedom in calculations. The t critical value at 95% confidence is 2.45. PFHxA was not measured in any samples. 183

Table S2.17 Statistical representation of C2–C6 PFCA on-site enrichment at the primary clarifier and aeration tank for nylon PAS and SIP PAS measurements. For nylon PAS calculations, a value of 4 was used for the DF, and for SIP PAS calculations a value of 2 was used for the DF. 184

Table S2.18 Ratio of average C2–C6 PFCA concentrations measured using nylon PAS to SIP PAS at three sites within the WWTP. Error shown is the propagated error associated with the ratio calculations, determined using the standard deviation between triplicate nylon PAS measurement and the relative error between duplicate SIP disk measurements. *PFPrA levels cannot be directly compared as the two methods used different internal standards to quantify PFPrA: PFPrA in SIPs was quantified using $^{13}\text{C}_3$ -PFPrA for the LC-MS/MS, while for nylon PAS $^{13}\text{C}_1$ -TFA was used for the IC-MS.....184

Table S2.19 Statistical comparison of C2–C6 PFCA atmospheric concentrations measured at a WWTP using nylon PAS (n = 3) and SIP disks (n = 2). A value of 3 was used for the DF and the t critical value at the 95% confidence interval was 3.18.....185

Table S2.20 Recoveries (%) of 20 ng each of native compounds TFA, PFPrA, TFMS, PFETs, PFPeS, and 25 ng each of surrogate standards $^{13}\text{C}_2$ -TFA, $^{13}\text{C}_3$ -PFPrA, and $^{13}\text{C}_4$ -PFBS in blank SIP disks prior to extraction. 185

Table S2.21 Statistical comparison of C4–C10 PFCAs and PFOS atmospheric concentrations measured at a WWTP using SIP PAS in 2009 (n = 2) and 2023 (n = 2). A value of 2 was used for the DF and the t critical value at the 95% confidence interval was 4.30.....185

Table S3.1 Mean atmospheric mixing ratios (ppqv) and concentrations measured using replicate (n) nylon PAS. Mass loadings (pg/m^3) are also provided for SWAPIT measurements. Relative standard deviations (%) for replicate measurements are shown in brackets. 186

Table S3.2 Outcome (p values) of Welch t-test showcasing differences between C2–C5 PFCA concentrations measured at Pearson International Airport and surrounding three sites from November 2023 to March 2024. 187

Table S3.3 Outcome (p values) of Welch t-test showcasing differences between C2–C5 PFCA concentrations measured at York University (Site 1) and two nearby sites from November 2023 to March 2024. Significant differences at the 95% confidence interval are **bolded**.....187

Table S3.4 Outcome (p values) of Welch t-test showcasing differences between C2–C6 PFCA concentrations measured in Lab 1 compared with Lab 2, Office 1 and Office 2. With the exception of the bolded entry, all presented differences are significant at the 95% confidence interval.....187

Table S3.5 Outcome (p values) of Welch t-test showcasing differences C2–C6 PFCA concentrations measured in three indoor locations Lab 2 compared with Office 1 and Office 2. A value of 4 was used for degrees of freedom. Significant differences at the 95% confidence interval are **bolded**. 187

Table S3.6 Method limits of detection (mLOD) in mixing ratios (ppqv) for nylon PAS during selected deployments. SWAPIT: average deployment duration of 36 days (~1 month), Pearson International Airport: deployment duration 59 days (~2 months) at the airport (March to May) and one average deployment of 179 days (~6 months) in surrounding area, and indoor: average of 91 days (~3 months).....188

Table S4.1 Method limits of detection (mLODs) in ppqv for a 117 day (four month) average PAS deployment.....189

Table S4.2 Mean atmospheric mixing ratios (ppqv) and measured using replicate (n) nylon passive air samplers at locations along the St. Lawrence River, Quebec. Relative errors (%) are displayed for duplicate measurements (n = 2) and relative standard deviations (%) are displayed for triplicate measurements (n = 3). 189

Table S4.3 Ratio of PFPeA concentrations to PFBA at 14 sites along St. Lawrence River, Quebec and their statistical significance (Welch t-test). Instances where PFPeA was higher than PFBA are **bolded**. 190

Table S4.4 Statistical outcome for Shapiro-Wilk and Jarque-Bera tests on C2–C5 PFCA concentrations measured in PAS extracts (n = 40). A Shapiro-Wilk test statistic, W, closer to 1 indicates normality, while smaller values of W indicate deviation from normality. P values below 0.05 show that at the 95% confidence level, the PFCA concentration distributions do not follow a normal Gaussian distribution. A Jarque-Bera test statistic, JB, higher than the critical value, 4.097, indicates departure from normality. 191

Table S4.5 Upper inner ($Q3 + 1.5 \times IQR$) and outer fences ($Q3 + 3 \times IQR$) for C2–C5 PFCAs distribution in PAS extracts (n = 40), where IQR is the interquartile range, from the 25th to 75th percentiles of data distribution. The inner and outer fences are compared to the mean plus one, two, and three standard deviations (σ), representing 68.3%, 95.5, and 99.7% of a normal Gaussian data distribution, respectively, with closest values shown in **bold** font.....192

Table S4.6 Statistical outcome of Pearson Correlation between population size and gas-phase PFCA concentrations measured along the St. Lawrence River, QC. A Pearson coefficient (r) value between -0.1 and 0.1 indicates a negligible correlation. Significant relationships at the 95% confidence level, are shown in **bold** font.....192

List of Symbols and Abbreviations

%	percent
(g)	gaseous state
<	less than
>	greater than
±	plus or minus
≤	less than or equal to
≥	greater than or equal to
°C	degrees Celsius
•CH ₃	methane radical
•O(¹ D)	singlet state oxygen atom
•OH	hydroxyl radical
AAS	active air sampling / active air sampler
AFFF	aqueous-film forming foam
AIM-IC-MS	ambient ion monitoring ion chromatography mass spectrometer
A _{PSM}	planar area of the exposed portion of the passive sampler
BEH	ethylene-bridged hybrid
≥ C ₈	compound(s) with 8 or more carbons
C(O)F ₂	carbonyl fluoride
C ₂ –C ₆	two to six carbon compound(s)
C _A	concentration in air
CD	conductivity detector
CF ₃ (CF ₂) _n C(O)OH	perfluoroalkyl carboxylic acid
CF ₃ (CF ₂) _n C(O)X	perfluorinated acyl halide
CF ₃ (CF ₂) _n CF ₂ OH	perfluoroacyl fluoride
CF ₃ (CF ₂) _n CF ₂ OO•	perfluoro peroxy radical
CF ₃ (CF ₂) _n CHCl ₂	perfluorinated dichloroalkane
CF ₃ (CF ₂) _n CHClBr	perfluorinated chlorobromoalkane
CF ₃ (CF ₂) _n CHClOCHF ₂	perfluorinated chlorofluoroalkyl ether
CF ₃ (CF ₂) _n CHF ₂ CF ₃	perfluorinated alkene or a perfluorinated olefin
CF ₃ (CF ₂) _n CH ₂ Cl	perfluorinated chlorofluoroalkane
CF ₃ (CF ₂) _n H	perfluoroalkane
CFC	chlorofluorocarbon
CH ₄	methane
CIMS	chemical ionization mass spectrometry
C _p	molar concentration sorbed to particles
C _{PSM}	concentration in the passive sampler medium
D	molecular diffusion coefficient
e	base of natural logarithms
ER	enrichment ratio

ESI	electrospray ionization
FASAs	Perfluoroalkane sulfonamides
FASEs	Perfluoroalkane sulfonamidoethanols
FTALs	fluorotelomer aldehydes
FTOHs	fluorotelomer alcohols
g	grams
GAPS	Global Atmospheric Passive Sampling
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
GTA	Greater Toronto Area
h	hour
H ₂ O	water
H ₂ SO ₄	sulfuric acid
HAAAs	haloacetic acids
HCFC	hydrochlorofluorocarbons
HCl	hydrochloric acid
HDPE	high-density polyethylene
HF	hydrogen fluoride
HFC-134a	1,1,1,2-tetrafluoroethane, CF ₃ CH ₂ F
HFCs	hydrofluorocarbons, CF ₃ (CF ₂) _n CH ₂ F
HFO-1234yf	2,3,3,3-tetrafluoropropene
HFOs	hydrofluoroolefins
HNO ₃	nitric acid
HPLC-MS/MS	high performance liquid chromatography tandem mass spectrometry
hν	light energy
HV-AAS	high-volume active air sampler(s)
HX	hydrogen halide
IC	ion chromatography
IC-CD	ion chromatography-conductivity detector
IC-MS	ion chromatography-mass spectrometry
iLOD	instrument limit of detection
iLOQ	instrument limit of quantitation
IS	internal standard
J	diffusion flux
k	mass transfer coefficient
k'	retention factor
k _A	air-side mass transfer coefficient
k _{ads}	rate of adsorption
K _{AW}	air water partitioning coefficient
k _D	rate of diffusion
k _H	solubilization from the gas-phase

K_{OA}	octanol air partitioning coefficient
K_{OW}	octanol water partitioning coefficient
k_{PSM}	passive sampler medium-side mass transfer coefficient
K_{PSM-A}	passive sampler medium-air partition coefficient
k_R	reactive uptake
L	litre
LC	liquid chromatography
LC-MS(/MS)	liquid chromatography-(tandem) mass spectrometry
LOD	limit of detection
LOQ	limit of quantification
m	metre
M	molar (mol/L)
m/z	mass-to-charge ratio
mA	miliAmpere
MCA	monochloroacetic acid
MeOH	methanol
MFC	mass flow controller
min	minute
mLOD	method limit of detection
mLOQ	method limit of quantitation
mol	mole
MRM	multiple-reaction monitoring
MS	mass spectrometry / mass spectrometer
MS/MS	tandem mass spectrometry
MW	molecular weight
N	efficiency factor
n	number of replicates or repeating units
N_2	nitrogen gas
N_2O_5	dinitrogen pentoxide
Na^+	sodium ion
Na_2CO_3	sodium carbonate
NaOH	sodium hydroxide
NH_3	ammonia
NH_4^+	ammonium ion
NH_4Ac	ammonium acetate
NO	nitrogen oxide
NO_3^-	nitrate anion
O_2	molecular oxygen
O_3	ozone
OCPs	organochlorine pesticides
OH^-	hydroxide ion

PAHs	polycyclic aromatic hydrocarbons
PAS	passive air sampler
PBDEs	polybrominated diphenyl ethers
PCBs	polychlorinated biphenyls
PFAAs	Perfluoroalkyl acids
PFAS	Poly- and perfluoroalkyl substances
PFBA (C4)	Perfluorobutanoic acid
PFBS (C4)	perfluorobutane sulfonic acid
PFCAs	Perfluoroalkyl carboxylic acids
PFDA (C10)	Perfluorodecanoic acid
PFDoDA (C12)	Perfluorododecanoic acid
PFDoDS (C12)	perfluorodecane sulfonic acid
PFDS (C10)	perfluorodecane sulfonic acid
PFEtS (C2)	perfluoroethane sulfonic acid
PFHpA (C7)	Perfluoroheptanoic acid
PFHpS (C7)	perfluoroheptane sulfonic acid
PFHxA (C6)	Perfluorohexanoic acid
PFHxDA (C16)	perfluorohexadecanoic acid
PFHxS (C6)	perfluorohexane sulfonic acid
PFNA (C9)	Perfluorononanoic acid
PFNS (C9)	perfluorononane sulfonic acid
PFOA (C8)	Perfluorooctanoic acid
PFODA (C18)	perfluorooctadecanoic acid
PFOS (C8)	Perfluorooctane sulfonic acid
PFPeA (C5)	Perfluoropentanoic acid
PFPeS (C5)	perfluoropentane sulfonic acid
PFPrA (C3)	Pentafluoropropionic acid
PFPrS (C3)	perfluoropropane sulfonic acid
PFSAs	Perfluoroalkyl sulfonic acids
PFTeDA (C14)	Perfluorotetradecanoic acid
PFTTrDA (C13)	Perfluorotridecanoic acid
PFTTrDS (C13)	perfluorotridecane sulfonic acid
PFUnDA (C11)	Perfluoroundecanoic acid
PFUnDS (C11)	perfluoroundecane sulfonic acid
pH	negative logarithm of hydronium ion concentration
pKa	negative logarithm of the acid dissociation constant
PM	particulate matter
POPs	persistent organic pollutants
POSF	Perfluorooctyl sulfonyl
PP	polypropylene
ppqv	parts per quadrillion by volume

pptv	parts per trillion by volume
PSM	passive sampling medium
PTFE	polytetrafluoroethylene
PUF	polyurethane foam
QA/QC	Quality Assurance / Quality Control
R	peak-to-peak resolution
R_4N^+	quaternary ammonium cation
$RCOO^-$	carboxylic acid anion
RH	relative humidity
$ROO\bullet$	peroxy radicals
$RR'CHOO\bullet$	peroxy radical containing an alpha hydrogen
RSD	relative standard deviation
RT	room temperature
S/N	signal-to-noise ratio
SIM	selective ion monitoring
SIP	sorbent impregnated polyurethane-foam
SO_4^{2-}	sulfate anion
SPE	solid phase extraction
SRM	selected reaction monitoring
SS	surrogate standard
SVOCs	semi-volatile organic compounds
SWAPIT	Study of Winter Air Pollution in Toronto
$t_{\text{calculated}}$	statistical value for sample data in t-tests
TFA (C2)	trifluoroacetic acid
TFMS (C1)	trifluoromethane sulfonic acid
t_m	the retention time of an unretained compound
t_r	retention time of an analyte
t_{table}	statistical reference value in t-tests
UPLC-MS/MS	ultra performance liquid chromatography-tandem mass spectrometry
V_{air}	equivalent air volume
V_{PSM}	volume of the passive sampler medium
w_{av}	average width between two peaks
WWTP	Wastewater Treatment Plant
XAD	divinylbenzene–styrene copolymer
α	selectivity factor
Δ	change
Σ	sum
τ	atmospheric lifetime

Chapter 1. Introduction to perfluoroalkyl carboxylic acids in the atmosphere

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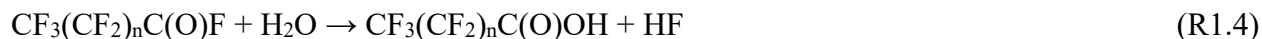
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1.1 Atmospheric transport and fate of pollutants

The atmosphere is a mixture of gases and particles, which are transformed, transported, and dispersed across the globe. The atmosphere is divided into four layers: the troposphere, stratosphere, mesosphere, and thermosphere (Seinfeld & Pandis, 2006). The troposphere is the lowest layer of the atmosphere, extending 10 to 15 km from Earth's surface to the tropopause, the boundary where the stratosphere begins. The atmospheric concentrations of all chemical species, including pollutants, are controlled by four types of processes: emissions (both natural and anthropogenic), chemistry, transport, and deposition (Jacob, 1999). Understanding these processes is essential in the determination of the effects of anthropogenic emissions on all of Earth's spheres: the atmosphere, hydrosphere, lithosphere, and biosphere.

Chemical reactions in the atmosphere can transform species and lead to the formation and deposition of pollutants. The formation of pollutants can occur by different types of reactions, including photolysis (R1.1), oxidation (R1.2), hydrolysis (R1.3, R1.4), and acid-base reactions (R1.5) (Finlayson-Pitts & Pitts, 2000; Seinfeld & Pandis, 2006).



In the atmosphere, the concentration of pollutants can be measured by mass loading (e.g. mass of pollutant per volume of air; pg/m^3) or mixing ratio (e.g. parts per quadrillion by volume; ppqv). The mixing ratio of a gas, defined as the number of moles of a gas per mole of air, is a better measure of atmospheric composition as it remains constant with changes in temperature or pressure (Jacob, 1999).

Transport through oceans is slow, on the order of decades to thousands of years. Transport in the troposphere is much faster, occurring on the order of a few weeks longitudinally to a year between hemispheres (Jacob, 1999). Particles and gases are eventually deposited back to Earth's surface through wet and dry deposition (Finlayson-Pitts & Pitts, 2000). Wet deposition occurs when

pollutants are first dissolved in fog, rain, or snow before impacting the surface. Dry deposition occurs when pollutants are transported to the surface and absorbed or adsorbed without having been dissolved in atmospheric water droplets.

A mass balance approach can be used to describe atmospheric levels of a pollutant (X), through a simple one-box atmospheric model, as shown in Figure 1.1 (Jacob, 1999). The model describes the abundance of X inside a box representing a part of the atmosphere (e.g. a small urban area, a country, or the global atmosphere), where transport is represented as a flow of X into the box (F_{in}) and out of the box (F_{out}), sources of X are its emissions (E) and chemical production (P), while sinks of X are its deposition (D) to Earth's surface, and loss through chemical reactions (L).

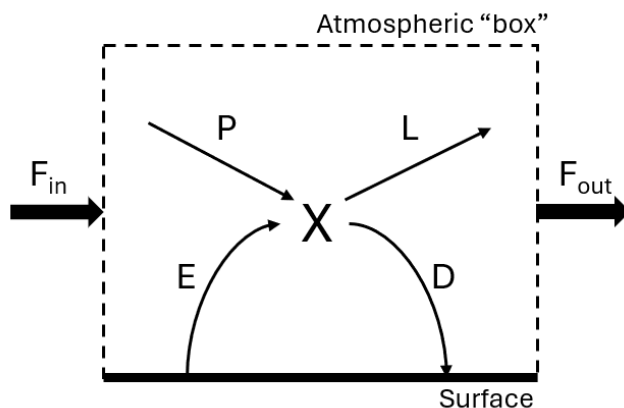


Figure 1.1 One-box model for a species X in the atmosphere, modified from Jacob (1999). F_{in} and F_{out} represent the flow of X into and out of the box, respectively. Emissions (E) and chemical production (P) are sources of X, and deposition (D) and chemical loss (L) are sinks of X.

The lifetime (τ) of a chemical is defined as the time it takes for its concentration to fall to one divided by the base of natural logarithms ($1/e$) of its initial value (Finlayson-Pitts & Pitts, 2000). Using a one-box model, the lifetime (s) of X in the box is the average time a molecule of X remains in the box, in other words, the ratio of the mass (kg) of X in the box to its total removal rate $F_{out} + L + D$ (kg/s) (Equation 1.1) (Jacob, 1999). The atmospheric lifetime of a gas molecule can vary from a few seconds to millions of years, depending on how efficiently it is removed (Seinfeld & Pandis, 2006). The change in the abundance of X inside the box is equal to the difference between its sources and sinks (Equation 1.2).

$$\tau = \frac{m}{F_{out} + L + D} \quad (E1.1)$$

$$\frac{dm}{dt} = \sum sources - \sum sinks = F_{in} + E + P - F_{out} - L - D \quad (E1.2)$$

Transport of pollutants in the atmosphere can be greatly affected by meteorological factors such as pressure gradients, wind, and precipitation, as well as the physical and chemical properties of the pollutant molecules. Some molecules exist in both the gas and particle (aerosol) phases, where the latter is a mixture of inorganic salts, water-soluble and -insoluble organic matter, and many other compounds (Tao et al., 2023). Aerosols can have separate aqueous and water-insoluble organic phases, into which molecules partition differently. Partitioning between gas and aerosol phases is influenced by factors such as relative humidity (RH), aerosol pH (ranging from – 1 to 7), and the physical properties of molecules.

A gas-particle partition coefficient, K_p , is used to describe the distribution of a molecule between the gas and particle phases and is defined as the ratio of molar concentrations of a molecule sorbed to particles (C_p) to that in the gas phase (C_a) (Equation 1.3) (Arp & Goss, 2009).

$$K_p = \frac{C_p}{C_a} \quad (E1.3)$$

Partitioning of molecules in the atmosphere can also be described by the air-water (K_{AW}), octanol-air (K_{OA}), and octanol-water (K_{OW}) partitioning coefficients (Tao et al., 2023). The preference of a molecule to partition to air is indicated by high values of K_{AW} and low values of K_{OA} . K_{OW} is often used as a proxy for biological tissues, with higher values meaning a molecule is more hydrophobic. The partitioning behaviour of pollutants can affect their rates of reactivity or deposition, and subsequently their atmospheric lifetime and global distribution (Arp & Goss, 2009).

1.2 Background on poly- and perfluoroalkyl substances (PFAS)

Poly- and perfluoroalkyl substances (PFAS) are a diverse class of more than 4700 fluorinated aliphatic anthropogenic compounds, now recognized as persistent environmental contaminants (OECD, 2018). PFAS contain a hydrophobic alkyl chain of varying length, that is either partially ('poly-') or fully ('per-') fluorinated and can be linear or branched (Buck et al., 2011). Due to their unique properties, such as chemical stability, surface tension lowering, and ability to create stable foams, PFAS have been widely used for more than 60 years in the manufacture of a variety of products such as aqueous-film forming foams (AFFF), fluoropolymers, polyurethane, inks,

lubricants, gasoline, and for surface coating of textiles, paper, kitchen utensils, food contact materials, and furniture (Kwiatkowski et al., 2020; Prevedouros et al., 2006; Sunderland et al., 2019). PFAS are widely detected in environmental media such as air (Genualdi et al., 2010) and precipitation (Scott et al., 2006), as well as in wildlife (Khalid et al., 2024) and humans (Kudzin et al., 2026). Almost all human blood samples collected worldwide contained trace levels (ng/mL) of PFAS (Fenton et al., 2021; Lindstrom et al., 2011). Some PFAS are bioaccumulative and have possible adverse effects in humans and animals, such as altered immune and thyroid function, liver and kidney disease, cancer, and detrimental outcomes to reproductive and developmental health (Fenton et al., 2021; Lau et al., 2004).

Some PFAS can degrade in the environment and transform into other types of PFAS but the strength and stability of the perfluorinated acid moiety makes it resistant to all forms of environmental degradation. This stability and persistence make the perfluoroalkyl acids (PFAAs), including perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) an important PFAS subgroup. Historically, the eight-carbon PFSA, perfluorooctane sulfonic acid (PFOS), and the eight-carbon PFCA, perfluorooctanoic acid (PFOA), were favoured in industry. Due to their persistence, toxicity, and bioaccumulative properties, in the early 2000s under the PFOA Stewardship Program, eight major chemical companies agreed to reduce emissions of PFOA and long-chain PFAS by 95% by 2010, with the goal of eliminating production by 2015 (Z. Wang et al., 2014). In 2009 PFOS, its salts, and derivatives were listed as persistent organic pollutants (POPs) under Annex B of the Stockholm Convention, restricting their production. The restrictions on eight-carbon PFAS caused a shift towards the use of fluorinated alternatives such as those consisting of ethers that interrupt the perfluorinated moieties, as well as PFAS containing fewer fluorinated carbon atoms, as substitutes (Janousek et al., 2019; Z. Wang et al., 2013, 2017).

The prevalent use of PFAS in industry has led to the accumulation of PFAAs in the environment, including in remote regions such as the Arctic (Persaud et al., 2024; Pickard et al., 2018, 2020). Volatile neutral PFAS like perfluoroalkane sulfonamido substances such as perfluoroalkane sulfonamides (FASAs) and perfluoroalkane sulfonamidoethanols (FASEs) as well as fluorotelomer compounds such as fluorotelomer alcohols (FTOHs) are subject to long-range atmospheric transport, with some undergoing atmospheric oxidation to form PFSAs and PFCAs as terminal products (Ellis et al., 2004; Thackray et al., 2020).

1.3 Perfluoroalkyl carboxylic acids

1.3.1 Nomenclature, background, and physical properties

Perfluoroalkyl carboxylic acids contain a hydrophilic functional group and a hydrophobic alkyl chain (Figure 1.2). PFCAs have been widely detected in environmental matrices such as air (Ahrens et al., 2011; Young et al., 2024), precipitation (Persaud et al., 2026; Scott et al., 2006), surface water (Liu et al., 2023), tap water (Lee, Roberts, et al., 2025; Ye et al., 2023) as well as in humans (Muir et al., 2025; Zheng et al., 2023).

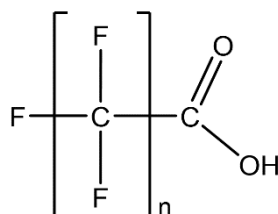


Figure 1.2 General structure of a perfluoroalkyl carboxylic acid.

Based on their alkyl chain length, PFCAs fall into two categories: compounds with eight or more carbons ($\geq \text{C}_8$) are termed long-chain and those containing two to seven carbons ($\text{C}_2\text{--C}_7$) are termed short-chain (Buck et al., 2011). A subcategory of short-chain PFCAs, representing those with a chain length of two or three carbons (C_2, C_3) is called ultrashort-chain (Bjornsdotter et al., 2020). Varying chain lengths give rise to behavioural differences between categories; ultrashort- and short-chain PFCAs are highly water soluble and stable and have been demonstrated to accumulate more in aquatic environments (Arp & Goss, 2009; Cahill, 2022; Cahill et al., 2001), while long chain PFCAs have been proven to bioaccumulate in the food chain (Martin, Mabury, Solomon, et al., 2003). Longer chain PFCAs have a higher tendency to partition into organic hydrophobic phases (Tao et al., 2023). Bioaccumulation is directly related to hydrophobicity, and because hydrophobicity increases with increasing size or chain length, PFCAs with greater than eight fluorinated carbons are considered bioaccumulative (Conder et al., 2008). Some PFCAs, such as PFOA, are known to be harmful to animals; in rats PFOA has been found to increase the incidence of cancers and cause weight loss, liver enlargement and changes in lipid metabolism (Fenton et al., 2021).

At environmentally-relevant pHs of various media (e.g. water, atmospheric aerosol, etc.), the majority of PFCA molecules are likely to be in their ionized state and partition preferentially into aqueous phase due to their low acid-dissociation (pKa) values (Tao et al., 2023). For example, at pH 7, more than 99.994% of PFOA molecules are anionic (Prevedouros et al., 2006). The anionic forms of PFCAs have high water solubility, low vapor pressure, and moderate sorption to solids, leading to their accumulation in water. The anionic forms can also be found in the organic phase and/or water contained in aerosols suspended in the atmosphere. The strength and stability of the carbon-fluorine bonds (>450 kJ/mol) make PFCAs extremely persistent in the environment, resistant to hydrolysis, photolysis, microbial degradation and metabolism (Prevedouros et al., 2006). PFCAs only have two small terminal environmental sinks: transport to deep ocean and sediment burial.

1.3.2 Sources and fate of PFCAs in the atmosphere

PFCAs are released into the environment from both direct and indirect sources, all of anthropogenic origin (Joudan et al., 2021). Direct sources include the manufacture and use of PFCAs, fluoropolymers, and a multitude of other products made with PFCA additives such as fire-fighting foams and lubricants (Prevedouros et al., 2006). In addition to their direct release into the environment from their manufacture and industrial use, PFCAs can be formed indirectly from the environmental degradation of PFAS precursors such as fluorotelomer-based chemicals, and compounds containing PFCA impurities such as perfluorooctyl sulfonyl-based (POSF) products. Some point sources of PFCA or PFCA precursor emissions are chemical and material production facilities, wastewater treatment plants (Houtz et al., 2016; Shoeib et al., 2016), landfills (Ahrens et al., 2011), airports (Awad et al., 2011), and military bases (Andrews et al., 2021).

A multitude of PFAS compounds can undergo atmospheric degradation to form PFCAs as terminal products (Young & Mabury, 2010). A simplified workflow of PFAS precursor transformation pathways leading to PFCA formation is provided in Figure 1.3.

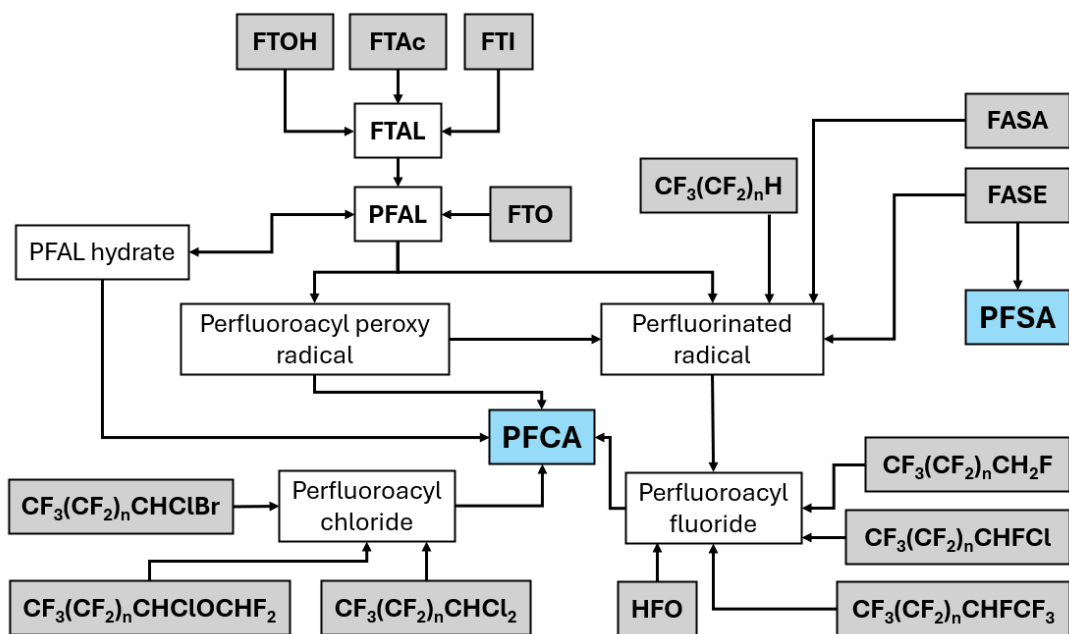
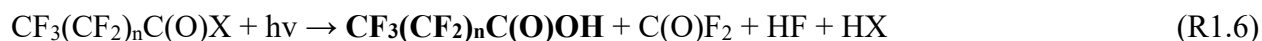


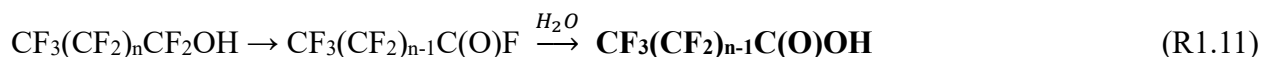
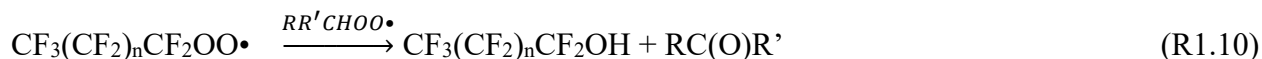
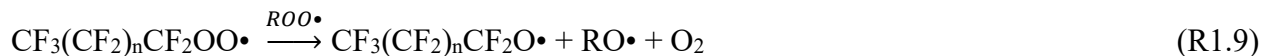
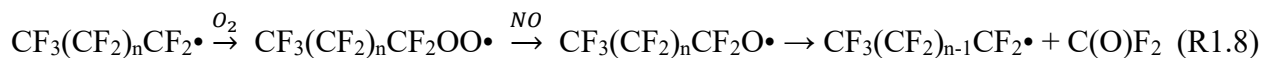
Figure 1.3 Simplified diagram of PFAS precursor atmospheric transformation pathways leading to PFCA and PFSA formation, modified from Young and Mabury (2010). Commercially produced compounds are shaded in gray.

One of the major formation pathways of PFCAs in the atmosphere is through the degradation of perfluoroacyl halides, via photolysis (R1.6) or hydrolysis (R1.7), to form the corresponding **PFCA**, $\text{CF}_3(\text{CF}_2)_n\text{C}(\text{O})\text{OH}$.



Perfluoroacyl halides can be formed from the atmospheric oxidation of mixed halides such as $\text{CF}_3(\text{CF}_2)_n\text{CHFCl}$, hydrofluoroolefins (HFOs), or perfluorinated radicals (Young & Mabury, 2010). Perfluorinated radicals, $\text{CF}_3(\text{CF}_2)_n\text{CF}_2\bullet$, are formed from the atmospheric oxidation of PFAS, and their major environmental fate is an “unzipping” mechanism to yield a carbonyl fluoride, $\text{C}(\text{O})\text{F}_2$ (R1.8) (Wallington et al., 1994). In remote areas where levels of NO are lower, reaction of the perfluoro peroxy radical, $\text{CF}_3(\text{CF}_2)_n\text{CF}_2\text{OO}\bullet$, with peroxy radicals ($\text{ROO}\bullet$) can be important. One possible pathway is the formation of a perfluoro alkoxy radical (R1.9) which ultimately forms COF_2 as in Reaction 1.8. If the $\text{ROO}\bullet$ contains an alpha hydrogen ($\text{RR}'\text{CHOO}\bullet$),

a perfluorinated alcohol can be formed (R1.10). Perfluorinated alcohols are unstable and lose HF to form perfluoroacyl fluorides, which hydrolyze to form **PFCAs** (R1.11) (Ellis et al., 2004).



The atmospheric lifetimes of PFCA precursors vary widely, from as little as four days for fluorotelomer aldehydes (FTALs), to 10–20 days for FTOHs, to 14 years for a hydrofluorocarbon (HFC), like HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$) (Young & Mabury, 2010). PFCAs are expected to have short atmospheric lifetimes, on the order of a few days, depositing back to the surface through wet and dry deposition (Persaud et al., 2026; Pickard et al., 2020; Young et al., 2024). Neutral volatile precursor compounds have longer atmospheric lifetimes and can undergo long range transport to remote regions such as the Arctic, where they form PFCAs as terminal degradation products, followed by fast deposition processes (Pickard et al., 2018, 2020; Thackray et al., 2020; Wong et al., 2018).

Due to the recent phase-out of long-chain PFAS, increasing concentrations of ultrashort- and short-chain PFAS have been detected in the environment (Janousek et al., 2019). Compared with long-chains, short-chain PFAS can be just as persistent and even more mobile in the environment, leading to an increase in their environmental detection and abundance (Janousek et al., 2019). In addition to the sources of PFCAs previously mentioned, ultrashort-chain PFCAs trifluoroacetic acid (TFA) and perfluoropropionic acid (PFPrA) can also be formed from atmospheric degradation of chlorofluoro-carbon (CFC) replacements, HFCs and hydrochlorofluorocarbons (HCFCs) (Wallington et al., 1994). Ultrashort- and short-chain PFCAs, in particular TFA, can be formed from many more PFAS compounds compared to the longer chain PFCAs (Young & Mabury, 2010). For example, HFOs such as 2,3,3,3-tetrafluoropropene (HFO-1234yf), manufactured as replacements for restricted HFCs like HFC-134a, are expected to react with hydroxyl radicals in the atmosphere forming TFA in almost 100% yield (Luecken et al., 2010). Among all PFCAs, TFA is by far the most abundant, dominating measurements in air (Vanhouwaert et al., 2025), ice cores

(Pickard et al., 2020), surface water (Miao et al., 2025), drinking water (Neuwald et al., 2022), beverages (Freeling & Mira de Orduña Heidinger, 2025; Lee, Butt, et al., 2025), indoor dust (Zheng et al., 2023), and human serum (Cheng et al., 2025). Although current environmental concentrations of TFA are thought to be harmless to humans and animals, TFA concentrations are expected to accumulate indefinitely due to a lack of environmental sinks (Arp et al., 2024; Cahill, 2022; Joudan et al., 2021). Most existing studies on PFCAs have overlooked TFA and PFPrA, leaving a substantial gap in the global evaluation of PFAS contamination that warrants further investigation.

1.4 Sampling techniques for determination of PFCAs

Atmospheric measurements can be conducted indirectly through wet and total deposition. Most measurements have been of total deposition, including both wet and dry fractions, with no way to distinguish between the two. Automated samplers with lids which only open when sensing moisture (i.e. precipitation), allowed for the collection of wet deposition separately from total deposition (Colussi et al., 2024; Persaud et al., 2026). In this way dry deposition can be estimated as the difference between total and wet deposition. However, wet and total deposition measurements cannot provide information on gas-particle partitioning as both are collected at the same time. To address this limitation, some studies have employed active air sampling techniques to directly measure atmospheric PFCAs with the goal of better understanding their gas-particle partitioning (Ahrens et al., 2012; Wu et al., 2019).

Active sampling techniques such as high-volume active air samplers (HV-AAS) and annular diffusion denuders have been used to conduct atmospheric measurements of semi-volatile organic compounds (SVOCs), POPs, and PFAS, including PFCAs (Ahrens et al., 2012; Barber et al., 2007; Wong et al., 2018). In these techniques, air is pulled through a filter which collects particle-phase compounds, allowing the gas-phase compounds to be collected on a sorbent downstream. Although HV-AAS have the ability to measure the gas- and particle-phases separately, due to the collection of the particle phase before the gas phase, they are subject to notable sampling artifacts for PFCAs and PFASs (Young & VandenBoer, 2023). One type of sampling artifact, termed “blow-on” occurs when gas-phase compounds sorb to the filter or trapped particulate matter instead of reaching the

sorbent-based gas sampler, resulting in an overestimation of the particle-phase. The second type of sampling artifact, termed “blow-off”, occurs when particle-phase molecules on the filter volatilize and are collected on the sorbent downstream, or are displaced by atmospheric gaseous acids, such as hydrochloric acid (HCl), with both resulting in an underestimation of the particle-phase.

Annular diffusion denuder samplers do not suffer from the aforementioned sampling artifacts due to the collection of the gas-phase first, followed by the particle-phase (Martin, Mabury, Wong, et al., 2003; Young & VandenBoer, 2023). As air is pumped into the denuder, gases are collected on a reactive coating that is selective for the target compounds, while the particles have such high inertia that they pass through the denuder and are collected by impaction or interception on a filter (MacInnis et al., 2016). Ahrens et al. (2012) assessed the performance of HV-AAS and a diffusion denuder for the measurement of C4–C12 PFCAs and C4–C10 PFSA. They found that diffusion denuder concentrations of PFCAs and PFSA in the gas-phase were ~2.5 times higher, while the particle-phase were ~4 times lower than HV-AAS measurements. Nevertheless, the high cost, high maintenance, and power requirements of both active sampling methods have limited possible sampling locations and prevent large-scale sampling of atmospheric PFCAs. Understanding the gas–particle partitioning of PFCAs in the atmosphere is critical, as it provides insight into their environmental fate, particularly their potential for long-range transport relative to removal processes such as wet and dry deposition.

1.4.1 Passive air sampling: theory and advantages

Passive air sampling approaches offer a cost-effective, non-intrusive, user-friendly, low maintenance, and power-free alternative to active sampling. Passive air samplers can be deployed in multiple locations simultaneously, allowing for the determination of temporal trends or spatial variability in time-averaged air concentrations of chemicals (Wania & Shunthirasingham, 2020). Networks of samplers can be deployed, varying in scale: local and urban, regional, national, international, or global. Another common application for PAS is the measurement of analyte concentrations along a transect of sampling sites where a change in air concentration is expected, with the goal of identifying or quantifying the influence of point sources. The relatively compact size and lack of noise make PAS particularly well-suited to indoor sampling as well, with the potential to aid in the determination of inhalation exposure sources.

Passive air sampling involves the diffusive uptake of chemicals in a sorbent over time (Gorecki & Namiesnik, 2002; Seethapathy et al., 2008). There are several passive air sampler (PAS) designs, each consisting of a barrier and a sorbent (Seethapathy et al., 2008). For diffusion samplers, the barrier is a static layer of the surrounding medium, while for permeation samplers, the barrier is a non-porous membrane. Transport is driven by the difference in analyte chemical potential across the barrier, which occurs when analyte molecules are captured by the medium or sorbent, creating a concentration or vapor-pressure gradient across the barrier. Net transport through either barrier type occurs due to diffusional mass transfer, described by Fick's first law of diffusion (E1.4) (Tyrrell, 1964). Fick's first law of diffusion describes the one-dimensional flow, J , in moles or grams per unit area per unit time across a reference plane in terms of the diffusion coefficient, D , and the concentration, c , in moles or grams per unit volume.

$$J = -D \, dc/dx \quad (\text{E1.4})$$

Fick's first law of diffusion can be applied to both types of passive samplers (E1.5). Here, J represents the diffusion flux ($\text{mol m}^{-2} \text{s}^{-1}$), D is the diffusion coefficient of the analyte (m^2/s), and ΔC is the change in concentration of the analyte (mol/m^3), and L is the length of the analyte diffusion pathway (m) (Kawashima et al., 2021).

$$J = D \times \frac{\Delta C}{L} \quad (\text{E1.5})$$

The uptake curve of an analyte to the sorbent has three phases, the kinetically controlled linear uptake phase, the transitional curvi-linear uptake phase, and the thermodynamically controlled equilibrium phase. Depending on the sampler design, barrier type, sorbent, and sampling duration, a passive sampler can function in the kinetic or equilibrium regions, or in an intermediate state between the two (Seethapathy et al., 2008). Kinetic samplers aim to remain in the kinetically controlled uptake phase during the entire length of deployment, while equilibrium samplers aim for the analyte concentration in the sorbent to reach equilibrium with the analyte concentration in air (Wania & Shunthirasingham, 2020). The calculations of analyte air concentrations differ between the two sampler types.

Diffusional mass transfer for both types of samplers can be described by Equation 1.6. The amount of analyte (M) transported by diffusion in time, t , can be described in terms of the molecular diffusion coefficient of the analyte, D (m^2/day), the cross section of the diffusion path, A (m^2), the

total length of the diffusion path, L (m), and the analyte concentration in the air, C_A , (mol/m^3). The term DA/L , which has units of volume over time, is often considered to be the sampling rate (Gorecki & Namiesnik, 2002). This relationship applies when the concentration gradient is linear and the collection efficiency is 100%.

$$M = \frac{DA}{L} \times C_A \times t \quad (\text{E1.6})$$

Fick's law of diffusion can be used to estimate sampling rates, however, possible analyte losses to other parts of the sampler and a collection efficiency lower than 100% can lead to uncertainty, thus it is necessary to calibrate each sampler for the uptake of every analyte of interest (Gorecki & Namiesnik, 2002). Calibration can be achieved by exposing the sampler to a known concentration of the analyte for varying amounts of time, and calculating the sampling rate based on the amount of analyte collected over time. An uptake curve can then be generated by plotting the change in the mass of a chemical collected on a sorbent with increasing length of deployment (Wania & Shunthirasingham, 2020). Once the PAS is calibrated for the uptake of each analyte of interest, their air concentrations can be determined.

Since the analyte concentration at the sorbent surface is close to zero, the amount of analyte collected by diffusion samplers in the kinetic phase is proportional to its air concentration and the sampling time, allowing for simple determination of time-weighted average analyte concentrations where the air concentration is equal to the mass on the sorbent divided by the product of sampling rate and deployment duration (Gorecki & Namiesnik, 2002). Important conditions of this calculation are that the sorbent does not let collected molecules escape and the sampling rate remains constant and in the linear phase throughout sampling. This is often achieved using adsorption or chemisorption-based sorbents, such as nylon PAS for atmospheric acids (Bytnerowicz et al., 2001, 2005; Place et al., 2018; Vanhauwaert et al., 2025). For analytes in the curvi-linear or equilibrium phase at the end of sampling, the calculation becomes more difficult (See Section 1.4.1.1).

Some environmental variables such as temperature and wind can impact the PAS sampling rates. Molecular diffusion coefficients increase with temperature, thus as temperature increases, an increase in sampling rates is expected (Gorecki & Namiesnik, 2002). This may lead to bias in measurements, the extent of which depends on the change in the rate of diffusion relative to the

temperature during calibration. For example, a temperature change of 25 °C, from 10 °C to 35 °C, leads to an error of $\pm 10\%$ (Place et al., 2018). Wind speed can also impact PAS sampling rates, and a combination of wind speed and direction can affect the distribution of air masses sampled by the PAS, with this effect being highly dependent on the sampler shelter design (Melymuk et al., 2011; Wania & Shunthirasingham, 2020).

1.4.1.1 PUF, SIP

The polyurethane foam (PUF) sorbent has been employed in the collection of POPs for over 50 years (Wania & Shunthirasingham, 2020). Shoeib and Harner (2002) introduced the PUF disk for passive sampling of SVOCs. Currently, this sampler design is the most popular PAS for atmospheric SVOCs and POPs due to its affordability, ease of handling, and high capacity for SVOCs. Numerous studies have used PUF PAS to measure POPs such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs), as well as polycyclic aromatic hydrocarbons (PAHs) in air (Melymuk et al., 2011, 2021; Schuster et al., 2021; Shoeib & Harner, 2002). To increase the uptake capacity of PUF to more volatile chemicals such as FTOHs, Shoeib et al. (2008) embedded polyurethane foam with ground-up XAD-4 (divinylbenzene–styrene copolymer) powder to obtain PUF-XAD disks, renamed sorbent impregnated polyurethane (SIP) foam disks (Figure 1.4).

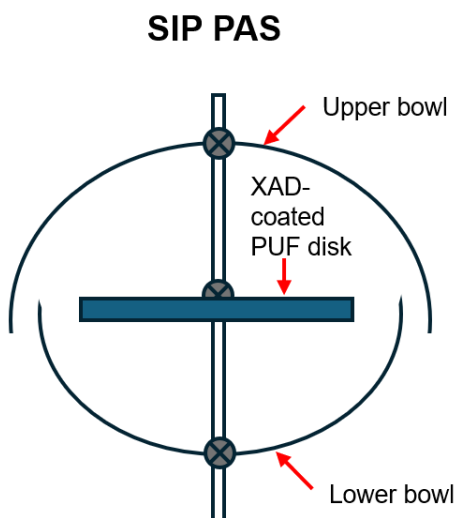


Figure 1.4 Design of SIP PAS, modified from Wania & Shunthirasingham (2020).

The addition of XAD powder to PUF disk has been reported to improve sorption of volatile PFAS by two orders of magnitude, presumably due to the increased surface area available for this interfacial interaction process (Shoeib et al., 2008).

The calculation of air concentrations is not straightforward, relying on several assumptions. Permeation samplers such as those utilizing PUF or SIP disks may be viewed as uniform, porous compartments into which chemicals can diffuse and/or dissolve (Shoeib & Harner, 2002). Mass transfer across the passive sampling medium (PSM)-air interface can be described by Equation 1.7, where k represents the overall mass transfer coefficient, k_A and k_{PSM} denote the air-side and PSM-side mass transfer coefficients, respectively, and K_{PSM-A} is the PSM-air partition coefficient.

$$\frac{1}{k} = \frac{1}{k_A} + \frac{1}{k_{PSM} \times K_{PSM-A}} \quad (E1.7)$$

For nonpolar organic chemicals, K_{PSM-A} is expected to be comparable in magnitude to the octanol-air partition coefficient, K_{OA} , for a nonpolar substrate like PUF or XAD (Shoeib & Harner, 2002). For chemicals that have large values of K_{OA} , the term $1/(k_{PSM}K_{PSM-A})$ becomes negligible, and mass transfer to the passive sampler is governed by air-side resistance (i.e. k is approximately equal to k_A). Uptake of chemicals by the sorbent is equivalent to the rate of uptake minus the rate of loss. This can be described by Equation 1.8, where V_{PSM} is the volume of the PSM (cm^3), C_{PSM} and C_A are concentrations (ng/m^3) in the PSM and air, respectively, and A_{PSM} is the planar geometric area of the exposed portion of the passive sampler (cm^2).

$$V_{PSM} \left(\frac{dC_{PSM}}{dt} \right) = k_A A_{PSM} \left(C_A - \frac{C_{PSM}}{K_{PSM-A}} \right) \quad (E1.8)$$

When the concentration of chemical in the PSM reaches equilibrium, such that C_{PSM}/K_{PSM-A} is equal to C_A , there is no net uptake and C_{PSM} becomes constant. Equation 1.8 can be solved analytically to determine the concentration in the PSM (E1.9).

$$C_{PSM} = K_{PSM-A} \times C_A \times \left(1 - \exp \left[- \left(\frac{A_{PSM}}{V_{PSM}} \times \frac{k_A}{K_{PSM-A}} \right) \times t \right] \right) \quad (E1.9)$$

The equivalent air volume (V_{air}) for a passive air sampler is a measure of the amount of air that it has sampled after a given exposure period. To calculate air concentrations for permeation samplers at equilibrium, the PSM-air partition coefficient can be defined as the equivalent air volume that contains the same mass of analyte as one unit volume of PSM at equilibrium (i.e. K_{PSM-A} is equal

to V_{air}/V_{PSM} , which is equal to C_{PSM}/C_A) (Shoeib et al., 2008). Therefore, the equivalent air volume can be determined by replacing terms in Equation 1.9, to produce Equation 1.10.

$$V_{air} = K_{PSM-A} \times V_{PSM} \times \left(1 - \exp \left[- \left(\frac{A_{PSM}}{V_{PSM}} \times \frac{k_A}{K_{PSM-A}} \right) \times t \right] \right) \quad (E1.10)$$

The PSM-air partition coefficient is specific to each chemical and must be empirically derived. Although previous studies have determined K_{PSM-A} for short- and long-chain PFCAs and PFSAAs through side-by-side field deployments with HV-AAS (Ahrens et al., 2013), as explained previously, HV-AAS suffers from sampling artifacts, possibly leading to bias in the determination of K_{PSM-A} . The derived equations were also modelled after the behaviour of neutral SVOCs and make several assumptions that may not apply to other compound classes. The assumption that the uptake is controlled by the air-side mass-transfer coefficient (k_A) may not hold for all chemicals as sampler-side resistance within the SIP may influence their uptake. In addition, the chemical and physical properties of ionic compounds are not considered, and the samplers may behave kinetically at all times as a result.

The use of combined sorbents like SIP disks adds time-consuming preparation steps with the possibility of contamination to the methodological process, as well as the added difficulty in reproducing and maintaining the exact properties of embedded material (e.g. total surface area and particle size distribution of ground XAD in sorbent pores). Furthermore, the addition of XAD powder is likely to introduce complexity to the uptake kinetics with respect to a sampler side resistance (Wania & Shunthirasingham, 2020). In addition, the double bowl design is not entirely effective at preventing winds from impacting on the SIP disk and allows for entry and accumulation of particle-bound compounds. There are some inconsistencies among different studies regarding the fraction of particle-phase analytes sampled by SIP PAS (Melymuk et al., 2014). Still, in a prior study by Markovic et al. (2015) the design was determined to be capable of acquiring a representative air sample for ambient particles. Additionally, a year-long gas-particle partitioning study measured similar whole air concentrations of short- and long-chain PFCAs and PFSAAs using HV-AAS compared with SIP PAS, indicating that the particle fraction sampled by SIPs is representative of the ambient conditions, even if the phase distribution is biased in the HV-AAS (Ahrens et al., 2013). As such, SIP PAS are treated as whole air samplers, sampling both gas- and particle-phases.

Under the Global Atmospheric Passive Sampling (GAPS) network, Environment and Climate Change Canada has been monitoring persistent organic pollutants using SIP PAS globally in more than 50 countries since 2004 (Genualdi et al., 2010; Saini et al., 2023). SIP PAS have been used to measure air concentrations of volatile neutral PFAS such as FASEs, FASAs, and FTOHs, as well as ionic PFAS such as PFCAs and PFSAs (Ahrens et al., 2011; Saini et al., 2023; Shoeib et al., 2008, 2016). However, to date, SIP PAS have only measured short- and long-chain PFCAs and PFSAs, containing four or more carbons ($\geq C_4$). Thus, there is a gap in the literature as ultrashort-chain PFCAs, in particular TFA, are found in much higher concentrations in the atmospheric environment (Pickard et al., 2020; Vanhauwaert et al., 2025; Young et al., 2024).

1.4.1.2 Nylon PAS

Passive air samplers with nylon sorbents have been used in the collection of atmospheric acids like HCl and nitric acid (HNO_3) since the 1980s (Perrino et al., 1988; Sturges & Harrison, 1989). PAS with nylon filters have been used to measure atmospheric gas-phase HNO_3 ($\text{HNO}_{3(g)}$) (Bytnerowicz et al., 2001, 2005; Place et al., 2018). These PAS were calibrated for $\text{HNO}_{3(g)}$ using a continuous stirred tank (Padgett et al., 2004), and subsequently deployed in an urban location in California (Bytnerowicz et al., 2005) and in remote regions of Newfoundland and Labrador (Place et al., 2018). Remote deployments demonstrated the passive sampler's capability in measuring $\text{HNO}_{3(g)}$ at ultra-trace levels as low as 9 parts-per-trillion by volume (pptv) over a 35-day period. Following the design described by Place et al. (2018), nylon PAS were used for the measurement of gas-phase PFCAs ($\text{PFCA}_{(g)}$). First, in a preliminary study, Carmichael (2022) detected $\text{TFA}_{(g)}$ in nylon PAS extracts deployed in Toronto and Halifax, but the remaining PFCAs were below detection limits. Next, our research group's current nylon PAS sampler design (Figure 1.5), modified to utilize a polypropylene overlying filter instead of polytetrafluoroethylene (PTFE), was calibrated for the uptake of $\text{TFA}_{(g)}$ through an extensive atmospheric chamber calibration experiment (see Chapter 2, Section 2.2.5) (Vanhauwaert et al., 2025). Nylon PAS were used to measure ultra-trace (ppqv to pptv) gas-phase ultrashort- and short-chain PFCAs in various locations across Canada, with subsequent analysis by gas chromatography-mass spectrometry (GC-MS), ion chromatography with conductivity detection (IC-CD), or ion chromatography-mass spectrometry (IC-MS) (Clouthier et al., 2026; Vanhauwaert et al., 2025).

The nylon filter and the overlying PP filter are encased in a petri dish filter pack and attached via hook and loop fastener inside the weatherproof cap (Figure 1.5a). A detailed schematic of the components including dimensions of the weatherproof cap can be found in Chapter 2, Section 2.2.1.

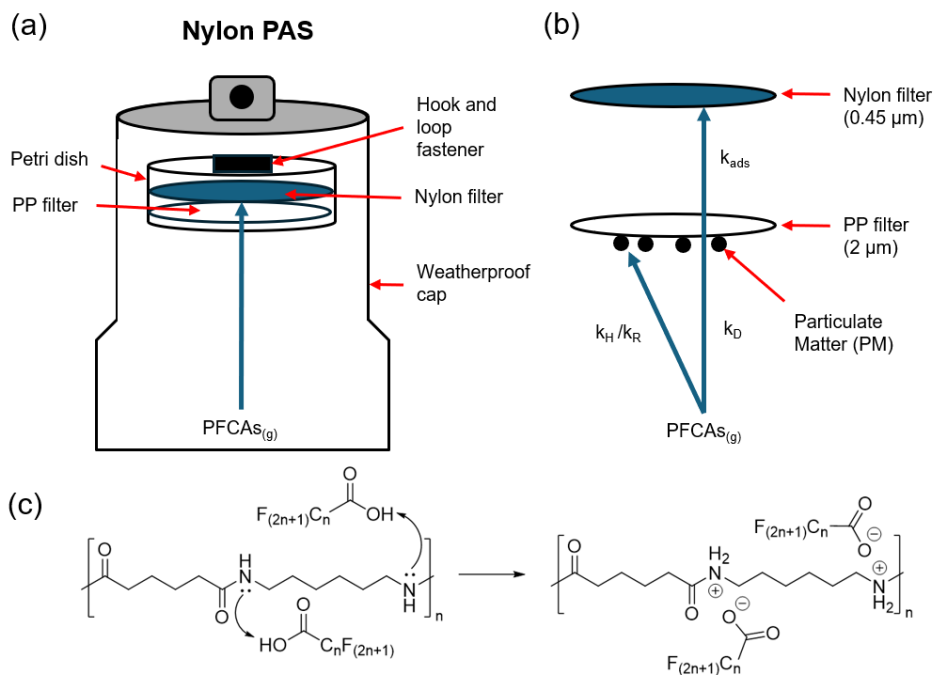


Figure 1.5 (a) Passive air sampler components (simplified) with blue arrow showing direction of air flow, modified from Vanhauwaert et al (2025). (b) The uptake rate of PFCAs_(g) is determined by their rate of diffusion (k_D) through the PP filter and their rate of adsorption (k_{ads}) to the nylon filter and may be impacted by the solubilization (k_H) or reactive uptake (k_R) of gas-phase acids to the PP filters when water or particulate matter have accumulated, with blue arrows representing air flow. (c) Proposed reactive uptake mechanism whereby atmospheric acids, including PFCAs (F_(2n+1)C_nCOOH where $n \geq 1$), sorb to the nylon filters through an acid-base reaction.

The overlying PP filter physically blocks particles from reaching the nylon filter, minimizing contamination (Figure 1.5b). Gas molecules diffuse through the PP filter and reach the nylon filter, onto which gas-phase acids, including PFCAs_(g), selectively chemisorb. This creates a concentration gradient between the two filters, which aids in the continuous diffusion of acids to the nylon filter. The uptake rate of PFCAs_(g) is determined by their rate of diffusion (k_D) through the PP filter and their rate of adsorption (k_{ads}) to the nylon filter and may be impacted by their

solubilization (k_H) or reactive uptake (k_R) to the PP filters on moisture or particulate matter (PM) (Bytnerowicz et al., 2005; Place et al., 2018).

The exact uptake mechanism remains unclear; however, it is likely that atmospheric acids are adsorbed through an acid–base reaction whereby the amino group accepts a proton from the carboxylic acid, becoming positively charged, while the deprotonated acid anion subsequently binds to the protonated amino group (Figure 1.5c), synonymous to the mechanism of ion exchange in condensed phase systems (Boyer et al., 2021; Du et al., 2014).

Nylon PAS offer several advantages over conventional active and passive sampling techniques. In comparison to active air sampling techniques, use of passive samplers like nylon PAS can be advantageous due to their affordability, compact size, unobtrusiveness, ease of use, and no power requirements. In addition to their increased utility compared with active air samplers, nylon PAS stand out among passive sampler types due to their high selectivity toward all strong acids in the gas-phase, including ultrashort-chain PFCAs. Their capability in collecting and providing simple and accurate measurements of gas-phase TFA and PFPrA addresses a critical gap in the literature. Past PAS measurements utilizing SIP disks have primarily targeted PFCAs with four or more carbons. This focus was mainly driven by reliance on the most widely used analysis technique, reversed-phase liquid chromatography–mass spectrometry (LC-MS), which does not effectively retain highly polar compounds such as TFA and PFPrA. As emissions of precursor compounds continue to rise, environmental concentrations of TFA and PFPrA are expected to increase, underscoring a growing societal need to monitor their atmospheric abundance and the factors driving their presence.

1.5 Separation theory: liquid chromatography

Liquid chromatography is the most widely used separation technique. In simplest terms, a liquid sample is injected into a liquid mobile phase, pumped into a column containing a stationary phase which separates the sample into its components. Each component is detected upon exiting the column, with the resulting detector signal plotted against time in a chromatogram (Snyder et al., 2010). For each peak in the chromatogram, the retention factor, k' , can be defined in terms of

retention time in Equation 1.11, where t_r is the retention time of the analyte and t_m is the retention time of an unretained compound (Harris, 2010).

$$k' = \frac{t_r - t_m}{t_m} \quad (\text{E1.11})$$

Two main factors determine how effectively compounds are separated in chromatography, the difference in elution times between peaks and the peak width. Greater separation in time and narrower peaks result in better resolution and improved separation. The peak-to-peak resolution (R) is defined as the separation between peaks (Δt_r) divided by the average width of the two peaks (w_{av}). Baseline separation requires a resolution value of at least 1.5 be obtained. The efficiency of a stationary phase is measured using theoretical plates, the height equivalent to a theoretical plate (H), and the number of theoretical plates (N), where N can be defined as the column length (L) divided by H.

Plate height (H) is proportional to the variance of a chromatographic band and can be approximated by the van Deemter equation (E1.12), where μ is the linear flow rate of the mobile phase, A is the multiple paths parameter, B/μ is the longitudinal diffusion, $C\mu$ is the mass transfer parameter. In packed columns, all three terms contribute to band broadening (Harris, 2010).

$$H \propto A + \frac{B}{\mu} + C\mu \quad (\text{E1.12})$$

The fundamental resolution equation (E1.13) expresses resolution as a function of three parameters: the efficiency factor, N, the retention factor, k' , and the selectivity factor (α).

$$R = \left(\frac{\sqrt{N}}{4} \right) \left(\frac{k'}{k' + 1} \right) \left(\frac{\alpha - 1}{\alpha} \right) \quad (\text{E1.13})$$

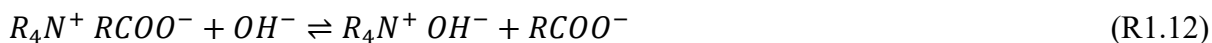
Each of the three parameters can be altered to improve the resolution of analytes (Snyder et al., 2010). The largest N occurs when H is minimized (e.g. by altering mobile phase, flow rate and/or stationary phase) and/or L is maximized (e.g. by using a longer column), depending on practical requirements of the system like pressure limits. An increase in k' , to an optimal value between 1 and 10, can be achieved by altering the mobile phase composition or changing it as a function of time in a gradient. When k' is small ($k' < 5$) an increase in k' leads to a large increase in resolution (R) between neighbouring peaks since R is proportional to $\frac{k'}{k' + 1}$. An increase in α can be achieved by altering the relative partitioning between analytes through changes in mobile phase composition

or the chemistry of the column stationary phase (i.e. its intermolecular interactions). A column with smaller particle size would likely enhance selectivity through reduced diffusion path lengths and narrower peaks. In addition to increasing N , k' , and α , a chromatographic separation method can be optimized through modification of other method parameters such as flow rate and temperature. The mobile phase flow rate affects the speed at which molecules travel through the column. Higher flow rates lead to shorter separation times, narrower peaks and increased pressure. Changes in temperature alter the diffusivity in both mobile and stationary phases. In general, increased temperature increases the rate of exchange and diffusion for solute ions between mobile phase and stationary phase. For separation of acids or bases, a buffer must be added to the mobile phase to control its pH.

1.5.1 Ion chromatography theory and coupling to mass spectrometer

Ion chromatography (IC) is a specialized form of liquid chromatography, designed for the analysis of charged species (ions). Separation is based on the interaction of cations and anions in the mobile phase and sample with charged groups on the stationary phase (Harris, 2010). For instance, anion exchange stationary phases contain cationic functional groups able to interact with anions present in the sample and with competing anions in the mobile phase. The identity of the competing ion and its concentration relative to the analyte determines the strength of the mobile phase and the selectivity of the separation. The strength of the mobile phase increases with increasing competing ion concentration and binding strength. The mobile phase can be pumped through the column using either isocratic or gradient modes. In isocratic elution, the mobile phase composition and the concentration of the competing ions remains constant throughout the entire chromatographic process (Weiss, 2019). In contrast, gradient elution involves a gradual increase in the mobile phase competing ion concentration during separation, resulting in an increase in elution strength over time.

The selectivity coefficient, K , describes the relative selectivity of a stationary phase for two ions. Reaction 1.12 and Equation 1.14 illustrate an IC setup utilizing a stationary phase containing quaternary ammonium groups (R_4N^+), a carboxylic acid ($RCOO^-$) analyte, and hydroxide (OH^-) as the competing ion provided by the mobile phase (Weiss, 2004).



$$K = \frac{[R_4N^+ OH^-][RCOO^-]}{[R_4N^+ RCOO^-][OH^-]} \quad (E1.14)$$

Selectivity is driven by the effective charge density (i.e. magnitude of ion charge and size of the hydrated ion) and polarizability (i.e. ability of maximum charge to appear at any point on the surface of the ion) (Michalski, 2016). Analytes with higher ion charge have a higher affinity for the functional group on the stationary phase and so are retained in a stronger way. Similarly, larger ion size and polarizability lead to increased electrostatic interaction with the ionic groups fixed in the stationary phase.

The Van Deemter considerations for IC (E1.15) are similar to those for LC, where the A term is related to particle diameter and shape, the B term is relatively small, and for the C term, mobile phase diffusivity (C_m) and the degree to which the analyte can penetrate the stationary phase (C_s) must be considered.

$$H \propto A + \frac{B}{\mu} + C_m \mu + C_s \mu \quad (E1.15)$$

When analyzing a sample containing anionic analytes (e.g. PFCAs) via ion chromatography, the sample is first injected onto either a concentrator column or a loop (Figure 1.6). Concentrator columns are used to concentrate analytes in large sample volumes (e.g. 0.5 – 2 mL) prior to injection (Weiss, 2004). The mobile phase delivers the sample through a guard column which protects and extends the life of the analytical column by collecting any sample components that would normally be deposited on the analytical column. After exiting the guard column, the mobile phase delivers the sample to the analytical column where it is separated into its components. While travelling through the analytical column, the ions in the mobile phase compete with the sample ions for the exchange sites of the stationary phase and cause the sample ions to move down the column. Due to differing affinities for the exchange sites, the sample ions move at different rates down the column and are eventually separated (Fritz, 1987). The mobile phase and separated analytes (effluent) then enter the suppressor, which removes conductive ions, thereby reducing the background conductivity and increasing the sensitivity. The separated analytes then pass through a detector, with the conductivity detector (CD) being the most popular option in ion chromatography (Weiss, 2019). The CD produces a chromatogram based on analyte conductivity.

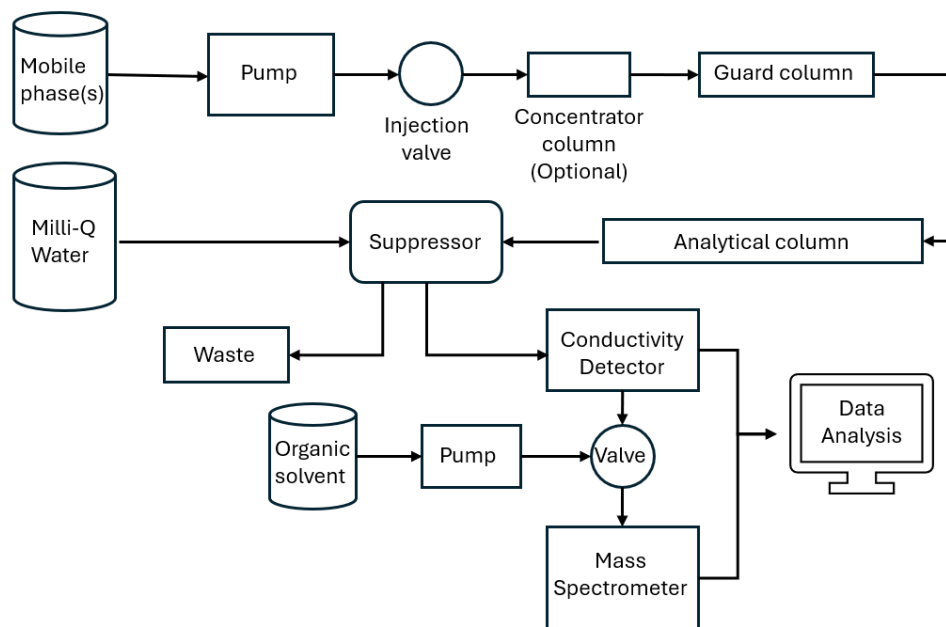


Figure 1.6 Schematic of an IC-CD-MS (IC-MS) system. Arrows display the flow of the mobile phase.

Coupling the traditional IC-CD setup with a mass spectrometer (MS) affords higher selectivity and sensitivity (Bigard et al., 2023). The combination is not trivial because the ionic mobile phase, an aqueous basic or acidic solution containing non-volatile salts, has the potential to cause salt buildup on the MS electrospray ionisation source, rendering it incompatible with the MS system. Thus, this combination would not be possible without the suppressor, which selectively removes the non-volatile mobile phase salts present in high concentration and neutralizes the mobile phase into water, an MS-compatible eluent. Before reaching the MS, an organic solvent is added to the flow, typically acetonitrile or methanol, to enhance solvent evaporation, sensitivity, and spray stability. Next, the effluent is sprayed into the ion source, commonly electrospray ionization (ESI), generating a mist of fine droplets which are directed towards the mass spectrometer entrance. After ionization, the ion stream flows into the mass analyzer, most commonly a quadrupole, which has an oscillating direct current voltage and a radio frequency applied to four rods parallel to the ion stream, causing the ions to be rapidly attracted and repelled by each rod (Harris, 2010). The combination of current and radio frequency allows ions of one specific mass-to-charge (m/z) ratio to maintain the correct flight path to exit the mass analyzer and strike the detector, while all others are eliminated. Ions of the selected m/z strike the detector, producing a current that is amplified

into a signal sent to the data analysis software. Importantly, Selective Ion Monitoring (SIM) mode can be utilized in MS to increase the selectivity for the analyte m/z ratios and decrease the response to everything else.

Analyses utilizing MS with ESI are subject to matrix effects, where the use and choice of internal standard is crucial to the accuracy of analysis (Furey et al., 2013). Although the exact mechanism is unknown, the common assumption is that interfering compounds present at high concentrations can raise the viscosity and surface tension of droplets formed during ESI, limiting the analytes' access to the droplet surface and reducing their transfer into the gas phase. Competition may occur between the analyte and remaining sample components (i.e. matrix) for the available charge, leading to differences in analyte response between standards and samples. Depending on the conditions under which ionization and ion evaporation occur, this interaction can either reduce the formation efficiency of the target analyte ion (ion suppression) or enhance it (ion enhancement). This phenomenon is referred to as matrix effects and it can greatly affect the reproducibility, linearity and accuracy of the method and lead to errors in quantitation. Quantitation of each analyte against its own mass-labelled internal standard is the best way to mitigate matrix effects (Furey et al., 2013). Since the analyte and its mass-labelled internal standard have nearly identical molecular structures, they will elute at the same retention time and any matrix effects encountered during analysis will be the same for both compounds, thereby compensating for any matrix effects.

IC-MS is an efficient analytical technique for analyzing ionic or ionizable compounds in complex matrices. One of the biggest advantages of IC-MS compared with the traditional GC-MS and high-performance liquid chromatography (HPLC) mass spectrometry techniques is the ability to directly inject aqueous samples without sample preparation steps such as derivatization or sample cleanup such as solid phase extraction (SPE) (Bigard et al., 2023). This greatly simplifies sample preparation and eliminates steps that often lead to substantial sample loss and possible contamination. Furthermore, IC has a high retention capacity toward highly polar molecules and organic acids, making IC-MS particularly well suited for analysis of ultrashort- and short-chain PFCA's.

1.5.2 High performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS)

HPLC is a versatile chromatographic technique capable of separating a wide variety of compounds, including neutral, polar, and non-polar molecules (Snyder et al., 2010). It is well suited for the analysis of hydrophobic organic compounds, such as long-chain PFCAs, as well as species that may be too strongly retained on anion-exchange columns, including PFSAAs. Additionally, HPLC offers many separation modes, allowing for greater flexibility in method development. Among these, reversed phase chromatography, characterized by a nonpolar stationary phase and a polar mobile phase, is the most frequently used HPLC mode, including for the analysis of traditional PFAAs (Ahrens et al., 2011; Shoeib et al., 2016; Taniyasu et al., 2005; Yamashita et al., 2008).

Ionized polar acidic analytes, such as ultrashort-chain PFCAs, are not well retained on conventional reversed-phase columns. Other chromatographic modes, including anion-exchange and hydrophilic interaction have been used to separate acidic compounds (Walter et al., 2021). However, these approaches have notable limitations, such as difficulty separating mixtures of acids, bases, and neutrals, as well as long column equilibration times. An alternative strategy is the use of mixed-mode stationary phases, which combine the properties of both reversed phase and anion-exchange chromatography. Mixed mode columns may be based on silane-bonded silica or ethylene-bridged hybrid (BEH) organic/inorganic particles stationary phases. Mixed-mode chromatography has yielded promising results for ultrashort-chain PFAAs (Montes et al., 2020; Y. Wang et al., 2024; Zhang et al., 2018; Zheng et al., 2023), although extending this approach to analysis of the longer chain homologues remains challenging. Recently, a direct injection LC-MS/MS method utilizing a mixed-mode column successfully quantified ultrashort-, short-, and long-chain PFAAs simultaneously in tap water, surface water, and precipitation (Lee, Roberts, et al., 2025).

Compared with a single quadrupole in MS, the use of a triple quadrupole detector in tandem mass spectrometry (MS/MS) provides greater selectivity for the target analytes. The triple quadrupole (QqQ) consists of two mass-analyzing quadrupoles Q1 and Q3 and a quadrupole collision cell q2 with no mass separation function (Zimmer, 2003). To quantify trace amounts of an analyte of interest, the ionized analyte molecules are selected with the first mass analyzer (Q1). The charged

analyte ions are allowed to pass into the collision cell (q2) where they collide with gas molecules, resulting in fragment ions passed to the exit and neutral molecules which are evacuated in the collision gas flow. The fragment ions are focused into the second mass analyzer (Q3) where typically only the product ion with the highest intensity is selected for monitoring, resulting in a chromatogram. Monitoring a fragmentation reaction of one analyte is termed selected reaction monitoring (SRM). To quantify multiple analytes simultaneously, a separate reaction (precursor ion $\rightarrow$ product ion) is monitored for each analyte; termed multiple reaction monitoring (MRM). Two or three product ions are typically monitored for each analyte, aiding in accurate identification, with the ion of highest intensity used for quantification, denoted the quantifier ion. The ions with the second (and third) highest intensities are used only for confirmation of analyte identity and are denoted the qualifier ion(s). Analyte peak identification can be achieved by retention time matching against an analytical standard, and verifying the ratio of qualifier to quantifier ions in the sample is within the acceptable percentage compared to that in an analytical standard.

In HPLC-MS/MS, as in IC-MS, ESI is a commonly used ionization source which is susceptible to matrix effects (Section 1.5.1). One advantage of MS/MS compared with MS is the higher analyte selectivity afforded by the second quadrupole. Even if a matrix constituent shares the same precursor mass-to-charge ratio (m/z) as the analyte and reaches Q2, it may not undergo the same fragmentation reactions, thus lowering the chances of interference.

1.6 Quality assurance and quality control strategies for analytical measurements

PFCAs are present at ultra-trace levels (ppqv to pptv) in the environment, and at such low concentrations, accurate analysis is challenging and requires robust method quality assurance and quality control (QA/QC) strategies. QA/QC parameters including selectivity, precision, accuracy, limit of detection (LOD), limit of quantification (LOQ), and linearity must be determined and optimized (Harris, 2010). Selectivity is the method's ability to distinguish the analyte from all other species in the sample, avoiding interference. Selectivity can be improved by optimizing the separation method to ensure analytes elute separately from other analytes and matrix components.

Precision shows how close replicate measurements are to each other and is measured by analyzing replicates of standards or samples and calculating the average, standard deviation, and relative standard deviation (%RSD). Accuracy describes how close a measurement is to the true value and is typically measured by spiking the sample matrix with a known concentration of analyte and calculating the % recovery. Accuracy can also be demonstrated by comparison against a certified reference material or by comparing results from two or more different analytical methods, termed a method intercomparison. LOD is defined as the lowest concentration at which the instrument can detect but not accurately quantify the analyte. At the detection limit there is a 1% chance of determining that a blank contains analyte above the detection limit (false positive). If a sample contains analyte at the detection limit, there is a 50% chance of determining the analyte is absent (false negative). LOQ is defined as the lowest concentration that can be accurately quantified. Because atmospheric mixing ratios of PFCAs occur at ultra-trace levels, the analytical method must achieve extremely low limits of detection, at the single- to double-digit ppqv levels. With IC-MS instrumentation, this sensitivity can be obtained through large-volume (e.g. 750 μ L) sample preconcentration on a concentrator column followed by detection with a single quadrupole MS. LC-MS/MS methods typically use much lower injection volumes (e.g. 1–10 μ L) and reach comparable detection limits through multiple sample concentration and solvent-exchange steps combined with triple quadrupole MS/MS detection.

Linearity describes how closely a calibration curve approximates a straight line, indicating that the instrument response is directly proportional to the analyte concentration. Linearity is directly linked to analyte quantitation and calibration: external, internal, or standard addition (Harris, 2010). The preferred method of calibration to avoid any matrix effects is standard addition, which involves addition of increasing volumes of a standard to equal volumes of the sample to prepare at least five spiked samples. Plotting the signal versus the concentration of added standard allows for explicit calculation of analyte concentration in the sample, whether matrix effects exist or not. However standard addition is very time-consuming and requires substantial sample volume for the replicate analyses and additions. Internal calibration involves adding an internal standard (i.e. a compound of known concentration that behaves similarly to the analyte) to the sample in a constant quantity, followed by a single analytical determination of the target analyte and internal standard. The ratio of analyte to internal standard response is calculated and can be plotted for known amounts to obtain a calibration curve. Internal standards are especially useful when sample losses

are known to occur during sample preparation because the ratio of analyte to standard stays the same as the same percentage is lost from each.

One of the most common obstacles to the accuracy of analysis are matrix effects. Several strategies may be employed to remove or reduce matrix effects, including selective extraction, effective sample clean-up, and optimization of the separation method to obtain full separation of analytes from matrix components (Furey et al., 2013). Selective extraction and sample clean-up may lead to analyte loss and so are not attractive options for ultra-trace analysis. Optimizing the separation method can be a good way to reduce matrix effects, however it can be time-consuming and lead to long analysis times. Other methods to reduce matrix effects are the use of calibration approaches such as external calibration using matrix-matched samples, standard addition, or mass-labelled internal standards, as well as sample dilution. Both standard addition and calibration using matrix-matched samples require large sample volumes which are typically not available when analyzing ultra-trace contaminants, as the extraction volumes are kept small to achieve sample concentrations above the instrument detection limits. For a similar reason, dilution is not the preferred choice when working at ultra-trace levels. As described in Section 1.5.1, use of each analyte's own mass-labelled internal standard is the best way to mitigate matrix effects (Furey et al., 2013).

1.7 Objectives

The first objective of this work is to improve and validate our nylon PAS analysis method by optimizing several analytical and field-associated QA/QC parameters. First, issues arising from the analytical method are assessed and resolved, greatly improving the accuracy of analyte quantitation. These include resolving interferences with $^{13}\text{C}_2$ -TFA, TFA and PFPrA, as well as evaluating the performance of the $^{13}\text{C}_1$ -TFA, and $^{13}\text{C}_4$ -PFBA internal standards against the gold standard of $^{13}\text{C}_1$ -PFPrA in quantifying PFPrA. Next, several experiments are conducted on the extraction and deployment methods, with the aim of providing greater certainty in our measurements of gas-phase PFCAs. Improvements include the evaluation of the extraction method at two environmentally relevant concentrations, the calibration of our nylon PAS for the uptake of PFBA using an enclosed atmospheric chamber and a controlled delivery of gas-phase PFBA, and the assessment of potential sampling biases for field-deployed PAS. Last, a novel intercomparison

with SIP PAS is conducted at a wastewater treatment plant with the aim of enhancing our understanding of whole air composition in PFCA emissions from a point source and evaluating the performance and comparability of the two passive sampling methods for measuring ultrashort- and short-chain PFCAs.

The second objective of this work is to deploy nylon PAS at several locations within the Greater Toronto Area (GTA), to quantify gas-phase PFCAs at multiple locations simultaneously and gain insight to the distribution of PFCAs in a large urban city. First, measurements are performed at three locations spanning a distance of 40 km across the GTA as part of the Study of Winter Air Pollution in Toronto campaign. Next, nylon PAS are deployed at a suspected PFAS point source, Pearson International Airport, and at three nearby sites in pursuit of studying aircraft and airport-derived PFCA emissions compared to the surrounding urban environment, representing the first atmospheric measurements of ultrashort-chain PFCAs at an airport. Next, measurements are conducted in four indoor locations: a chemistry laboratory with a history of PFAS usage, an instrumental laboratory, an academic office, and an office in a private residence, with the aim of determining potential indoor inhalation exposure risks. This represents the most comprehensive indoor passive sampling campaign to date for ultrashort-chain PFCAs.

The third and final objective of this work is to deploy nylon PAS at 14 locations along the St. Lawrence River and Estuary in Quebec, representing the largest sampling endeavor to date targeting ultrashort-chain PFCAs in air. This study aims to quantify the abundance of PFCAs in the habitats of the endangered St. Lawrence beluga whales and provide insight into the sources, behaviour, and distribution of PFCAs across a large spatial area spanning nearly 600 km.

1.8 References

- Ahrens, L., Harner, T., Shoeib, M., Koblizkova, M., & Reiner, E. J. (2013). Characterization of two passive air samplers for per- and polyfluoroalkyl substances. *Environmental Science and Technology*, 47(24), 14024–14033. <https://doi.org/10.1021/es4048945>
- Ahrens, L., Harner, T., Shoeib, M., Lane, D. A., & Murphy, J. G. (2012). Improved characterization of gas-particle partitioning for per- and polyfluoroalkyl substances in the atmosphere using annular diffusion denuder samplers. *Environmental Science and Technology*, 46(13), 7199–7206. <https://doi.org/10.1021/es300898s>
- Ahrens, L., Shoeib, M., Harner, T., Lee, S. C., Guo, R., & Reiner, E. J. (2011). Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environmental Science and Technology*, 45(19), 8098–8105. <https://doi.org/10.1021/es1036173>
- Andrews, D. Q., Hayes, J., Stoiber, T., Brewer, B., Campbell, C., & Naidenko, O. V. (2021). Identification of point source dischargers of per- and polyfluoroalkyl substances in the United States. *AWWA Water Science*, 3(5). <https://doi.org/10.1002/aws2.1252>
- Arp, H. P. H., & Goss, K. U. (2009). Gas/particle partitioning behavior of perfluorocarboxylic acids with terrestrial aerosols. *Environmental Science and Technology*, 43(22), 8542–8547. <https://doi.org/10.1021/es901864s>
- Arp, H. P. H., Gredelj, A., Glüge, J., Scheringer, M., & Cousins, I. T. (2024). The Global Threat from the Irreversible Accumulation of Trifluoroacetic Acid (TFA). *Environmental Science and Technology*, 58(45), 19925–19935. <https://doi.org/10.1021/acs.est.4c06189>
- Awad, E., Zhang, X., Bhavsar, S. P., Petro, S., Crozier, P. W., Reiner, E. J., Fletcher, R., Tittlemier, S. A., & Braekevelt, E. (2011). Long-term environmental fate of perfluorinated compounds after accidental release at Toronto airport. *Environmental Science and Technology*, 45(19), 8081–8089. <https://doi.org/10.1021/es2001985>
- Barber, J. L., Berger, U., Chaemfa, C., Huber, S., Jahnke, A., Temme, C., & Jones, K. C. (2007). Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of Environmental Monitoring*, 9(6), 530. <https://doi.org/10.1039/b701417a>
- Bigard, A., Cardinael, P., & Agasse, V. (2023). Anion Exchange Chromatography Coupled to Electrospray-Mass Spectrometry: An Efficient Tool for Food, Environment, and Biological Analysis. *Critical Reviews in Analytical Chemistry*, 53(7), 1591–1603. <https://doi.org/10.1080/10408347.2022.2036942>
- Bjornsdotter, M. K., Yeung, L. W. Y., Karrman, A., & Jogsten, I. E. (2020). Challenges in the analytical determination of ultra-short-chain perfluoroalkyl acids and implications for environmental and human health. *Anal. Bioanal. Chem*, 412(20), 4785–4796. <https://doi.org/10.1007/s00216-020-02692-8>
- Boyer, T. H., Fang, Y., Ellis, A., Dietz, R., Choi, Y. J., Schaefer, C. E., Higgins, C. P., & Strathmann, T. J. (2021). Anion exchange resin removal of per- and polyfluoroalkyl substances (PFAS) from impacted water: A critical review. *Water Research*, 200, 117244. <https://doi.org/10.1016/j.watres.2021.117244>

- Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., Voogt, P. D., Jensen, A. A., Kannan, K., Mabury, S. A., & van Leeuwen, S. P. J. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management*, 7(4), 513–541. <https://doi.org/10.1002/ieam.258>
- Bytnerowicz, A., Padgett, P. E., Arbaugh, M. J., Parker, D. R., & Jones, D. P. (2001). Passive sampler for measurements of atmospheric nitric acid vapor (HNO₃) concentrations. *TheScientificWorldJournal*, 1, 815–822. <https://doi.org/10.1100/tsw.2001.323>
- Bytnerowicz, A., Sanz, M. J., Arbaugh, M. J., Padgett, P. E., Jones, D. P., & Davila, A. (2005). Passive sampler for monitoring ambient nitric acid (HNO₃) and nitrous acid (HNO₂) concentrations. *Atmospheric Environment*, 39(14), 2655–2660. <https://doi.org/10.1016/j.atmosenv.2005.01.018>
- Cahill, T. M. (2022). Increases in Trifluoroacetate Concentrations in Surface Waters over Two Decades. *Environmental Science and Technology*, 56(13), 9428–9434. <https://doi.org/10.1021/acs.est.2c01826>
- Cahill, T. M., Thomas, C. M., Schwarzbach, S. E., & Seiber, J. N. (2001). Accumulation of Trifluoroacetate in Seasonal Wetlands in California. *Environmental Science & Technology*, 35(5), 820–825. <https://doi.org/10.1021/es0013982>
- Carmichael, L. (2022). *Determining the sampling rates for a new nylon passive sampler to estimate the atmospheric concentrations of nitric acid and perfluoroalkyl acids pollutants* [Master's Thesis, York University]. <http://hdl.handle.net/10315/40980>
- Cheng, L., Teagle, S., Enders, J. R., Weed, R. A., Nichols, H. B., Knappe, D. R. U., & Hoppin, J. A. (2025). Historical Blood Serum Samples from Wilmington, North Carolina: The Importance of Ultrashort-Chain Per- and Polyfluoroalkyl Substances. *Environmental Science & Technology*. <https://doi.org/10.1021/acs.est.5c08146>
- Clouthier, J., Vandenboer, T., & Young, C. (2026). Direct-inject suppressed ion chromatography-mass spectrometry method with online preconcentration for short- and ultra short-chain perfluoroalkyl carboxylic acids in fresh water. *Analytical Methods*. <https://doi.org/10.1039/D5AY02105G>
- Colussi, A. A., Persaud, D., Lao, M., Place, B. K., Hems, R. F., Ziegler, S. E., Edwards, K. A., Young, C. J., & Vandenboer, T. C. (2024). Cost-effective off-grid automatic precipitation samplers for pollutant and biogeochemical atmospheric deposition. *Atmospheric Measurement Techniques*, 17(12), 3697–3718. <https://doi.org/10.5194/amt-17-3697-2024>
- Conder, J. M., Hoke, R. A., De Wolf, W., Russell, M. H., & Buck, R. C. (2008). Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environmental Science and Technology*, 42(4), 995–1003. <https://doi.org/10.1021/es070895g>
- Du, Z., Deng, S., Bei, Y., Huang, Q., Wang, B., Huang, J., & Yu, G. (2014). Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review. *Journal of Hazardous Materials*, 274, 443–454. <https://doi.org/10.1016/j.jhazmat.2014.04.038>

- Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., & Wallington, T. J. (2004). Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science and Technology*, 38(12), 3316–3321. <https://doi.org/10.1021/es049860w>
- Fenton, S. E., Ducatman, A., Boobis, A., DeWitt, J. C., Lau, C., Ng, C., Smith, J. S., & Roberts, S. M. (2021). Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environmental Toxicology and Chemistry*, 40(3), 606–630. <https://doi.org/10.1002/etc.4890>
- Finlayson-Pitts, B. J., & Pitts, J. N. (2000). *Chemistry of the upper and lower atmosphere: Theory, experiments, and applications*. Academic Press.
- Freeling, F., & Mira de Orduña Heidinger, R. (2025). Tracking Trifluoroacetate (TFA) through Time: A 78-Year Record from Archived Wines. *Environmental Science & Technology*, 59(49), 26762–26769. <https://doi.org/10.1021/acs.est.5c10868>
- Fritz, J. S. (1987). Ion Chromatography. *Analytical Chemistry*, 59(4), 335–344.
- Furey, A., Moriarty, M., Bane, V., Kinsella, B., & Lehane, M. (2013). Ion suppression; A critical review on causes, evaluation, prevention and applications. *Talanta*, 115, 104–122. <https://doi.org/10.1016/j.talanta.2013.03.048>
- Genualdi, S., Lee, S. C., Shoeib, M., Gawor, A., Ahrens, L., & Harner, T. (2010). Global Pilot Study of Legacy and Emerging Persistent Organic Pollutants using Sorbent-Impregnated Polyurethane Foam Disk Passive Air Samplers. *Environmental Science & Technology*, 44(14), 5534–5539. <https://doi.org/10.1021/es1009696>
- Gorecki, T., & Namiesnik, J. (2002). Passive sampling. *Trends Anal. Chem.*, 21(4), 276–291. [https://doi.org/10.1016/S0165-9936\(02\)00407-7](https://doi.org/10.1016/S0165-9936(02)00407-7)
- Harris, D. C. (2010). *Quantitative Chemical Analysis* (8. ed). W. H. Freeman and Company.
- Houtz, E. F., Sutton, R., Park, J. S., & Sedlak, M. (2016). Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Research*, 95, 142–149. <https://doi.org/10.1016/j.watres.2016.02.055>
- Jacob, D. J. (1999). *Introduction to Atmospheric Chemistry*. Princeton University Press.
- Janousek, R. M., Mayer, J., & Knepper, T. P. (2019). Is the phase-out of long-chain PFASs measurable as fingerprint in a defined area? Comparison of global PFAS concentrations and a monitoring study performed in Hesse, Germany from 2014 to 2018. *TrAC - Trends in Analytical Chemistry*, 120. <https://doi.org/10.1016/j.trac.2019.01.017>
- Joudan, S., De Silva, A. O., & Young, C. J. (2021). Insufficient evidence for the existence of natural trifluoroacetic acid. *Environ. Sci.: Processes Impacts*, 23, 1641–1649. <https://doi.org/10.1039/d1em00306b>
- Kawashima, H., Ogata, R., & Gunji, T. (2021). Laboratory-based validation of a passive sampler for determination of the nitrogen stable isotope ratio of ammonia gas. *Atmospheric Environment*, 245. <https://doi.org/10.1016/j.atmosenv.2020.118009>

- Khalid, N. K., Le Calvez, M., Lemire, M., Dinh, Q. T., Fontaine, J., Lair, S., & Sauvé, S. (2024). Occurrence of 80 per and polyfluorinated alkyl substances (PFAS) in muscle and liver tissues of marine mammals of the St. Lawrence Estuary and Gulf, Quebec, Canada. *Frontiers in Environmental Chemistry*, 5. <https://doi.org/10.3389/fenvc.2024.1403728>
- Kudzin, G. P., Dodds, J. N., Kirkwood-Donelson, K. I., Schiffenbauer, A., Sarkar, K., Noroozi Farhadi, P., Miller, F. W., Johnson, D., Chappel, J., Jarmusch, A. K., Rider, L. G., & Baker, E. S. (2026). Evaluating Legacy and Emerging PFAS in Human Blood Collected from 2003 to 2021. *Environmental Science & Technology*, 60(4), 3068–3079. <https://doi.org/10.1021/acs.est.5c13753>
- Kwiatkowski, C. F., Andrews, D. Q., Birnbaum, L. S., Bruton, T. A., Dewitt, J. C., Knappe, D. R. U., Maffini, M. V., Miller, M. F., Pelch, K. E., Reade, A., Soehl, A., Trier, X., Venier, M., Wagner, C. C., Wang, Z., & Blum, A. (2020). Scientific Basis for Managing PFAS as a Chemical Class. *Environmental Science and Technology Letters*, 7(8), 532–543. <https://doi.org/10.1021/acs.estlett.0c00255>
- Lau, C., Butenhoff, J. L., & Rogers, J. M. (2004). The developmental toxicity of perfluoroalkyl acids and their derivatives. *Toxicology and Applied Pharmacology*, 198(2), 231–241. <https://doi.org/10.1016/j.taap.2003.11.031>
- Lee, H., Butt, C. M., Lodge, S., Ye, R., Nistorescu, I., Young, C., & VandenBoer, T. (2025). *Quantitation of ultrashort- and short-chain PFAS in beverages by a direct injection LC-MS/MS method*. SCIEX. <https://sciex.com/tech-notes/food-beverage/food-and-beverage/quantitation-of-ultrashort-and-short-chain-pfas-in-beverages-by-a-direct-injection-lc-ms-ms-method>
- Lee, H., Roberts, S., Butt, C. M., Lodge, S., Ye, R., Young, C., & VandenBoer, T. (2025). *Simultaneous quantitation of ultrashort-, short- and long-chain PFAS in water by a single direct injection LC-MS/MS method*. SCIEX. <https://sciex.com/tech-notes/environmental-industrial/water-and-soil/simultaneous-quantitation-of-ultrashort-short-and-long-chain-pfas-in-water-by-a-single-direct-injection-lc-ms-ms-method>
- Lindstrom, A. B., Strynar, M. J., & Libelo, E. L. (2011). Polyfluorinated compounds: Past, present, and future. *Environmental Science and Technology*, 45(19), 7954–7961. <https://doi.org/10.1021/es2011622>
- Liu, J., Zhao, Z., Li, J., Hua, X., Zhang, B., Tang, C., An, X., & Lin, T. (2023). Emerging and legacy perfluoroalkyl and polyfluoroalkyl substances (PFAS) in surface water around three international airports in China. *Chemosphere*, 344, 140360. <https://doi.org/10.1016/j.chemosphere.2023.140360>
- Luecken, D. J., Waterland, R. L., Papasavva, S., Taddonio, K. N., Hutzell, W. T., Rugh, J. P., & Andersen, S. O. (2010). Ozone and TFA Impacts in North America from Degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), A Potential Greenhouse Gas Replacement. *Environmental Science & Technology*, 44(1), 343–348. <https://doi.org/10.1021/es902481f>
- MacInnis, J. J., VandenBoer, T. C., & Young, C. J. (2016). Development of a gas phase source for perfluoroalkyl acids to examine atmospheric sampling methods. *Analyst*, 141(12), 3765–3775. <https://doi.org/10.1039/c6an00313c>

- Markovic, M. Z., Prokop, S., Staebler, R. M., Liggio, J., & Harner, T. (2015). Evaluation of the particle infiltration efficiency of three passive samplers and the PS-1 active air sampler. *Atmospheric Environment*, 112, 289–293. <https://doi.org/10.1016/j.atmosenv.2015.04.051>
- Martin, J. W., Mabury, S. A., Solomon, K. R., & Muir, D. C. G. (2003). Bioconcentration and Tissue Distribution of Perfluorinated Acids in Rainbow Trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.*, 22(1), 196–204. <https://doi.org/10.1002/etc.5620220126>
- Martin, J. W., Mabury, S. A., Wong, C. S., Noventa, F., Solomon, K. R., Alae, M., & Muir, D. C. G. (2003). Airborne haloacetic acids. *Environmental Science and Technology*, 37(13), 2889–2897. <https://doi.org/10.1021/es026345u>
- Melymuk, L., Bohlin, P., Sánka, O., Pozo, K., & Klánová, J. (2014). Current challenges in air sampling of semivolatile organic contaminants: Sampling artifacts and their influence on data comparability. *Environmental Science and Technology*, 48(24), 14077–14091. <https://doi.org/10.1021/es502164r>
- Melymuk, L., Nizzetto, P. B., Harner, T., White, K. B., Wang, X., Tominaga, M. Y., He, J., Li, J., Ma, J., Ma, W. L., Aristizábal, B. H., Dryer, A., Jiménez, B., Muñoz-Arnanz, J., Odabasi, M., Dumanoglu, Y., Yaman, B., Graf, C., Sweetman, A., & Klánová, J. (2021). Global intercomparison of polyurethane foam passive air samplers evaluating sources of variability in SVOC measurements. *Environmental Science and Policy*, 125, 1–9. <https://doi.org/10.1016/j.envsci.2021.08.003>
- Melymuk, L., Robson, M., Helm, P. A., & Diamond, M. L. (2011). Evaluation of passive air sampler calibrations: Selection of sampling rates and implications for the measurement of persistent organic pollutants in air. *Atmospheric Environment*, 45(10), 1867–1875. <https://doi.org/10.1016/j.atmosenv.2011.01.011>
- Miao, X., Ma, W., Tian, Y., Luo, H., Xing, Y., Zhan, L., Pan, Y., Sheng, N., & Dai, J. (2025). Environmental Occurrence, Source Identification, and Health Hazards of Ultrashort-Chain PFAS in the Yangtze River Delta. *Environmental Science & Technology*. <https://doi.org/10.1021/acs.est.5c09274>
- Michalski, R. (2016). Principles and Applications of Ion Chromatography. In R. Michalski (Ed.), *Application of IC-MS and IC-ICP-MS in Environmental Research* (1st ed., pp. 1–46). Wiley. <https://doi.org/10.1002/9781119085362.ch1>
- Montes, R., Rodil, R., Placer, L., Wilms, J. M., Cela, R., & Quintana, J. B. (2020). Applicability of mixed-mode chromatography for the simultaneous analysis of C1–C18 perfluoroalkylated substances. *Analytical and Bioanalytical Chemistry*, 412(20), 4849–4856. <https://doi.org/10.1007/s00216-020-02434-w>
- Muir, D. C. G., Freeling, F., Nilsson, S., Bugsel, B., Bowles, K., Hobson, P., Toms, L.-M., & Mueller, J. F. (2025). Trifluoroacetic Acid in Australian Human Urine Samples. *Environmental Science & Technology Letters*. <https://doi.org/10.1021/acs.estlett.5c00678>
- Neuwald, I. J., Hübner, D., Wiegand, H. L., Valkov, V., Borchers, U., Nödler, K., Scheurer, M., Hale, S. E., Arp, H. P. H., & Zahn, D. (2022). Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated. *Environmental Science and Technology*, 56(10), 6380–6390. <https://doi.org/10.1021/acs.est.1c07949>

- OECD. (2018). *Summary report on the new comprehensive global database of per- and polyfluoroalkyl substances (PFASs)* (OECD Series on Risk Management 39). <https://doi.org/10.1787/1a14ad6c-en>
- Padgett, P. E., Bytnerowicz, A., Dawson, P. J., Riechers, G. H., & Fitz, D. R. (2004). Design, Evaluation and Application of a Continuously Stirred Tank Reactor System for Use in Nitric Acid Air Pollutant Studies. *Water, Air, and Soil Pollution*, 151(1–4), 35–51. <https://doi.org/10.1023/B:WATE.00000009890.74470.fa>
- Perrino, C., De Santis, F., & Febo, A. (1988). Uptake of nitrous acid and nitrogen oxides by nylon surfaces: Implications for nitric acid measurement. *Atmospheric Environment* (1967), 22(9), 1925–1930. [https://doi.org/10.1016/0004-6981\(88\)90081-9](https://doi.org/10.1016/0004-6981(88)90081-9)
- Persaud, D., Criscitiello, A. S., Spencer, C., Lehnher, I., Muir, D. C. G., De Silva, A. O., & Young, C. J. (2024). A 50 year record for perfluoroalkyl acids in the high arctic: Implications for global and local transport. *Environmental Science: Processes and Impacts*, 26(9), 1543–1555. <https://doi.org/10.1039/d4em00219a>
- Persaud, D., Joudan, S., VandenBoer, T. C., & Young, C. J. (2026). Atmospheric Removal of Trifluoroacetic Acid by Dry and Wet Deposition: A Multiyear Analysis in Toronto. *Environmental Science & Technology Letters*, 13(2), 261–267. <https://doi.org/10.1021/acs.estlett.5c01100>
- Pickard, H. M., Criscitiello, A. S., Persaud, D., Spencer, C., Muir, D. C. G., Lehnher, I., Sharp, M. J., De Silva, A. O., & Young, C. J. (2020). Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations. *Geophysical Research Letters*, 47(10). <https://doi.org/10.1029/2020GL087535>
- Pickard, H. M., Criscitiello, A. S., Spencer, C., Sharp, M. J., Muir, D. C. G., De Silva, A. O., & Young, C. J. (2018). Continuous non-marine inputs of per- and polyfluoroalkyl substances to the High Arctic: A multi-decadal temporal record. *Atmospheric Chemistry and Physics*, 18(7), 5045–5058. <https://doi.org/10.5194/acp-18-5045-2018>
- Place, B. K., Young, C. J., Ziegler, S. E., Edwards, K. A., Salehpoor, L., & VandenBoer, T. C. (2018). Passive sampling capabilities for ultra-trace quantitation of atmospheric nitric acid (HNO₃) in remote environments. *Atmospheric Environment*, 191, 360–369. <https://doi.org/10.1016/j.atmosenv.2018.08.030>
- Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). Sources, fate and transport of perfluorocarboxylates. *Environmental Science and Technology*, 40(1), 32–44. <https://doi.org/10.1021/es0512475>
- Saini, A., Chinnadurai, S., Schuster, J. K., Eng, A., & Harner, T. (2023). Per- and polyfluoroalkyl substances and volatile methyl siloxanes in global air: Spatial and temporal trends. *Environmental Pollution*, 323. <https://doi.org/10.1016/j.envpol.2023.121291>
- Schuster, J. K., Harner, T., Eng, A., Rauert, C., Su, K., Hornbuckle, K. C., & Johnson, C. W. (2021). Tracking POPs in Global Air from the First 10 Years of the GAPS Network (2005 to 2014). *Environmental Science and Technology*, 55(14), 9479–9488. <https://doi.org/10.1021/acs.est.1c01705>

- Scott, B. F., Spencer, C., Mabury, S. A., & Muir, D. C. G. (2006). Poly and perfluorinated carboxylates in north American precipitation. *Environmental Science and Technology*, 40(23), 7167–7174. <https://doi.org/10.1021/es061403n>
- Seethapathy, S., Górecki, T., & Li, X. (2008). Passive sampling in environmental analysis. *Journal of Chromatography A*, 1184(1–2), 234–253. <https://doi.org/10.1016/j.chroma.2007.07.070>
- Seinfeld, J. H., & Pandis, S. N. (2006). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (3rd ed.). John Wiley & Sons Inc.
- Shoeib, M., & Harner, T. (2002). Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environmental Science and Technology*, 36(19), 4142–4151. <https://doi.org/10.1021/es020635t>
- Shoeib, M., Harner, T., Sum, C. L., Lane, D., & Zhu, J. (2008). Sorbent-impregnated polyurethane foam disk for passive air sampling of volatile fluorinated chemicals. *Analytical Chemistry*, 80(3), 675–682. <https://doi.org/10.1021/ac701830s>
- Shoeib, M., Schuster, J., Rauert, C., Su, K., Smyth, S. A., & Harner, T. (2016). Emission of poly and perfluoroalkyl substances, UV-filters and siloxanes to air from wastewater treatment plants. *Environmental Pollution*, 218, 595–604. <https://doi.org/10.1016/j.envpol.2016.07.043>
- Snyder, L. R., Kirkland, J. J., & Dolan, J. W. (2010). *Introduction to Modern Liquid Chromatography* (3rd ed.). John Wiley & Sons, Inc. <https://doi.org/10.1007/s13361-010-0021-8>
- Sturges, W. T., & Harrison, R. M. (1989). The use of nylon filters to collect hcl: Efficiencies, interferences and ambient concentrations. *Atmospheric Environment* (1967), 23(9), 1987–1996. [https://doi.org/10.1016/0004-6981\(89\)90525-8](https://doi.org/10.1016/0004-6981(89)90525-8)
- Sunderland, E. M., Hu, X. C., Dassuncao, C., Tokranov, A. K., Wagner, C. C., & Allen, J. G. (2019). A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects. *Journal of Exposure Science and Environmental Epidemiology*, 29(2), 131–147. <https://doi.org/10.1038/s41370-018-0094-1>
- Taniyasu, S., Kannan, K., Man, K. S., Gulkowska, A., Sinclair, E., Okazawa, T., & Yamashita, N. (2005). Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *Journal of Chromatography A*, 1093(1–2), 89–97. <https://doi.org/10.1016/j.chroma.2005.07.053>
- Tao, Y., VandenBoer, T. C., Ye, R. X., & Young, C. J. (2023). Exploring controls on perfluorocarboxylic acid (PFCA) gas-particle partitioning using a model with observational constraints. *Environmental Science: Processes and Impacts*, 25(2), 264–276. <https://doi.org/10.1039/d2em00261b>
- Thackray, C. P., Selin, N. E., & Young, C. J. (2020). A global atmospheric chemistry model for the fate and transport of PFCAs and their precursors. *Environmental Science: Processes and Impacts*, 22(2), 285–293. <https://doi.org/10.1039/c9em00326f>

- Tyrrell, H. J. V. (1964). The origin and present status of Fick's diffusion law. *Journal of Chemical Education*, 41(7), 397. <https://doi.org/10.1021/ed041p397>
- Vanhouwaert, E., Carmichael, L., Nistorescu, I., Crilley, L., Shunthirasingham, C., Hung, H., Young, C., & Vandenboer, T. C. (2025). Selective ultra-trace atmospheric passive sampling of gaseous perfluoroalkyl carboxylic acids. *Environmental Science: Processes & Impacts*. <https://doi.org/10.1039/d5em00297d>
- Wallington, T. J., Schneider, W. F., Worsnop, D. R., Nielsen, O. J., Sehested, J., Debruyn, W. J., & Shorter, J. A. (1994). Environmental impact of CFC replacements—Sources of short chain PFCAs. *Environmental Science & Technology*, 28(7). <https://doi.org/10.1021/es00056a714>
- Walter, T. H., Alden, B. A., Field, J. A., Lawrence, N. L., Osterman, D. L., Patel, A. V., & DeLoffi, M. A. (2021). Characterization of a highly stable mixed-mode reversed-phase/weak anion-exchange stationary phase based on hybrid organic/inorganic particles. *Journal of Separation Science*, 44(5), 1005–1014. <https://doi.org/10.1002/jssc.202001136>
- Wang, Y., Liu, M., Vo Duy, S., Munoz, G., Sauv  , S., & Liu, J. (2024). Fast analysis of short-chain and ultra-short-chain fluorinated organics in water by on-line extraction coupled to HPLC-HRMS. *Science of the Total Environment*, 943. <https://doi.org/10.1016/j.scitotenv.2024.173682>
- Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C., & Hungerb  hler, K. (2014). Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: Production and emissions from quantifiable sources. *Environment International*, 70, 62–75. <https://doi.org/10.1016/j.envint.2014.04.013>
- Wang, Z., Cousins, I. T., Scheringer, M., & Hungerb  hler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFASs) and their potential precursors. *Environment International*, 60, 242–248. <https://doi.org/10.1016/j.envint.2013.08.021>
- Wang, Z., Dewitt, J. C., Higgins, C. P., & Cousins, I. T. (2017). A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environmental Science and Technology*, 51(5), 2508–2518. <https://doi.org/10.1021/acs.est.6b04806>
- Wania, F., & Shunthirasingham, C. (2020). Passive air sampling for semi-volatile organic chemicals. *Environmental Science: Processes and Impacts*, 22(10), 1925–2002. <https://doi.org/10.1039/d0em00194e>
- Weiss, J. (2004). *Handbook of Ion Chromatography* (3rd ed.). Wiley-VCH.
- Weiss, J. (2019). *Gradient Elution of Ionic Compounds* (S. Kromidas, Ed.; pp. 111–159). Thermo. <https://doi.org/10.1002/9783527812745.ch4>
- Wong, F., Shoeib, M., Katsoyiannis, A., Eckhardt, S., Stohl, A., Bohlin-Nizzetto, P., Li, H., Fellin, P., Su, Y., & Hung, H. (2018). Assessing temporal trends and source regions of per- and polyfluoroalkyl substances (PFASs) in air under the Arctic Monitoring and Assessment Programme (AMAP). *Atmospheric Environment*, 172, 65–73. <https://doi.org/10.1016/j.atmosenv.2017.10.028>

- Wu, J., Jin, H., Li, L., Zhai, Z., Martin, J. W., Hu, J., Peng, L., & Wu, P. (2019). Atmospheric perfluoroalkyl acid occurrence and isomer profiles in Beijing, China. *Environmental Pollution*, 255, 113129. <https://doi.org/10.1016/j.envpol.2019.113129>
- Yamashita, N., Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P. K. S., & Kannan, K. (2008). Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. *Chemosphere*, 70(7), 1247–1255. <https://doi.org/10.1016/j.chemosphere.2007.07.079>
- Ye, R. X., Di Lorenzo, R. A., Clouthier, J. T., Young, C. J., & VandenBoer, T. C. (2023). A Rapid Derivatization for Quantitation of Perfluorinated Carboxylic Acids from Aqueous Matrices by Gas Chromatography-Mass Spectrometry. *Analytical Chemistry*, 95(19), 7648–7655. <https://doi.org/10.1021/acs.analchem.3c00593>
- Young, C. J., Joudan, S., Tao, Y., Wentzell, J. J. B., & Liggio, J. (2024). High Time Resolution Ambient Observations of Gas-Phase Perfluoroalkyl Carboxylic Acids: Implications for Atmospheric Sources. *Environmental Science and Technology Letters*, 11(12), 1348–1354. <https://doi.org/10.1021/acs.estlett.4c00897>
- Young, C. J., & Mabury, S. A. (2010). Atmospheric perfluorinated acid precursors: Chemistry, occurrence, and impacts. *Reviews of Environmental Contamination and Toxicology*, 208, 1–109. https://doi.org/10.1007/978-1-4419-6880-7_1
- Young, C. J., & VandenBoer, T. C. (2023, October). PFAS: Unraveling the analytical challenges: Separations and selectivity for measurements of atmospheric PFAS. *Separation Science*. <https://www.sepscience.com/separations-and-selectivity-for-measurements-of-atmospheric-pfas-7951>
- Zhang, B., Zhai, Z., & Zhang, J. (2018). Distribution of trifluoroacetic acid in gas and particulate phases in Beijing from 2013 to 2016. *Science of the Total Environment*, 634, 471–477. <https://doi.org/10.1016/j.scitotenv.2018.03.384>
- Zheng, G., Eick, S. M., & Salamova, A. (2023). Elevated Levels of Ultrashort- and Short-Chain Perfluoroalkyl Acids in US Homes and People. *Environmental Science and Technology*, 57(42), 15782–15793. <https://doi.org/10.1021/acs.est.2c06715>
- Zimmer, D. (2003). Introduction to quantitative liquid chromatography-tandem mass spectrometry (LC-MS-MS). *Chromatographia*, 57(S1), S325–S332. <https://doi.org/10.1007/BF02492124>

Chapter 2. Method development and validation of nylon passive air samplers for measurement of gas-phase PFCAs

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Author Contributions:

IN prepared, with TCV editing the chapter/manuscript. IN performed all experiments and analyses under the guidance of TCV, except those specifically noted below where collaborators were involved.

CJY and TCV conceptualized the work and acquired the funding. CJY and TCV provided the resources to support this work.

IN conducted the chamber experiments; EV assembled the chamber components and developed the chamber use procedures presented in Section 2.2.5. Parts of Sections 2.2.1.3 and 2.2.5 are reproduced or adapted from:

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For the SWAPIT and Pearson International Airport (YYZ) campaigns, HH and CS were associated with funding to support the participation of IN and helped with project design and logistics. Due to security clearances and various adjacent site access requirements, SWAPIT sample deployment and collection was conducted by DP and sampler deployment and collection at Pearson International Airport was conducted by RR.

For the WWTP intercomparison, all nylon PAS field work was done by EV. SIP PAS were deployed and collected by JM and analyzed by IN under the supervision and guidance of AS. SS and TH aided in project design.

2.1 Introduction

2.1.1 Perfluoroalkyl carboxylic acids (PFCAs)

Perfluoroalkyl carboxylic acids (PFCAs) are widely detected in environmental media such as air (Vanhouwaert et al., 2025) and rainwater (Taniyasu et al., 2008), as well as in wildlife (Khalid et al., 2024) and humans (Fenton et al., 2021), even though they are not naturally occurring (Joudan et al., 2021). PFCAs can be categorized based on chain length: PFCAs containing eight or more carbons ($\geq C8$) are termed long-chain, those with less than eight carbons ($< C8$) are named short-chain, and a subset of short-chain PFCAs, those with three carbons or less ($\leq C3$) are termed ultrashort-chain (Buck et al., 2011). Due to the bioaccumulative and toxic nature of long-chain PFCAs and perfluoroalkyl sulfonic acids (PFSAs) (Fenton et al., 2021), restrictions on their production and use were implemented (Janousek et al., 2019). Consequently, manufacturers turned to the use of structurally similar replacement compounds, such as those with fewer fluorinated carbons, the ultrashort- ($C2$, $C3$) and short-chain ($C4$ – $C6$) PFCAs (Janousek et al., 2019; Z. Wang et al., 2013, 2017). These fluorinated alternatives were thought to be safer due to their lower bioaccumulation potential in humans; however, studies have shown that ultrashort- and short-chain PFAS can be just as persistent and even more mobile in the environment (Janousek et al., 2019). The $C2$ PFCA, trifluoroacetic acid (TFA), has been demonstrated to accumulate in plants, including crops (Freeling & Bjornsdotter, 2023). Compared to long-chains, ultrashort-chain PFCAs are much higher in abundance in the environment (Arp et al., 2024; Persaud et al., 2026; Pickard et al., 2020), meaning that our exposure to them can be higher even if their half-lives in the human body are shorter (Cheng et al., 2025).

Due to the strength of the carbon-fluorine bonds, PFCAs are extremely stable and do not degrade under the conditions typical of Earth's environment (Young & Mabury, 2010). PFCAs are released into the environment directly, from their manufacture and industrial use, and indirectly from the environmental degradation of precursor compounds such as fluorotelomer alcohols (FTOHs) as well as hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), which can form the $C2$ and $C3$ PFCAs, TFA and perfluoropropanoic acid (PFPrA) (Bjornsdotter et al., 2020; Joudan et al., 2021; Young & Mabury, 2010). Many PFCA precursors are highly mobile, readily undergoing long range atmospheric transport, leading to PFCA deposition from the atmosphere into terrestrial and aquatic systems far away from the emission location of their volatile parent

compound(s), leading to global contamination (Pickard et al., 2018; Thackray et al., 2020; Wong et al., 2018). Thus, atmospheric measurement of PFCAs, in particular those with six or fewer carbons, is becoming increasingly important.

2.1.2 Sampling techniques for the measurement of atmospheric PFCAs

Under typical environmental conditions, PFCAs are largely found in the gas phase, with limited partitioning into the aqueous particle phase (i.e. aerosols). The extent of gas-particle partitioning and dissociation of PFCAs depends on liquid water content, pH, and the physical properties of PFCAs, with the particle fraction increasing with chain length (Tao et al., 2023; Thackray et al., 2020). Previous atmospheric measurements have used active sampling techniques such as high volume active air samplers (HV-AAS), which provide information on the gas- and particle- phase distribution (Ahrens et al., 2012; Wong et al., 2018). However, HV-AAS have disadvantages such as sampling artifacts due to the collection of particles before gases, which can theoretically result in both over- and underestimation of concentrations that are dependent on the composition of the atmospheric matrix (Ahrens et al., 2012). Diffusion denuder samplers negate these issues by collecting the gas-phase first, followed by the particle-phase (Martin et al., 2003; Young & VandenBoer, 2023). However, both active sampling methods are expensive, difficult to operate, and require power. These challenges have limited sampling locations and prevented large-scale surveys of the atmospheric abundance and variability of gaseous and/or particulate PFCAs.

Passive air samplers (PAS) overcome the challenges of active air samplers, as they are affordable, easy to use, and operate without power (Gorecki & Namiesnik, 2002; Place et al., 2018; Wania & Shunthirasingham, 2020). Additionally, PAS are suitable for deployment in remote areas, in large numbers, and so have the potential to obtain large spatial scale measurements of atmospheric abundance and variability. In the past, polyurethane foam (PUF) disks, with or without the addition of XAD resin have been utilized for atmospheric measurements of total PFAS found in both the gas and particulate phases (Karásková et al., 2018; Shoeib et al., 2008). Due to the low sorption and/or recovery of PFCAs and other volatile PFAS onto PUF, they were combined with XAD, a polystyrene resin, as PUF-XAD, and then renamed as sorbent-impregnated polyurethane foam (SIP) disks. These have been reported to improve sorption of volatile PFAS by two orders of magnitude (Shoeib et al., 2008), but have not been validated in their performance for the collection of ultrashort-chain PFCAs. SIP disks also require extensive sample preparation, long multi-step

extraction methods using solvents, as well as multiple concentration and evaporation steps (Ahrens et al., 2011) which can lead to sample loss, making these methods highly dependent on the use of internal standards (IS) added prior to extraction for recovery correction, as well as expensive mass spectrometers where isotopically-labeled IS are used. To date, passive air samplers utilizing SIP disks (SIP PAS) have only been used to measure PFAS with $\geq C4$ and thus were never calibrated for the uptake of ultrashort-chain PFCAs (Ahrens et al., 2013), such as TFA and PFPrA, which are present at much higher concentrations in the atmosphere (Vanhouwaert et al., 2025).

PAS with nylon filters have been successfully used to measure gas phase nitric acid (HNO_3) (Bytnerowicz et al., 2001, 2005; Place et al., 2018) and TFA (Carmichael, 2022). More recently, the entire suite of ultrashort- and short-chain ($C2-C6$) PFCAs_(g) were measured by Vanhouwaert et al. (2025) in the atmosphere from sites across Canada using nylon PAS. Gas phase acids such as PFCAs selectively chemisorb onto the nylon filters, making these passive air samplers well suited for the measurement of PFCAs at mixing ratios down to the parts per quadrillion (ppqv) range in the atmosphere. In addition, the samplers' preparation and extraction procedures are simple, and when analyzing with ion chromatography systems, do not require strong solvents or any evaporation steps, thus minimizing sample loss. Our nylon PAS, adapted from the design by Place et al. (2018), have been calibrated for the uptake of TFA through an extensive atmospheric chamber calibration experiment (Vanhouwaert et al., 2025). Through this calibration, the linear uptake rate for TFA was determined, and with the aid of Fuller's Law, the predicted linear uptake rates for the remaining PFCAs ($C3-C6$) were estimated.

2.1.3 Objectives

The goal of this work is to validate the nylon PAS for the measurement of gas-phase $C2-C6$ PFCAs. To do so, several method quality assurance and quality control processes were evaluated and optimized. First, a major interference with the $^{13}C_2$ -TFA IS peak was assessed for how it might limit our quantitative workflow. Second, due to the unavailability of the mass-labelled IS for PFPrA, an assessment of the quantitative performance of our method by using TFA and the $C4$ PFCA (perfluorobutanoic acid, PFBA) mass-labelled IS, $^{13}C_1$ -TFA and $^{13}C_4$ -PFBA, was evaluated, as a $C4$ -IS has been typically assumed to be quantitative (70–130%) in the literature, but not validated. Third, an extraction method for $C2-C6$ PFCAs from both nylon and polypropylene (PP)

filters was validated. The overlying PP filters, designed to allow gas phase PFCAs to pass through, were inspected for the uptake of gaseous PFCAs.

Following this, we turned our attention to the optimization of the field deployment of our PAS. The nylon PAS were calibrated for the uptake of PFBA, while simultaneously confirming the value of our previously measured TFA uptake rate. Next, the potential for sampling bias arising from the duration of PAS deployment due to co-sampling of other atmospheric acids was assessed, as this issue was raised by Reviewers on our published methodology. Finally, a first step towards method intercomparison of our nylon PAS and SIP PAS was undertaken at a wastewater treatment plant (WWTP). A WWTP was targeted because in the past WWTPs have been found to be point sources for PFAS into both the aquatic and atmospheric environments and because higher PFAS concentrations in the effluent compared to the influent suggest that WWTPs do not effectively destroy PFAS (Ahrens et al., 2011; Gewurtz et al., 2024; Houtz et al., 2016; Shoeib et al., 2016). However, none of these studies include atmospheric measurements of ultrashort-chain PFCAs at WWTPs. This intercomparison also includes the methodological workflows ending in ion chromatography-mass spectrometry (IC-MS) and ultrahigh pressure liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) quantitative determinations.

2.2 Methods

2.2.1 Materials and Chemicals

2.2.1.1 IC-MS analysis

Sodium carbonate (Na_2CO_3 , $\geq 99.5\%$, ACS reagent grade), glycerol ($>99\%$), and sodium hydroxide (NaOH) solution (49-51% in water) were purchased from Sigma Aldrich (ON, Canada). Methanol (MeOH, Optima LC-MS) was obtained from Fisher Chemical (ON, Canada) and used for IC-MS analysis. Methanol (HPLC grade, $\geq 99.9\%$) was obtained from Sigma Aldrich (ON, Canada) and used for rinsing glassware. PFBA ($>97\%$) was purchased from Sigma Aldrich (MO, US). The sodium salts of TFA ($>98\%$) and PFPrA ($>99\%$) were obtained from Sigma Aldrich; sodium salts of PFBA ($>98\%$), perfluoropentanoic acid (PFPeA, $>97\%$) and perfluorohexanoic acid (PFHxA, $>98\%$) were obtained from Synquest (FL, US). Individual 1000 $\mu\text{g/mL}$ stock solutions of each

sodium salt PFCA were prepared in ultrapure Milli-Q water (18.2 M Ω ·cm at 25 °C, Direct 8; EMD Millipore), and subsequently combined and diluted to prepare working stock solutions.

Mass-labelled $^{13}\text{C}_1$ -TFA (T786038) and $^{13}\text{C}_1$ -PFPrA were purchased from Toronto Research Chemicals (ON, Canada) and dissolved separately in MeOH to 50 mg/mL. Mass-labelled $^{13}\text{C}_2$ -TFA-sodium salt (99%, 50 $\mu\text{g/mL}$ in MeOH) was purchased from Cambridge Isotope Laboratories, Inc. Mass-labelled $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_3$ -PFPeA, and $^{13}\text{C}_2$ -PFHxA were obtained as individual 50 $\mu\text{g/mL}$ solutions in MeOH from Wellington Laboratories (ON, Canada; MPFBA, M3PFPeA, and MPFHxA). Subsets of these compounds were combined and diluted with Milli-Q water into one solution for use as IS for IC-MS analysis.

2.2.1.2 UPLC-MS/MS analysis

A list of PFAS compounds used for UPLC-MS/MS analysis and their acronyms and analysis details can be found in Appendix A, Table S2.1.

A mixture of native PFAS; C4–C14, C16, C18 PFCAs and C4, C6, C8 and C10 PFSA (PFAC-MXB) was purchased from Wellington Laboratories. The C2 and C3 PFCAs (TFA, >98%; PFPrA, >98%) and sodium salts of C2 (PFEtS, >98%), C3 (L-PFPrS, >98%), C11 (L-PFUdS, >98%), and C13 PFSA (L-PFTrDS, >98%) were purchased from Wellington Laboratories as individual 50 $\mu\text{g/mL}$ solutions in MeOH. The C5 PFSA (PFPeS, APFOA025S) and sodium salts of C7 and C9 PFSA (PFHpS, APFOS008S; PFNS, APFOS009S) were purchased as individual 100 $\mu\text{g/mL}$ solutions in MeOH, and the C12 PFSA (PFDoDS, APFOS038SCN) was purchased as a 100 $\mu\text{g/mL}$ solution in ACN from Chromatographic Specialties Inc.

A mass labelled PFAS mixture containing $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_5$ -PFNA, $^{13}\text{C}_2$ -PFDA, $^{13}\text{C}_2$ -PFUnDA, $^{13}\text{C}_2$ -PFDoDA, $^{18}\text{O}_2$ -PFHxS, and $^{13}\text{C}_4$ -PFOS (MPFAC-MXA) was purchased from Cambridge Isotope Laboratories Inc. This was used as a surrogate standard mixture, added prior to extraction. Mass-labelled $^{13}\text{C}_4$ -PFBS (99%, potassium salt, cat# CLM-9523-S), $^{13}\text{C}_3$ -PFPrA (99%, cat# CLM-11324-A-S), and $^{13}\text{C}_2$ -TFA (99%, sodium salt, cat# CLM-11046-S) were obtained as individual 50 $\mu\text{g/mL}$ in MeOH solutions from Cambridge Isotope Laboratories Inc. These mass-labelled standards were obtained after sample extraction and only added to samples analyzed with the C1–C3 PFAS method prior to injection.

2.2.1.3 Nylon passive air samplers

The VandenBoer Group has adapted the custom-built passive air samplers (PAS) from the design by Place et al. (2018), which was used to measure $\text{HNO}_3(\text{g})$. The filter pack assembly consists of a Petri dish (60×15 mm, Fisher Scientific), a nylon membrane filter (47 mm, 0.45 μm , Satorius, Fisher Scientific, P/N 2500647N), two polytetrafluoroethylene (PTFE) rings, (52×2 mm, McMaster Carr, P/N 8547K33), a polypropylene (PP) filter (47 mm, 2.0 μm , Tisch, Tisch Scientific, SKU: SF14908), and an acrylic or polycarbonate ring (53×4 mm, McMaster Carr, P/N 8486K541) which holds everything together inside an inverted Petri dish (Figure 2.1) (Vanhauwaert et al., 2025).

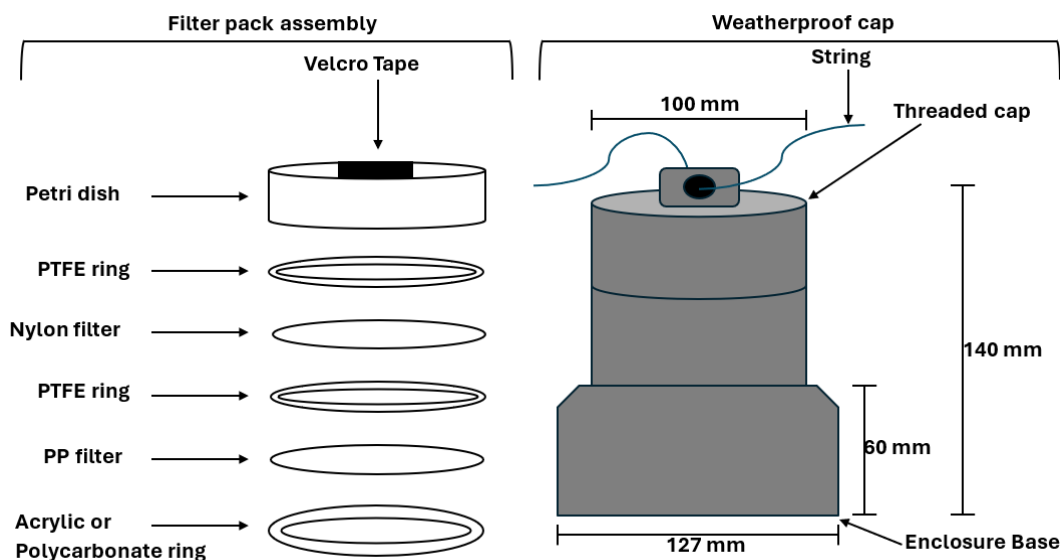


Figure 2.1 Passive air sampler components and assembly order. After assembly, the filter pack is affixed inside the weatherproof cap. Reproduced from Vanhauwaert et al. (2025) with permission from the Royal Society of Chemistry.

The PAS filter pack is enclosed in weatherproof cap (composed of a 4"×3" reducing pipe coupling and 3" ABS fitting clean out adapter with plug; IPEX, 4×3ABSCOU 027366, 3ABSFITCO 027708) which protects it from wind and precipitation. The weatherproof cap, originally black, was spray-painted silver (Rust-Oleum Universal, SKU: #1000520681) to reflect sunlight, and reduce the temperature in the filter pack assembly from radiative heating of the ambient air.

2.2.2 Preparation, deployment, and extraction of nylon PAS

The washing, assembly, and deployment procedures for nylon PAS were originally adapted from Place et al. (2018) and further developed by us in Vanhauwaert et al. (2025). Before the PAS are assembled, the nylon and PP filters are placed inside separate 1 L HDPE wide mouth bottles (Avantor, VWR, Cat. # 414004-115) and rinsed 6 times with deionized water (Milli-Q water), then both filter types are allowed to soak in solutions overnight; the PP filters in Milli-Q water, and the nylon filters in 0.015 M Na₂CO₃ in Milli-Q water to remove any bound acid impurities. Following that, filters of both types are rinsed with Milli-Q water 6 times and left to soak overnight in Milli-Q water. Prior to assembly, the PTFE and PC rings are placed inside a 1 L HDPE bottle and rinsed 6 times with Milli-Q water. The remaining PAS components, the Petri dishes and lids, are each rinsed separately 6 times with Milli-Q water.

The nylon and PP filters are allowed to air dry between two Kimtech® Kimwipes for 1.5 to 2 hours before assembly. All other components are allowed to air dry and/or are fully dried using Kim Wipes before assembly. Clean latex gloves and tweezers are used for assembly. A PTFE ring is placed inside a Petri dish to support the sampling filter, followed by the nylon sampling filter, another PTFE support ring, then a PP overlying filter to prevent intrusion of particles or atmospheric debris, and finally an acrylic or polycarbonate ring that holds everything in place as a friction lock. Lastly, the Petri dish lid is secured with lab tape, the PAS is sealed in a Ziploc® bag and stored in the freezer to reduce diffusive sampling until deployment.

The PAS are deployed in triplicate to reduce random error by providing the minimum assessment of measurement precision, while also representing a practical balance with the labour required for assembly, deployment, and analysis. When deployed, each PAS is taken out of the Ziploc® bag, the lid is removed, and it is attached to the inside of the weatherproof cap with hook and loop fasteners (Figure S2.1 in Appendix A). The weather shields are hung on a stable structure (e.g. post, fence, tree branch). The field blanks are only exposed to the air at the sampling site for ~10 seconds, then reconnected to the lids with the lab tape and returned to the Ziploc® bags. When PAS are collected from the field, the deployment steps are completed in reverse; the weatherproof cap is taken down, the PAS are removed, the lids are taped on, the PAS placed inside Ziploc® bags and then stored in the freezer until extraction and analysis. Deployment details of the PAS are provided in Appendix A, Table S2.2.

To extract, each nylon filter is gently rolled into a cone and placed inside a clean, dry Falcon™ tube. Extraction solvent (3 or 4 mL of 3 mM NaOH in Milli-Q water) is added to each tube, the tubes are sonicated for at least 15 minutes, then stored in the fridge overnight. If the polypropylene (PP) filters are to be analysed, they are extracted in the same way as the nylon filters, otherwise the PP filters are set aside to be washed and reused. The following day, clean tweezers are used to squeeze out all of the liquid from the filters prior to their removal from the extract.

2.2.3 Instrumental Analysis of PFCAs

2.2.3.1 Ion chromatography-mass spectrometry (IC-MS)

The sample extracts were analyzed for the C2–C6 PFCAs_(g) via ion chromatography-mass spectrometry (IC-MS). The ion chromatography system is composed of a Thermo Scientific™ Dionex™ ICS-6000 system outfitted with dual pump and dual column and detector compartments. The autosampler uses a 5 mL syringe to inject either 750 µL of the sample on an anion-selective concentrator column (Thermo Scientific™ Dionex™ IonPac™ TAC-ULP1, 5×23mm, 18 µm dp, 6% DVB), or 250 µL of the sample using a loop. A Thermo Scientific™ Dionex™ IonPac™ AG/AS24 guard (2×50 mm, 11 µm dp) and analytical column combination (2×250 mm, 7 µm dp, 55% DVB, alkanol quaternary ammonium exchanger) were used for the separation. A 2 mm Thermo Scientific™ Dionex™ ADRS 600 Dynamically Regenerated Suppressor is operated in external water mode to remove Na⁺ and OH⁻ from the eluent before reaching the conductivity detector and mass spectrometer. Milli-Q water is supplied to the suppressor at a flow of 1 mL/min. The suppressed eluent then flows through a conductivity detector before combining with 0.2 mL/min Optima methanol and entering the Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer. The single quadrupole mass spectrometer was operated in negative electrospray ionisation mode (ESI-) at 450 °C, performed in selective ion monitoring (SIM) with an ion transfer tube at 250 °C. The operating parameters for IC-MS analysis of C2–C6 PFCAs are summarized in Table 2.1.

Ten-point calibration standards were prepared for C2–C6 PFCAs in Milli-Q water, ranging from 0.01–10 ng/mL. For analysis of any standards, blanks, or samples, 800 µL of the solution was transferred to a 1 mL polypropylene IC-MS vial (Agilent, PN: 5182-0567), IS (100 µL) was added, and the solution was vortexed. To correct for matrix effects and instrument fluctuations, the peak areas of each PFCA were normalized against its corresponding mass-labelled IS, except for PFPrA,

which was quantified using $^{13}\text{C}_1$ -PFPrA, $^{13}\text{C}_1$ -TFA IS or $^{13}\text{C}_2$ -TFA, depending on availability. Due to an isobaric matrix interference with the $^{13}\text{C}_2$ -TFA IS at m/z 115, TFA was often quantified in a separate run, using the 250 μL loop and longer more selective separation method.

Table 2.1 Operating parameters for IC-MS analysis using the concentrator column and loop with long or short gradients. Mobile phase A: Milli-Q water; and mobile phase B: 100 mM NaOH in Milli-Q water.

Concentrator– short			Loop – long		Concentrator– long	
Injection volume (μL)	750		250		750	
Flow (mL/min)	0.35		0.35		0.35	
Suppressor current (mA)	57		57		57	
Column temperature ($^{\circ}\text{C}$)	28		25		25	
Mobile phase gradient:	<u>Time</u> <u>(min)</u>	<u>%B</u>	<u>Time</u> <u>(min)</u>	<u>%B</u>	<u>Time</u> <u>(min)</u>	<u>%B</u>
	0.00	25	0.00	10	0.00	10
	6.0	25	7.0	10	7.0	10
	10.9	52	10.0	27	10.0	27
	14.0	52	16.5	32	16.5	32
	14.5	60	20.0	50	20.0	50
	24.0	60	22.0	60	22.0	60
	24.1	10	31.0	60	31.0	60
	26.5	End	31.0	10	31.0	10
			33.0	End	33.0	End

2.2.3.2 Ultra Performance Liquid Chromatography-tandem Mass Spectrometry (UPLC-MS/MS)

In this work, previously extracted SIP disks were analyzed. Details on the preparation, assembly, deployment and extraction procedures for SIP PAS can be found in Shoeib et al. (2016). Briefly, samples were extracted with an accelerated solvent extraction system (ASE, ASE 350, Dionex Corporation, Sunnyvale, CA, USA) with a 33 mL capacity ASE cell using three cycles of 60–65 mL acetonitrile under the following conditions: 100 $^{\circ}\text{C}$, 5 min static cycle with a 100% flush and 240 s purge. This was concentrated using TurboVap (Biotage, Charlotte, NC, USA) to ~ 1 mL at 40 $^{\circ}\text{C}$, rinsed with acetonitrile and concentrated again to 0.5 mL. This was followed by transfer to 15 mL polypropylene tubes, an acetonitrile rinse, then reduction under nitrogen (N_2) gas to a final volume of 1 mL. Extracts were further purified using a carbon-column cleanup (100 mg of ENVI-Carb, 100-400 mesh, Supelco, St. Louis, MO) using acetonitrile (4 mL) as the elution solvent. This

was followed by further reduction under N₂ gas to ~1 mL and solvent exchange to MeOH, then reduction under N₂ to 0.5 mL. Prior to extraction, each SIP disk was spiked with mass-labelled surrogate standards (SS) containing ¹³C-PFCAs (C4, C6, C8, C9, C10, C11, C12) and ¹⁸O₂- and ¹³C₈-PFSAs (C6 and C8) to allow calculation of analyte recovery during extraction and analysis. Recovery correction for the ultrashort PFCAs with mass labelled IS has not typically been part of this methodology, instead relying on the assumption that the C4-IS sufficiently represents the behaviour of the method with respect to the C2 and C3 PFCA analytes. The WWTP SIP samples were spiked with 50 pg of the SS mix, and not the typical 500 pg here. An IS mixture containing ¹³C₈-PFOA and ¹³C₈-PFOS, in a final spike mass of 500 pg each, was added to each standard and sample prior to Ultra Performance Liquid Chromatography-Tandem Mass Spectrometry (UPLC-MS/MS) instrumental analysis.

Extracts from SIP disks were analyzed for C2–C14, C16, C18 PFCAs and C1–C13 PFSAs using Waters Acquity I-class UPLC coupled with a Xevo TQ-S triple quadrupole mass spectrometer (MS/MS) (Waters, Boston, MS, USA), using electrospray ionization (ESI) operating in negative ion mode. A list of the ions monitored for PFAS is given in the Appendix, Table S2.1.

Table 2.2 Mobile phase gradient for UPLC-MS/MS analysis of PFCAs and PFSAs.

Ultrashort-chain			Short- and Long-chain	
Injection volume (μL)	3		1	
Flow (mL/min)	0.3		0.5	
Mobile Phase	A: 0.025% acetic acid in water B: 20 mM NH ₄ Ac in MeOH		A: 10 mM NH ₄ Ac in water B: 10 mM NH ₄ Ac in MeOH	
Mobile phase gradient	<u>Time (min)</u>	<u>%B</u>	<u>Time (min)</u>	<u>%B</u>
	Initial	20	Initial	2
	3.00	80	3.00	95
	4.00	80	3.10	100
	4.10	100	4.00	100
	5.00	100	4.10	2
	5.10	20	6.70	2
	8.00	20	N/A	N/A

Short- and long-chain PFAS, namely C4–C14, C16, C18 PFCAs and C4–C13 PFSAs, were analyzed using a previously established gradient method of 0.5 mL/min methanol and water, both containing 10 mM aqueous ammonium acetate solution (NH₄Ac) (Table 2.2). Ultrashort-chain PFCAs (C2 and C3) and C1 – C3 PFSAs, were analyzed using a novel method developed for this

work, utilizing a gradient of water containing 0.025% acetic acid and MeOH with 20 mM NH₄Ac (Table 2.2). Additional method details are presented in Appendix A, Tables S2.3 and S2.4. A 6-point calibration curve for each PFCA and PFSA was used to quantify the data. Method blanks consisting of pre-cleaned SIP disks were extracted and analyzed using the same procedure as for field blanks and samples. A method blank and a check standard were run after every set of 10 samples including field blanks, to track performance of the instrument.

2.2.4 Expanded quality assurance and quality control from field observations

2.2.4.1 Interference with ¹³C₂ TFA internal standard

Sometimes samples contain non-PFAS compounds (i.e. interferents) which have the same mass-to-charge (m/z) ratio and MRM transition, as well as similar retention time, to the target analytes (Bangma et al., 2024). Such interferences with compounds of identical nominal masses for the mass resolution of a given mass spectrometer, for example $\Delta m/z < 1$ for the single quadrupole with unit mass resolution on the IC-MS, are termed isobaric. Co-elution of an interferent and analyte can lead to falsely elevated analyte concentration. In past IC-MS analyses, it was proven that the ¹³C₁-TFA IS works well and does not have any isobaric interferents (Vanhauwaert, 2024), however, approximately 1% of carbon exists as the ¹³C₁ isotope, which means ¹³C₁-TFA is present in samples prior to its addition as the IS. The ¹³C₂ isotope is not naturally occurring, so in theory, ¹³C₂-TFA could perform better as an internal standard. However, when using the short separation gradient with the concentrator column, the majority of PAS deployed at Toronto Pearson International Airport were found to contain an isobaric interferent at m/z 115, the same as ¹³C₂-TFA. In an effort to mitigate the interference, the samples were analyzed again, using an injection loop to reduce the abundance of matrix and a longer separation gradient to improve chromatographic resolution (Section 2.2.3.1, Table 2.1).

All PAS were extracted as described previously (Section 2.2.2). One PAS deployed indoors in an active chemistry laboratory was spiked with the ¹³C₂-TFA IS and analyzed via three IC-MS methods: using the concentrator column with both short and long separation methods, and the loop using the long separation method (Section 2.2.3.1, Table 2.1). The resulting chromatograms in the ¹³C₂-TFA channel (m/z 115) were compared between the methods with varying separation

selectivity to assess the presence and mitigation of isobaric interferences. Deployment details of the PAS are provided in Appendix A, Table S2.2.

2.2.4.2 Improving the quantitation of PFPrA

Contamination of the $^{13}\text{C}_1$ -PFPrA IS with TFA led to several issues regarding PFPrA quantitation. First, the $^{13}\text{C}_1$ -PFPrA IS could not be used to quantify PFPrA in the same analysis as TFA, thus a different IS had to be identified for best use when analyzing samples for PFPrA with the intent to perform quantification. Two options were the mass-labelled PFCAs closest to PFPrA in size and physical properties, $^{13}\text{C}_1$ -TFA and $^{13}\text{C}_4$ -PFBA. The result from each IS was compared against the result obtained using the TFA-contaminated $^{13}\text{C}_1$ -PFPrA. We used 800 μL each of triplicate PAS extracts from two Toronto sampling sites from the Study of Winter Air Pollution in Toronto (SWAPIT) campaign, High Park and Evergreen Brickworks, and each was spiked with 100 μL of an IS solution containing $^{13}\text{C}_1$ -TFA and $^{13}\text{C}_4$ -PFBA (final spike masses 2 ng and 0.5 ng, respectively) and analyzed by IC-MS. Separate 800 μL aliquots from the same PAS extracts were spiked with 100 μL of the $^{13}\text{C}_1$ -PFPrA IS and analyzed.

Second, PFPrA quantitation in PAS deployed at Pearson International Airport was difficult due to an isobaric interference with the $^{13}\text{C}_2$ -TFA IS. Samples were re-analyzed, using the loop and a longer separation gradient, and a comparison of TFA and PFPrA concentrations obtained with each method was conducted to determine which method was most robust. A second aliquot was taken from two Pearson Airport sample extracts and one Quebec City extract, spiked with $^{13}\text{C}_1$ -PFPrA and analyzed using the loop with long gradient to assess the performance of both the $^{13}\text{C}_2$ -TFA IS and the $^{13}\text{C}_1$ -PFPrA IS in samples under the same gradient conditions.

Third, due to observations of multiple peaks in the PFPrA channel (m/z 163) and a substantial shift in PFPrA retention time in several samples analyzed with the long gradient, a comparison of PFPrA and $^{13}\text{C}_1$ -PFPrA separations using the short and long gradients was undertaken on a PAS deployed in Quebec City. This comparison aimed to identify the PFPrA peak under the long gradient conditions; the results are presented in Appendix A. Deployment details can be found in Appendix A, Table S2.2.

The overall objective of the work in this section is to identify the most reliable method for accurate quantitation of PFPrA in our nylon PAS extracts.

2.2.4.3 Extraction efficiency of C2–C6 PFCAs from nylon filters

The extraction efficiency of our NaOH in Milli-Q water extraction solvent was determined for C2–C6 PFCAs at varying NaOH concentrations (0, 1, 2, 3, and 4 mM). In our previous work, 3 mM NaOH at ~4 °C was found to be the optimal extraction solvent for TFA, yielding quantitative recoveries of $83 \pm 2\%$ (Vanhauwaert, 2024). The same NaOH concentration at room temperature obtained an extraction efficiency of $73 \pm 3\%$, which was 10% lower than at 4 °C. In these earlier experiments 400 ng of TFA was spiked into method blanks ($n = 3$) containing NaOH in Milli-Q water and analyzed via IC-CD.

These initial experiments were expanded upon by determining the extraction efficiencies of the entire suite of C2–C6 PFCAs at varying extraction solvent NaOH concentrations (0, 1, 2, 3, and 4 mM) at 4 °C, in addition to the 3 mM NaOH at room temperature, at two environmentally relevant concentrations, denoted ‘high’ and ‘low’, using IC-MS. The high concentration spike consisted of 100 μ L of 200 ppb C3–C6 PFCA solution (equivalent to 20 ng C3–C6 PFCAs) spiked into a Falcon tube containing 4 mL of extraction solvent and a nylon filter ($n = 3$), which were sonicated for 20 min, then left undisturbed for at least 12 hours, either in the fridge (4 °C) or at room temperature. Measurement of TFA was not undertaken during this experiment so that PFPrA could be accurately quantified using its matched mass-labelled IS ($^{13}\text{C}_1$ -PFPrA) and is subjected to the same matrix effects as the native analyte. Method blanks ($n = 1$) and solvent blanks ($n = 3$) were also analyzed alongside the spiked samples. Method blanks consisted of 4 mL of the respective extraction solvent added to the nylon filter, sonicated for 20 min, then placed in the fridge overnight. Solvent blanks, which were the respective extraction solvents, were analyzed in triplicate for calculation of instrument detection limits.

A low concentration spike included TFA and was carried out in a similar fashion, which aimed to measure the extraction efficiencies at some of the lowest observed environmental concentrations from our initial surveys (Vanhauwaert et al., 2025). Nylon filters in 4 mL of extraction solvent (0, 1, 2, 3, or 4 mM NaOH) were spiked with 100 μ L of a solution containing C2–C6 PFCAs, equivalent to a final spike mass of 4 ng of TFA, 1 ng of PFPrA, and 0.5 ng of PFBA, PFPeA, and PFHxA. For each extraction solvent, method blanks ($n = 3$) and solvent blanks ($n = 3$) were analyzed. Due to the necessity of measuring TFA and PFPrA in the same analysis, the $^{13}\text{C}_2$ -TFA IS was used to track the recovery of and quantify PFPrA.

2.2.4.4 Inspection of overlying polypropylene filters

Previously used and cleaned overlying polypropylene (PP) filters were tested for any detectable amounts of PFCAs. Spike and recoveries on PP filters were conducted at ‘high’ and ‘low’ PFCA concentrations in a similar fashion to that presented in Section 2.2.4.3 for the nylon filters. The final spike masses were 20 ng C2–C6 PFCAs for the ‘high’ and 4 ng C2, 1 ng C3, 0.5 ng C4–C6 PFCAs for the ‘low’. Spiked 3 mM NaOH extraction solvent (4 mL) was added to Falcon tubes, each containing a PP filter ($n = 3$), which were sonicated for 20 min, then left undisturbed in the fridge (4 °C) for at least 12 hours.

To check for possible sampling bias stemming from PFCA air-water partitioning or reactive uptake on particulate matter on the overlying PP filters, those from PAS deployed at Pearson International Airport were also analyzed for C2–C6 PFCAs. Deployment details can be found in Appendix A, Table S2.2.

2.2.5 Chamber calibration of nylon passive air samplers for PFBA_(g)

Following previous nylon PAS calibration experiments for HNO_{3(g)} (Bytnerowicz et al., 2005; Padgett et al., 2004), calibration of our nylon-based PAS was recently accomplished for TFA, using an atmospheric chamber containing controlled and measured TFA mixing ratios, temperature and humidity levels, and denuders for orthogonal measurements to validate the measured sampling rate (Vanhauwaert et al., 2025).

The chamber procedures used in this work were initially developed for TFA calibration. The same custom-built enclosed atmospheric chamber used by us in Vanhauwaert et al. (2025) had certain components of the zero-air generator adapted from Crilley et al. (2023) (Figure 2.2) and was used in this work to calibrate the nylon PAS for uptake of PFBA_(g). A detailed standard operating procedure (SOP) for chamber use was followed and can be found in the MSc thesis appendices of Vanhauwaert (2024). Briefly, a control box (CCR, Model 400B, S/N 1041) was used to set the four mass flow controllers (MFCs) to the following desired flow rates to achieve 10 L/min into the chamber, and 9.7–9.8 L/min out. Inflow MFCs, in positions 2 and 4, were set to 2.5 L/min and 7.5 L/min, respectively; outflow MFCs, in positions 1 and 3, were set to 6 L/min and 3.8 L/min, respectively. The flow rates of each MFC were measured using a calibrated flow meter (MesaLabs,

Definer 220, S/N 132596) and adjusted as necessary to reach the desired values. Prior to the start of the chamber experiment, the chamber was cleaned by flushing with dry ($\sim 0\%$ RH) zero air bypassing the inflow impinger in position 4 for a minimum of two days. A permeation tube filled with native PFBA was placed inside the permeation oven (set to $70\text{ }^{\circ}\text{C}$) and allowed to equilibrate in the oven under nitrogen flow for at least 7 days before starting the chamber experiment. Our established in-house procedure for making PFCA permeation devices, as well as using our custom-built permeation oven are described in Vanhauwaert (2024) and Lao et al. (2020).

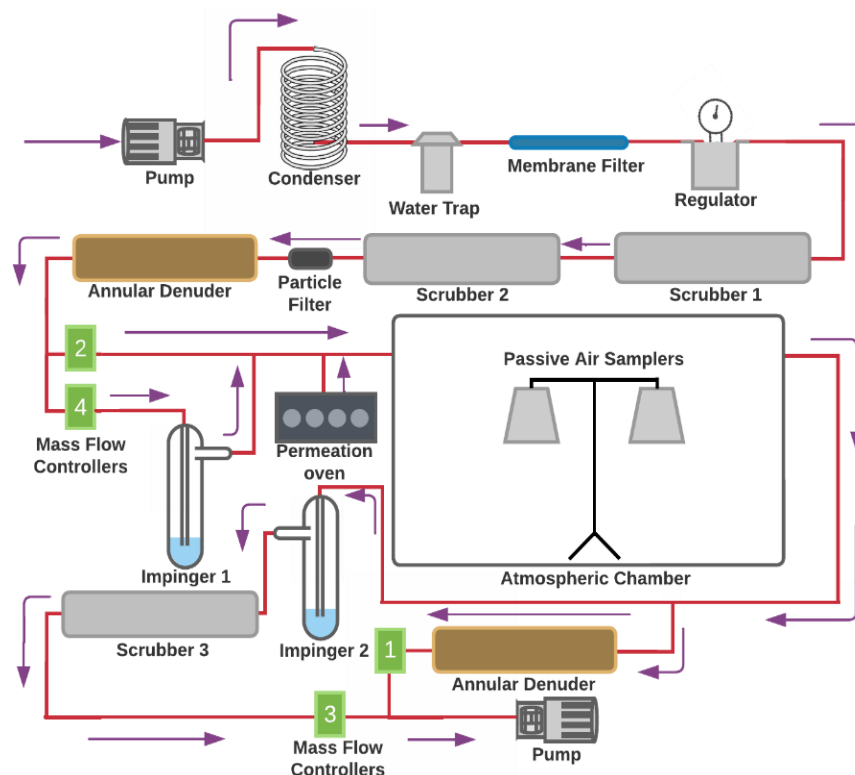


Figure 2.2 Schematic of enclosed atmospheric chamber setup. Purple arrows indicate direction of air flow. A permeation tube filled with native PFBA is placed in the permeation oven and a known amount of gas-phase PFBA is emitted into the chamber. Adapted from Vanhauwaert et al. (2025) with permission from the Royal Society of Chemistry.

Once the $\text{PFBA}_{(\text{g})}$ emission from the permeation tube equilibrated, the inflow impinger was filled with Milli-Q water and connected to the set gas flow and the permeation oven was connected, providing a steady supply of gas-phase PFBA into the chamber at a relative humidity set by the flow fraction through the water impinger. Two fans (Orion fans, OA4715-12TB) were placed inside to keep the contents well mixed. The chamber was then left in a flow-through state for 2–3

days to allow the walls and tubing to reach equilibrium with respect to both water vapour and PFBA_(g). Once the PFBA_(g) concentration in the chamber equilibrated, four sets of triplicate PAS, 12 in total, were placed inside the chamber, tied to retort stands. A field blank was exposed to the air inside the chamber for ~10 s, then capped and placed in the freezer. Three PAS were removed on each subsequent day, for a total of four days. After the removal of each set of triplicates, an outflow annular denuder (URG-2000-30x150-3CSS, University Research Glassware Corp, Chapel Hill, NC, USA) was replaced with a freshly cleaned and coated one. These denuders were used to collect and quantify PFBA_(g) in the chamber at each sampling point and correct for any loss of PFBA_(g) to the chamber walls. To ensure that temperature and relative humidity (%RH) were stable in the chamber during experiments, these parameters were measured using a Pimoroni Enviro+ sensor (ONA47D9XCF). An SOP for Pimoroni Enviro+ sensor use is provided in Appendix A, S2.2.

Our in-house procedure for quantitative PFCA collection using annular denuders, modified from the EPA Compendium Method IO-4.2 is described in detail by Ye et al. (2023). Briefly, the denuder is cleaned with Milli-Q water 5 times, then dried using zero air (Linde, ultra-zero air, purity 0.0UZ, Toronto, ON) at a flow of 2.5 L/min for at least 15 minutes. Following this, the denuder is coated with 15 mL of denuder coating solution (20 g/L Na₂CO₃ & 10 g/L of glycerol in 1:1 Milli-Q water: MeOH) and dried in the same manner. After sampling, the PFCAs are extracted using two aliquots of Milli-Q water (2×5 mL). A denuder field blank was collected by extracting a freshly cleaned and coated denuder in the same manner.

To summarize, our nylon PAS were calibrated for PFBA_(g) by placing four sets of triplicate PAS inside an atmospheric chamber containing gas-phase PFBA. Each set of triplicates was removed ~24 h after the previous set, and chamber PFBA concentrations were quantified using an annular denuder at the outflow. The chamber experiment was performed at a PFBA_(g) mixing ratio of 95 ± 10 pptv (equivalent to $0.82 \mu\text{g}/\text{m}^3$) at 30.0 ± 0.5 °C and a relative humidity (RH) of $43.8 \pm 2.2\%$. The experiment lasted four days, during which a total of 12 PAS and 4 annular denuders were used and collected. PAS were extracted prior to IC-MS analysis (Section 2.2.2), and the denuder extracts (blanks and samples) were diluted 20 times to eliminate matrix effects. PAS and diluted denuder extracts were spiked with 20 ng each of ¹³C₂-TFA and ¹³C₄-PFBA IS prior to IC-MS analysis using a sample loop.

2.2.6 Duration of PAS deployment and sampling bias

Three sets of triplicate nylon PAS were deployed at the same location on the grounds of Pearson International Airport for different sampling durations. Two sets were deployed for approximately two months each: November 2023 to January 2024, and January to March 2024, while a third set spanned the entire sampling period November 2023 to March 2024. This experiment was conducted to assess whether the much higher concentrations of other acids (e.g. HNO_3) typically found in the atmosphere would saturate or displace target analytes from the nylon filters during longer deployments, resulting in time and concentration dependent losses of target analytes and therefore systematic sampling bias. Deployment details can be found in Appendix A, Table S2.2.

2.2.7 Intercomparison between nylon and SIP PAS at a WWTP

In 2023 nylon PAS ($n = 3$) and SIP PAS ($n = 2$) were co-deployed at three sites within a Wastewater Treatment Plant (WWTP): at an upwind reference site (R), close to a primary clarifier (PC), and between aeration tanks (AT), as illustrated in Figure 2.3 (Vanhouwaert, 2024). Utilizing SIP disks, Ahrens et al., (2011) previously found this plant to be a source of PFAS to the atmosphere, including some PFCAs that their analytical method was capable of detecting ($\geq \text{C}_4$).

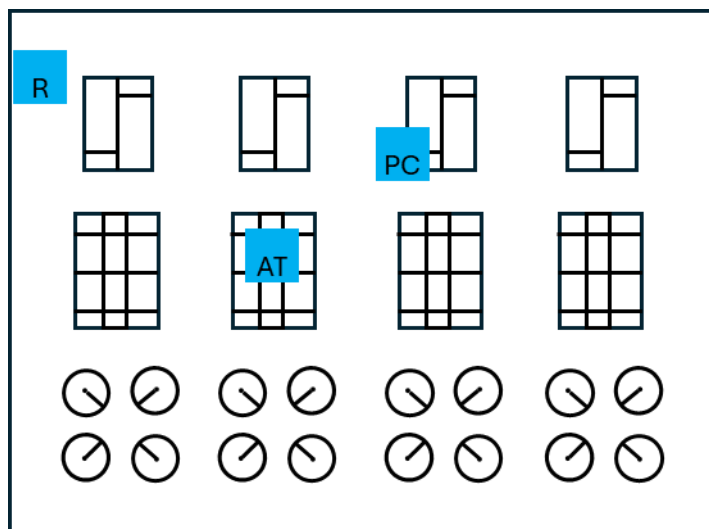


Figure 2.3 Nylon PAS ($n = 3$) and SIP disk ($n = 2$) sampling locations at the Wastewater Treatment Plant. Both types of passive samplers were deployed at a reference site (R), near a primary clarifier (PC), and between aeration tanks (AT).

The SIPs were deployed for two months, while the nylon PAS were replaced weekly or biweekly for a combined sampling period of one month. Three sets of triplicate nylon PAS were deployed in 1–2 week-long stages from May 25 to June 23, 2023. For each set of triplicate nylon PAS, a field blank was exposed to the air at the site for ~10 s as described in Section 2.2.2. Full deployment details for the nylon PAS are described by Vanhauwaert (2024). Duplicate double-dome type passive air samplers containing SIP disks were deployed at the three sites for two months from May 25 to July 27, 2023. SIP field blanks ($n = 3$) were collected by exposing the SIP disk in the dome housing for one minute at the site. The sum of the time-weighted C2–C6 PFCA concentrations, as established by our Pearson Airport sampling (Sections 2.2.6 and 2.3.6), measured by the nylon PAS were compared with the SIP measurements. The nylon PAS target the gas phase only, while the SIP disks can collect both gas and particulate PFCAs, often referred to as a whole air or total air sample. C2–C6 PFCA measurements from the two types of passive air samplers are compared here, providing the first method intercomparison between nylon and SIP PAS for gas and whole air matrices.

Concentrations of C4–C10 PFCAs and PFOS measured by SIP PAS in 2023 were compared with previous SIP PAS measurements taken at the same three locations within the WWTP in 2009 (Ahrens et al., 2011). The following sites from Ahrens et al. (2011) were selected for comparison as the closest sampling sites to those used in the current SIP PAS study: sites 1 and 2 as the reference site, 4 and 5 for the primary clarifier, and 8 and 9 between aeration tanks.

Nylon filter and SIP disk extracts were analyzed using IC-MS and UPLC-MS/MS, respectively. The following are notable differences in analyte quantitation between the two methods. Analysis of nylon PAS via IC-MS utilized the $^{13}\text{C}_1$ -TFA IS for TFA and PFPrA quantitation, while SIP disks analyzed via UPLC-MS/MS employed $^{13}\text{C}_2$ -TFA and $^{13}\text{C}_3$ -PFPrA for quantitation of TFA and PFPrA, respectively.

2.2.8 Data Analysis

2.2.8.1 IC-MS

The data was blank subtracted using the normalized concentrations of the site-specific field blank. The instrument limit of detection (iLOD) was calculated as three times the standard deviation of the peak area signals in the solvent blanks (800 μL Milli-Q water + 100 μL IS; $n = 3$). When there was no detectable signal in the blanks, the instrument limits of detection (iLOD) and quantitation

(iLOQ) were defined as having a signal-to-noise ratio (S/N) of 3 or 10, respectively. Signal-to-noise ratios were determined by dividing peak heights by the average standard deviation of the blank signals ($n = 3$) in the retention time window of each compound. The method limits of detection and quantitation (mLOD, mLOQ) were determined in the same manner, using method blanks which were clean and dry nylon filters extracted overnight with 4 mL of 3 mM NaOH in water instead of solvent blanks. Data below the detection limit was considered non-detect and replaced with $\frac{1}{2}$ detection limit when performing statistical analysis.

IC-MS analysis provides us with the PFCA mass present on each filter (and the average mass at each site). To convert the PFCA mass to atmospheric mixing ratios at each site, the passive samplers must be calibrated to determine the linear uptake rates of each PFCA onto the nylon filter. Using the atmospheric chamber techniques outlined in Section 2.2.5, Vanhauwaert et al. (2025) determined the TFA uptake rate to be $113 \pm 12 \frac{TFA_{(g)}(ng \cdot m^{-3}) \cdot t(h)}{TFA_{(filter)}(ng)}$, and used this value to estimate the uptake rates of C3–C6 PFCAs (Table 2.3). Fuller’s Law, presented in Equation 2.1, was employed for these calculations (Fuller et al., 1966).

$$\frac{\text{rate of effusion B in air}}{\text{rate of effusion C in air}} = \frac{\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{(\sqrt[3]{\sum A v_i} + \sqrt[3]{\sum B v_i})^2} \times \frac{(\sqrt[3]{\sum A v_i} + \sqrt[3]{\sum C v_i})^2}{\sqrt{\frac{1}{M_A} + \frac{1}{M_C}}} \quad (E2.1)$$

Here, the variables M_A , M_B , and M_C are the molar mass of gases A, B, and C, which are air, the compound of interest, and TFA respectively, and $\sum v_i$ is the sum of the diffusion corrected volumes of those gases (Fuller et al., 1966; Gu et al., 2018).

Table 2.3 Predicted and measured uptake rates of PFCAs, where those for C3–C6 were determined using Fuller’s law, based on the measured uptake rate for TFA from delivery of control gas quantities, as determined using an atmospheric chamber.

Compound	PFCA carbon number	Measured uptake rate	Predicted uptake rate
TFA	2	113 ± 12	-
PFPrA	3		139 ± 15
PFBA	4	$203 \pm 7^*$	161 ± 17
PFPeA	5		180 ± 19
PFHxA	6		197 ± 21

*See PFBA calibration in Section 2.3.5.

Concentrations of PFBA measured by nylon PAS determined using the predicted uptake rate were corrected by a factor of 1.26 as determined in our PFBA calibration, presented in Section 2.3.5.

The PFCA atmospheric mass loadings (C_x) (ng/m^3) can then be calculated using Equation 2.2, where M_x is the mass of ‘X’ on the nylon filter (ng), UR is the predicted or measured uptake rate

$\frac{PFCA_{(g)}(\text{ng}\cdot\text{m}^{-3})\cdot t(\text{h})}{PFCA_{(filter)}(\text{ng})}$, and t is the sampling time (h):

$$C_x = \frac{M_x \times UR}{t} \quad (\text{E2.2})$$

The mass loadings in ng/m^3 were then transformed into mixing ratios in parts-per-trillion or parts-per-quadrillion by volume (pptv and ppqv, respectively). Gas mixing ratios, defined as the number of moles of a gas (n_x) per mole of air (n_{air}) (E2.3), are a more appropriate measure of atmospheric composition, as they are not impacted by changes in temperature or pressure (Jacob, 1999).

$$C_x = \frac{n_x}{n_{\text{air}}} = \frac{C_x \times R \times T}{MW_x \times P \times V} \quad (\text{E2.3})$$

The moles of air can be calculated using the Ideal Gas Law and the mixing ratio (C_x) can be calculated using Equation 2.3, where n_x is the number of moles of compound X, C_x (ng/m^3) is its mass loading in ng/m^3 , MW_x is the molecular weight of X in ng/mol , V is the volume of air (m^3), P is the atmospheric pressure (Pa), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the average temperature (K) at the site during the period of PAS deployment. For these transformations, a value of 1 atm was assumed for the atmospheric pressure at all sites. Average temperature at each site was determined from daily meteorological data measured by the nearest weather station for the specific time periods corresponding to each sampler deployment (*Historical Data - Climate - Environment and Climate Change Canada*, 2025). The resulting value, expressed in moles of analyte per moles of air can be transformed into pptv by multiplying by 10^{12} or ppqv by 10^{15} .

2.2.8.2 UPLC-MS/MS

The data was blank corrected by subtracting the average concentration of each analyte in the field blanks ($n = 3$) from that in the samples. The recovery correction was applied on a sample-by-sample basis using the isotope dilution method based on the surrogate standards recoveries. The instrument limits of detection and quantitation (iLODs, iLOQs) were calculated as 3 times and 10 times the signal-to-noise ratio in the lowest calibration standard, respectively, and can be found in

Appendix A, Table S2.1. Due to the existence of only one lab blank, method limits of detection and quantitation were not calculated.

The UPLC-MS/MS analysis methods used in this work are largely based on those previously described by Ahrens et al. (2013). After blank correction, the PFAS mass per sample was converted to the corresponding air concentrations by dividing by the equivalent air volume (V_{air}), which is an estimate of the volume of air sampled during deployment. The formula for the calculation of V_{air} can be seen below, Equation 2.4:

$$V_{air} = K_{SIP-A} \times V_{SIP} \times \left(1 - \exp \left[- \left(\frac{A_{SIP}}{V_{SIP}} \times \frac{k_A}{K_{SIP-A}} \right) \times t \right] \right) \quad (E2.4)$$

where K_{SIP-A} is the SIP-air partition coefficient (dimensionless), V_{SIP} is the volume of the SIP disk (cm^3), A_{SIP} is the planar area of the exposed portion of the SIP disk (cm^2), k_A is the air-side mass transfer coefficient (dimensionless), and t is time (days). For analytes still in the linear phase at the end of the sampling period, V_{air} can be calculated by multiplying the sampling rate (R) by the deployment time in days (t) (E2.5).

$$V_{air} = R \times t \quad (E2.5)$$

The K_{SIP} values for the majority of short- and long-chain PFCAs and PFSAAs have been determined experimentally for SIP samplers, with the estimated value of V_{air} calculated using E2.4 in the GAPS template (Harner, 2021). The concentration of the analyte in the air (C_A) can then be determined by dividing the concentration measured per SIP disk (C_{SIP}) by V_{air} (E2.6).

$$C_A = \frac{C_{SIP}}{V_{air}} \quad (E2.6)$$

SIP disks have not been calibrated for C2, C3, C7, C18 PFCAs or C1–C3, C5, C7, C9, C11, C13 PFSAAs; as such, the equivalent air volumes for these compounds were calculated using the K_{SIP-A} values of similar compounds, as illustrated in Appendix A, Table S2.5.

The WWTP SIP samples were spiked with 50 pg of SS mix instead of the usual 500 pg, resulting in lower-than-expected recoveries for the majority of SS compounds. Recoveries for the mass-labelled PFHxS, PFHxA, PFHpA, PFNA, PFDA, and PFUnDA surrogate standards were below the instrument limit of quantitation, with recoveries below 10% in some samples. Any recoveries below the iLOD were replaced with $\frac{1}{2}$ iLOD in calculations. An external recovery correction was

applied to each of the native compounds, using the respective average surrogate standard recovery from across the full set of SIP samples to obtain better statistical representation (Appendix A, Table S2.6). Additional method details are provided in Appendix A, Tables S2.2, S2.3 and S2.4.

2.3 Results and Discussion

2.3.1 Resolving $^{13}\text{C}_2$ -TFA and TFA Interferences

Previously, TFA quantitation in PAS extracts was conducted using the $^{13}\text{C}_1$ -TFA internal standard. In this work, the $^{13}\text{C}_2$ -TFA IS was also used for TFA quantitation. When using our short elution separation method with the concentrator column, all analyzed PAS extracts were found to contain an isobaric interference at the same mass-to-charge ratio as $^{13}\text{C}_2$ -TFA (m/z 115). In many PAS deployed at Pearson International Airport, the interferent peak was over 10 times larger than the $^{13}\text{C}_2$ -TFA peak, with a peak-to-peak resolution below 1.0, making accurate quantitation extremely difficult (Figure 2.4a). Here it can be observed that the retention time of the large peak at 10.8 min expected to correspond to the IS does not match that of TFA at 10.4 min in a neat standard. Shifts in retention time are known to occur in ion chromatography depending on analyte concentration, so identification of the IS peak may not be robust when based on retention time alone even when compared to the IS peak in a neat standard.

The peak area, however, is much more informative as this is held constant when the IS does not occur naturally in a sample. A comparison found the $^{13}\text{C}_2$ -TFA IS peak in a neat standard has a similar retention time of ~10.4 min and peak area to the small shouldering peak observed at m/z 115, with the peak area in the standard larger by a factor of 1.4. This suggests that the shouldering peak belongs to the $^{13}\text{C}_2$ -TFA IS and the large peak at 10.8 min is an interference. Additional evidence of this interference is the much higher peak area of the large sample peak compared with the $^{13}\text{C}_2$ -TFA IS standard peak, by a factor of 5 (Figure 2.4a). Ionization enhancement is uncommon in ESI and so it is unlikely that the sample matrix would enhance the IS peak by a factor of five. In an effort to resolve the two peaks and accurately quantify $^{13}\text{C}_2$ -TFA, the samples were re-analyzed using the loop, as omission of the sample concentration step and a smaller injection volume (250 μL compared with 750 μL) has been determined by others in our group to improve the separation between isobaric interferences (Clouthier et al., 2025). With the loop,

injection of a smaller analyte mass can change the peak dimensions, resulting in narrower peaks and thus improved resolution between peaks.

In addition to the injection of a lower analyte mass, a longer mobile phase gradient with a shallower slope provides greater selectivity between coeluting compounds, and we combined both strategies on an aliquot of our sample, expecting improved resolution (Figure 2.4b) (Place et al., 2017; VandenBoer et al., 2012). Several observations can be drawn from this analysis: first, only one peak is observed in the $^{13}\text{C}_2$ -TFA channel (m/z 115), at a retention time of approximately 15.6 min, which matches that of both $^{13}\text{C}_2$ -TFA and TFA from the neat standard perfectly, with the interferent peak no longer present, likely eluting outside the retention window. The retention time and relative size of the sample $^{13}\text{C}_2$ -TFA peak are similar to, but lower than that of the standard peak, being smaller by a factor of 1.3. Second, two peaks separated by a minute are now observed in the TFA channel (m/z 113), showing that the changed selectivity helped resolve this isobaric interference, which was initially hidden by its coelution with TFA under the short gradient conditions.

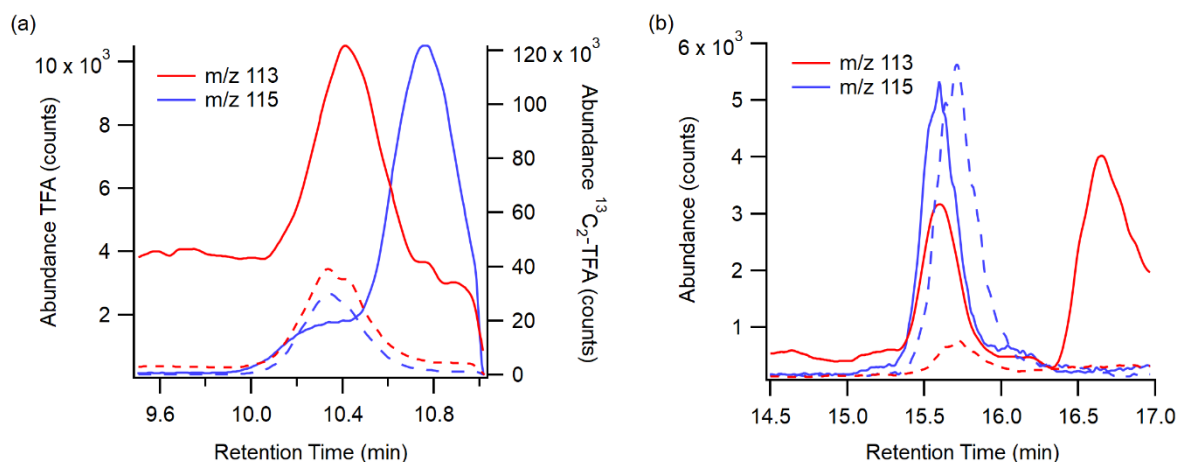


Figure 2.4 Chromatograms of TFA (red, m/z 113) and $^{13}\text{C}_2$ -TFA (blue, m/z 115) (solid lines) in an extracted PAS deployed at Pearson International Airport, with dashed lines depicting TFA and $^{13}\text{C}_2$ -TFA in a 250 ng/L standard. Panel (a) shows separation using the concentrator column (750 μL injection) and a short mobile phase gradient at 28 $^{\circ}\text{C}$, with a peak for m/z 115 at 10.8 min overlapping with a shouldering peak at 10.35 min, and (b) shows separation using a 250 μL loop injection and a long gradient at 25 $^{\circ}\text{C}$.

Use of the longer gradient and smaller injection volume resulted in an improved separation, with the $^{13}\text{C}_2$ -TFA interference resolved, likely eluting outside the retention window. The smaller injection volume lowered the peak area and width of both compounds, aiding in the obtained

resolution. The effect can be observed in the standard $^{13}\text{C}_2\text{-TFA}$ peak, for which area and width decreased by factors of 1.2 and 6, respectively, when utilizing the loop. The lower initial concentration of hydroxide (10 vs 25 mM) as the competing mobile phase ion and the slower increase in its concentration (0.8 vs 5.5 mM/min) during the longer gradient method led to an increase in the selectivity of the stationary phase, by generating longer retention times, and ultimately an improvement in separation through the retention factor k' . This aligns with the fundamental resolution equation (E2.7), which expresses resolution as a function of three parameters: the efficiency factor, N , the retention factor, k' , and the selectivity factor (α) (Place et al., 2017).

$$R = \left(\frac{\sqrt{N}}{4}\right) \left(\frac{k'}{k'+1}\right) \left(\frac{\alpha-1}{\alpha}\right) \quad (\text{E2.7})$$

Adjusting k' provided the most efficient and cost-effective approach to resolving the interference. Under the short gradient conditions, a k' value of ~ 3 was determined for TFA and $^{13}\text{C}_2\text{-TFA}$. Since resolution is proportional to $\frac{k'}{k'+1}$, modifying the mobile phase to increase k' leads to large increases in resolution when $k' < 5$. Alternative strategies, such as modifying the column or temperature, presented practical limitations. While employing a column with smaller particle size would likely enhance selectivity through reduced diffusion path lengths and narrower peaks, this approach incurs additional costs. Temperature optimization in ion chromatography is challenging, due to selectivity being directly related to the hydrated ion radius. Elevated temperatures typically accelerate the exchange rate of solute ions between mobile and stationary phases, thereby reducing retention (Michalski, 2016); however, these effects are ion-specific and unpredictable. Vanhauwaert (2024) reported increased retention and resolution for TFA and PFPrA at higher temperatures, while Place et al. (2017) observed decreased retention and both variable effects on the resolution of six alkylamine cations with increasing temperature.

Separation using the loop and longer gradient resolved the $^{13}\text{C}_2\text{-TFA}$ interference and indicated the presence of an isobaric interference at the same mass-to-charge ratio as TFA (m/z 113) in some samples. In this work, when using the $^{13}\text{C}_2\text{-TFA}$ IS, a separate analysis was conducted to quantify TFA using the loop and longer gradient, while C3–C6 PFCAs were quantified using the concentrator column and short gradient separation.

To investigate whether omission of the sample preconcentration step by utilizing the loop is necessary in resolving the $^{13}\text{C}_2\text{-TFA}$ interference, additional testing was conducted on indoor PAS extracts (Figure 2.5).

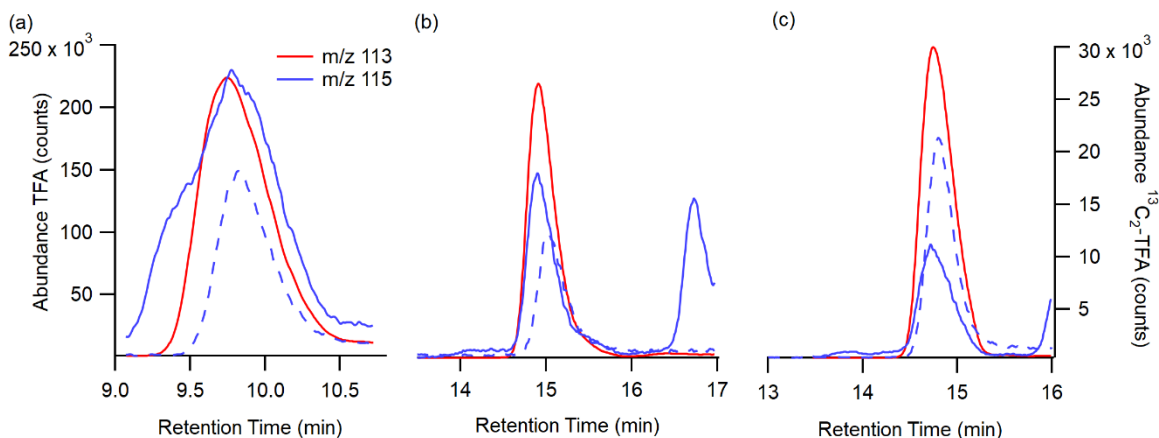


Figure 2.5 Chromatograms displaying TFA (red, m/z 113) and $^{13}\text{C}_2\text{-TFA}$ (blue, m/z 115) (solid lines) in an indoor PAS sample extract, with $^{13}\text{C}_2\text{-TFA}$ in a solvent blank overlaid (dashed lines), using three different analysis and separation methods: (a) Concentrator column with short separation gradient, (b) loop with long separation gradient, and (c) concentrator column with long separation gradient. Panels (b) and (c) show two separate peaks in the $^{13}\text{C}_2\text{-TFA}$ channel – the first belonging to $^{13}\text{C}_2\text{-TFA}$ and the second being an unknown isobaric interferent.

Here, use of the concentrator column and short gradient separation seems to be impacted by the co-elution of the isobaric interferent with $^{13}\text{C}_2\text{-TFA}$. The sample peak at m/z 115 is 2.5 times larger than in a solvent blank, and the shape is much wider than observed for TFA, suggesting co-eluting interference, rather than ionization enhancement, which is uncommon with ESI sources (Figure 2.5a). Like the Pearson Airport sample (Figure 2.4a), the large peak at m/z 115 exhibits a smaller shouldering peak, but instead the retention time of the main peak here matches that of TFA. This indoor isobaric interference was again completely resolved by using the loop and long gradient (Figure 2.5b), where two distinct peaks are observed at 15.0 min and 16.8 min, with the former matching the retention time of both TFA and the $^{13}\text{C}_2\text{-TFA}$ internal standard from a neat standard. The interference can be similarly resolved with the concentrator column and a longer gradient (Figure 2.5c). Unlike the Pearson Airport sample, no additional peaks were observed at m/z 113 in the indoor sample, suggesting that the detected TFA interferent (Figure 2.4b) is not uniformly present in PAS atmospheric samples, yet one for the $^{13}\text{C}_2\text{-TFA}$ IS is present. These results all

demonstrate the limitations of using a single quadrupole mass spectrometer and retention time alone to quantify TFA, even when including a mass-labelled IS in the method. Careful inspection of the chromatography and experience with the sample matrix, even when expected to be relatively simple like that of the atmosphere, are necessary to retain suitable method quality control. An alternate but costly solution is the utilization of a triple quadrupole mass spectrometer (MS/MS), which would improve the specificity of the analysis through precursor ion fragmentation and monitoring of one to two characteristic ion transitions per analyte (Jia et al., 2022). By targeting unique transitions rather than relying solely on the m/z ratio of the precursor ion, isobaric interferences can be effectively mitigated, as interfering compounds are unlikely to produce identical fragmentation patterns.

Quantitation of both $^{13}\text{C}_2$ -TFA and TFA was ultimately accomplished with a longer eluent gradient to improve method selectivity and compound resolution, albeit at the cost of demanding separate injections for quantification. The presence of a major co-eluting isobaric interference with the $^{13}\text{C}_2$ -TFA IS in all analyzed samples prevented analysis using our short separation method. Informal discussions among researchers in our group have tentatively identified the interferent as malic acid (after the loss of a water molecule in a dehydration reaction). Malic acid is a dicarboxylic acid commonly found in atmospheric aerosols (Röhrl & Lammel, 2002). The prevalence of this $^{13}\text{C}_2$ -TFA IS interferent is not yet clear, as it has not been observed in any water samples analyzed by direct injection using the concentrator column and a similar short concentration gradient (Clouthier et al., 2026). Identification of the unknown compound interfering with $^{13}\text{C}_2$ -TFA is beyond the scope of this work, as we have shown that its effects can be effectively mitigated through separation improvement. At the end of the day, the short separation method might be effective with the $^{13}\text{C}_1$ -TFA IS, however, one must take into account the stable isotope abundance as well as carefully assess the resulting chromatograms for any potential isobaric interferences for each atmospheric or environmental matrix analyzed until substantial experience is established to conclude whether one may be present.

2.3.2 Improving the quantitation of PFPrA

2.3.2.1 *Choice of internal standard for PFPrA quantitation*

The choice of internal standard can be extremely important to the accuracy of any analysis utilizing electrospray ionisation (ESI), with quantitation of each analyte against its own mass-labelled internal standard being the best way to mitigate matrix effects (Furey et al., 2013). Use of any other internal standard may lead to errors in quantitation, as differences in retention time can cause the analyte and internal standard to each be surrounded by a unique matrix composition, producing variation in ionization efficiencies. Due to the difficulty of obtaining a mass labelled PFPrA IS free from TFA contamination, an IS of similar structure and properties had to be used to quantify PFPrA in much of our early work on ultrashort PFCAs. Numerous studies reporting PFPrA concentrations in the literature use mass labelled PFBA IS to quantify PFPrA (Bjornsdotter et al., 2020; Janda et al., 2019; Joudan et al., 2024; Taniyasu et al., 2008; Vanhauwaert et al., 2025; Y. Wang et al., 2024; Zheng et al., 2023; Zou et al., 2024). However, PFBA has a different retention time than PFPrA in almost all analytical separations reported to date and should be expected to experience contrasting levels of matrix interference as a result, particularly for traditional LC methods where these analytes are all poorly retained and will be heavily impacted by unretained matrix. This could lead to altered ionisation efficiency through suppression or enhancement, and inaccurate quantitation.

An alternative choice is the mass-labelled TFA IS, which likely better replicates and accounts for differences in ionization as it is retained similarly to PFPrA in many methods. The $^{13}\text{C}_1$ -TFA and $^{13}\text{C}_4$ -PFBA IS were tested and compared for quantitative performance against the gold standard of $^{13}\text{C}_1$ -PFPrA IS for the quantitation of PFPrA in PAS samples deployed at two sites during the SWAPIT campaign: High Park and Evergreen Brickworks in the winter of 2024 (Figure 2.6).

The results show that the $^{13}\text{C}_1$ -TFA IS is an acceptable substitute for the $^{13}\text{C}_1$ -PFPrA IS (Figure 2.6) in our IC method, yielding statistically similar final PFPrA concentrations ($p > 0.05$, Student's t-test with equal variances, Table S2.7 in Appendix A), although the average PFPrA concentrations were ~20% lower for the samples from both sites. In contrast, quantifying with the PFBA IS resulted in significant underestimates of the atmospheric abundance of PFPrA ($p < 0.05$, Student's t-test, Table S2.7), with average PFPrA concentrations 67% (High Park) and 71% (Evergreen Brickworks) lower compared with PFPrA IS quantitation.

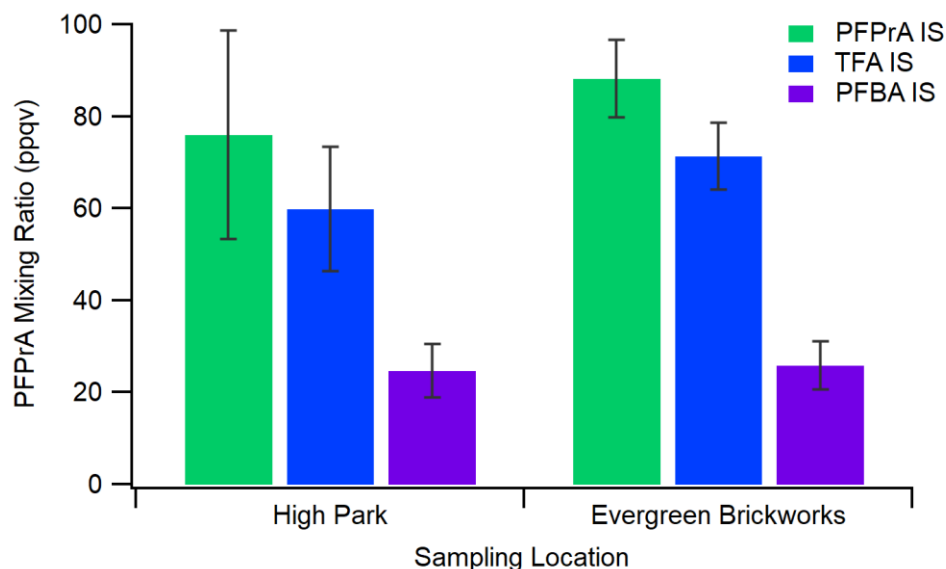


Figure 2.6 PFPrA mixing ratios (ppqv) measured at two SWAPIT sampling sites, High Park (n = 3) and Evergreen Brickworks (n = 3). PFPrA concentrations were quantified using the $^{13}\text{C}_1$ -PFPrA IS (green), $^{13}\text{C}_1$ -TFA IS (blue), and the $^{13}\text{C}_4$ -PFBA IS (purple). Error bars represent the standard deviation of triplicate measurements.

The reasoning behind these observations may be found in the separation of the PFCAs and major atmospheric anions such as sulfate (SO_4^{2-}) and nitrate (NO_3^-) (Figure 2.7). TFA and PFPrA have good separation from each other and from major anions, while PFBA elutes very close to nitrate and may be subjected to different matrix effects compared with PFPrA. The results suggest that the TFA IS experiences similar ionization efficiency effects to PFPrA with both showing suppression (Figure 2.6). In contrast, the PFBA IS exhibits enhancement that is almost certainly due to its proximity to nitrate, which is present in much higher abundance in the samples, with ambient measurements of winter HNO_3 atmospheric mixing ratios in Toronto exceeding those for PFBA by up to 4 orders of magnitude (Zbieranowski & Aherne, 2012). Evidence of enhancement of PFBA and suppression of TFA and PFPrA is illustrated in the increase in PFBA IS peak areas in the Evergreen Brickworks PAS by a factor of 1.4 and the decrease in TFA and PFPrA IS peak areas by factors of 1.5 and 1.9, respectively, as compared to their peak areas in the standards (Table S2.8).

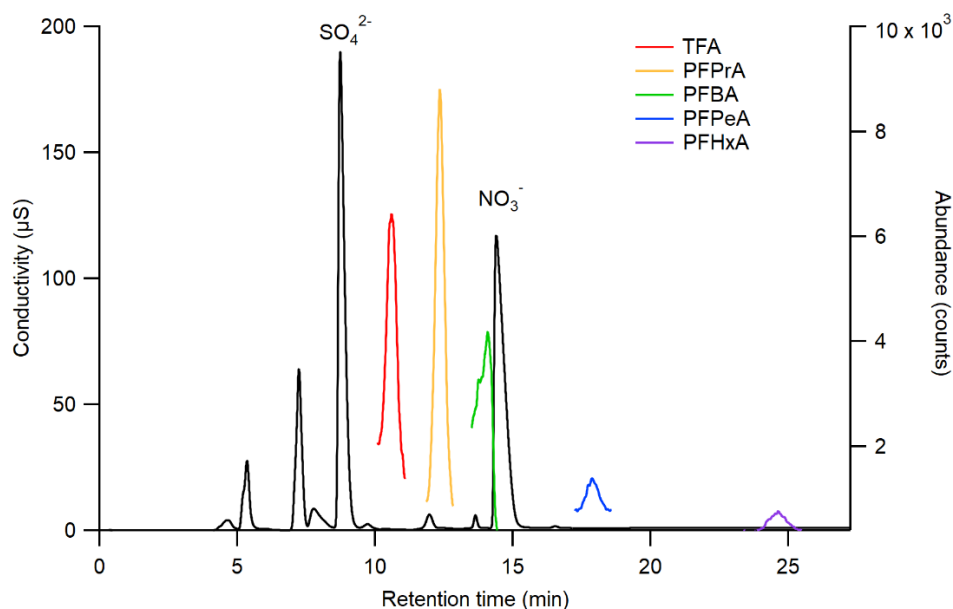


Figure 2.7 Chromatogram illustrating the separation of PFCAs (using our short gradient elution method for the concentrator column) in a PAS sample deployed at Evergreen Brickworks during the SWAPIT campaign (Jan. 29 – Mar. 11, 2024). The black trace is conductivity from the conductivity detector and the coloured traces are the PFCA mass abundances from the mass spectrometer, with the time delay of ~ 0.11 s between the two detectors corrected for. PFPeA and PFHxA were not detected in the sample so the mass abundances from the 100 ng/L and 50 ng/L standards were used for PFPeA and PFHxA, respectively.

To our knowledge, our research group has been the first to compare the effectiveness of alternate internal standards for the quantitation of PFPrA. In prior studies analyzing ultrashort-chain PFCAs, no importance is placed on the substitution of the mass-labelled PFPrA IS with an alternative compound (most often $^{13}\text{C}_4$ -PFBA), with the majority of studies examining aqueous matrices instead of the atmosphere and neither explaining nor justifying such a change (Janda et al., 2019; Taniyasu et al., 2008; Y. Wang et al., 2024; Zou et al., 2024). The internal standard experiments in this work demonstrate that in the absence of the PFPrA IS, the TFA IS is more suitable than the PFBA IS for the quantitation of PFPrA by IC. Consequently, in subsequent analyses, the $^{13}\text{C}_1$ TFA internal standard was used to quantify PFPrA, or the $^{13}\text{C}_1$ -PFPrA IS in some cases. It is important to note that the results presented in this section apply to the specific separation method conditions utilized and differences in the analytical setup (e.g. separation gradients, temperatures, columns) may give different results. In addition, these observations were conducted on samples from two similar urban locations, and samples obtained from more remote sampling locations with lower

concentrations of atmospheric ions (e.g. sulfate and nitrate), may not experience the same level of matrix effects.

2.3.2.2 *Working toward optimization of separation method for PFPrA quantitation*

In theory, analysis of a sample using two different separation methods should yield similar results, provided that both analyte calibration and quantitation methods are the same. In Section 2.3.1 an isobaric interference with the $^{13}\text{C}_2$ -TFA IS was resolved by performing a second analysis of each sample, using the loop and a longer gradient separation. Initially, we intended on using this long gradient method to quantify both TFA and PFPrA. However, a large discrepancy was observed between PFPrA concentrations determined using the short versus long gradient methods, with PFPrA levels measured in the airport samples higher by factors ranging from 1.9 to 6.5 using the short gradient (Table S2.9). The differences in TFA concentrations across both analysis methods were much more reproducible for all samples, with long gradient values higher by factors ranging only from 1.5 to 1.6 (Table S2.9), indicating that the $^{13}\text{C}_2$ -TFA interference was not also responsible for the observed variation in PFPrA levels.

To further investigate the discrepancy in the determination of PFPrA concentrations in the samples, the separation of TFA and PFPrA from atmospherically relevant anions (i.e. sulfate and nitrate) in the two methods was compared (Figure 2.8). When employing the short gradient method (Figure 2.8a), all five PFCAs have good separation from each other and the two other anions. In contrast, the long gradient separation (Figure 2.8b) led to the co-elution of PFPrA with sulfate, a compound demonstrated to cause ion suppression when in close proximity to TFA and PFPrA (Section 2.3.2.1). The longer gradient increased the retention factor (k') of PFPrA from 3.5 to 5.9. To better understand the effect of the co-elution of PFPrA with sulfate, a separate set of PAS extracts were spiked with $^{13}\text{C}_1$ -PFPrA and analyzed with the long gradient method.

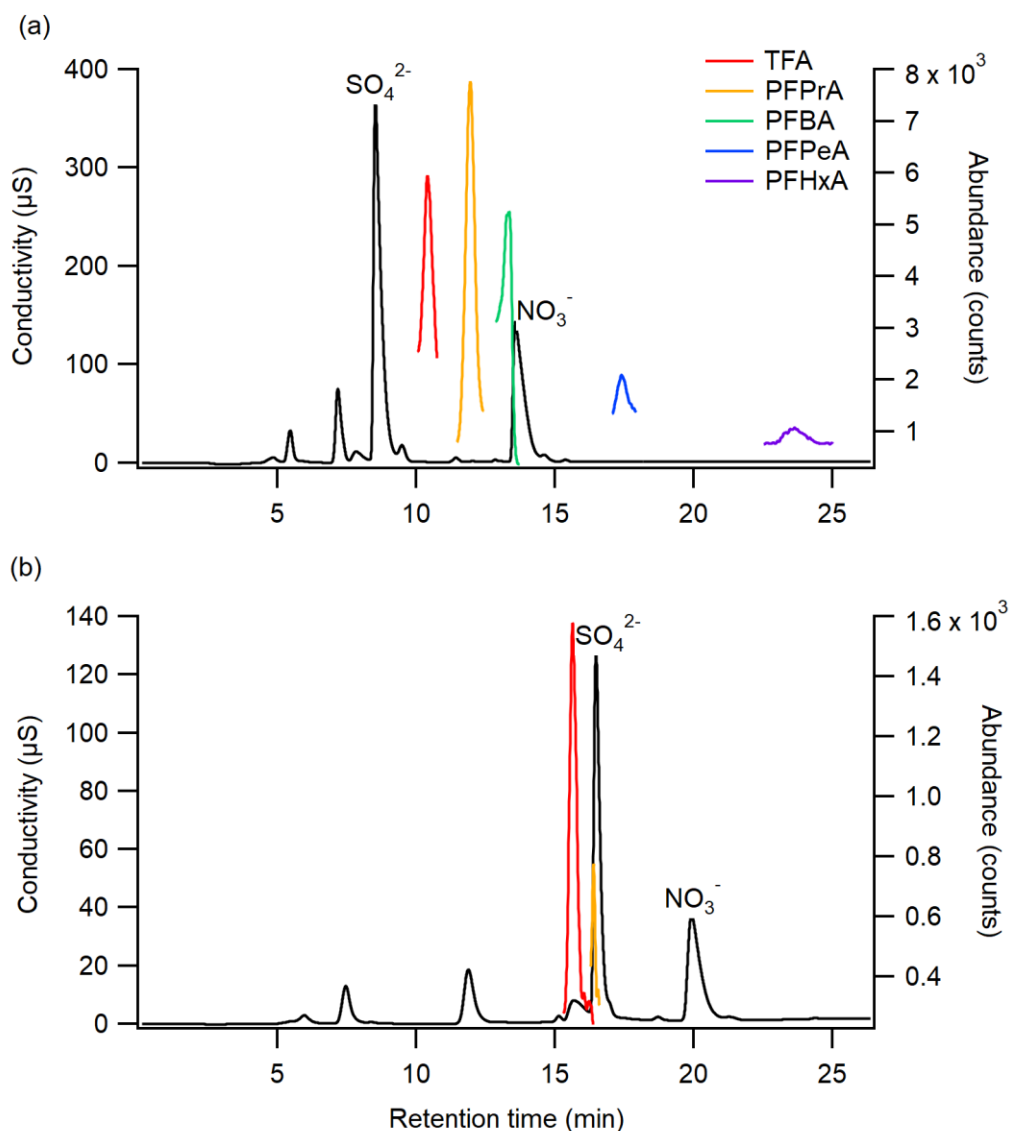


Figure 2.8 Chromatograms depicting the separation of PFCAs and major anions sulfate (SO_4^{2-}) and nitrate (NO_3^-) in a PAS sample deployed at Pearson International Airport utilizing (a) the concentrator column with a short gradient and (b) the loop with a long gradient. C4–C6 PFCAs were not included in (b) as they are generally present at levels too low to quantify using the loop.

Ion suppression was observed for the PFPrA IS in all three samples, evidenced by the decrease in peak areas in sample extracts by factors of 1.6, 2.4, and 3.3 relative to the peak area in a clean standard (Table S2.10). In prior analysis of the same samples spiked with $^{13}\text{C}_2$ -TFA, the TFA IS did not experience the same level of suppression, with peak areas in all three extracts similar to those in a standard (Table S2.10). Further analysis of one of the samples utilizing the concentrator column and short gradient method revealed that $^{13}\text{C}_1$ -PFPrA experienced minimal matrix effects,

with the sample peak area 1.1 times higher than in a standard. Since PFPrA and its mass-labelled IS have identical structures and elute at the same time, they experience the same ion suppression under the long gradient conditions, due to co-elution with sulfate. With the current long gradient method, accurate quantitation of PFPrA cannot be achieved without the use of the PFPrA IS. As this would mean an additional analytical run for all samples, we opted to quantify PFPrA using the best available option at a given time in this work, which included the $^{13}\text{C}_1$ -TFA, $^{13}\text{C}_2$ -TFA, or $^{13}\text{C}_1$ -PFPrA IS (depending on availability). This was done with the concentrator column and short gradient analyses, in which PFPrA displays good separation from all other compounds, and experiences minimal matrix effects.

Some additional strategies for reducing matrix effects are diluting the sample extracts, standard addition calibration, employing sample clean-up techniques or optimizing the chromatographic separation method (Furey et al., 2013). Since we are analyzing ultra-trace atmospheric contaminants and working close to our instrument detection limits, sample dilution is not an attractive option. Calibration via standard addition is a very time-consuming endeavor which cannot be employed for all samples in a reasonable time frame. In this specific case, it is also unlikely that the addition of a sample cleanup step such as solid phase extraction (SPE) would fix the issue of sulfate co-eluting with PFPrA. Seeing as sulfate is retained on our analytical column and elutes at a similar retention time to the strong acid PFCA analytes, it is safe to assume that these compounds exhibit similar intermolecular forces and would likely also be retained on an ion-exchange SPE sorbent (Gallo et al., 1995). Furthermore, SPE can lead to substantial analyte loss in samples, which combined with the absence of a mass-labelled IS for PFPrA, adds an extra source of error to the analysis (Jahnke & Berger, 2009).

We believe that optimization of the separation method can resolve the PFPrA interference. Future work in this subject should prioritize optimization of the concentrator column separation method to resolve both the $^{13}\text{C}_2$ -TFA IS interference (Section 2.3.1) and the co-elution of sulfate with PFPrA, while maintaining a good separation of C2–C6 PFCAs from one another and from all major atmospheric anions, achieving accurate quantitation in a single analytical run. Method optimization can be achieved through modification of parameters such as column packing, temperature, and mobile phase gradient. However, as explained in Section 2.3.1, altering the column can be costly, and effectively modifying the temperature can be difficult due to the ion-

specific nature of thermal effects. A better strategy is to alter the mobile phase gradient and consequently, k' , as a function of time to resolve the co-eluting peaks. During the long gradient run, PFPrA is no longer in the optimal k' regime ($k' > 5$) so further increases in k' will not lead to large increases in resolution. Changing the gradient program in such a way that k' of PFPrA is decreased with respect to the long gradient but k' of $^{13}\text{C}_2\text{-TFA}$ is increased compared to the short gradient will provide the ideal separation. Our initial methods were constrained to run times of ~30 min for use with our Ambient Ion Monitoring (AIM)-IC-MS instrument, but a method designed solely for IC-MS would not have this time constraint, affording greater flexibility to the gradient method optimization (VandenBoer et al., 2012). Following any modifications to the gradient separation conditions, we recommend that the IS evaluation experiment described in Section 2.3.2.1 be repeated, as changes to ionization efficiency may occur. Additional experimental observations determined from the analysis of PFPrA using the two gradient separation methods are presented in Appendix A, Figure S2.2.

The experiments and observations presented in this section have improved the quantitation of PFPrA in nylon PAS extracts. Utilization of the mass-labelled PFPrA IS represents the optimal analytical approach and remains the sole method capable of achieving accurate identification and quantification of PFPrA. Use of substitute internal standards such as mass-labelled TFA or PFBA may yield artificially suppressed PFPrA concentrations in samples. Nevertheless, no statistically significant difference was found between PFPrA concentrations determined using the TFA IS compared with the PFPrA IS, demonstrating that the $^{13}\text{C}_1\text{-TFA}$ IS serves as a suitable alternative. Theoretically, the $^{13}\text{C}_2\text{-TFA}$ IS should perform similarly well for PFPrA quantification, however, the presence of a co-eluting isobaric interference under our short gradient separation conditions currently compromises its use. A longer mobile phase gradient resolved the $^{13}\text{C}_2\text{-TFA}$ IS interference, however, this alternative separation method resulted in PFPrA co-eluting with sulfate, inducing substantial ion suppression for PFPrA across the majority of samples, rendering PFPrA quantitation inaccurate. Currently, our short gradient separation method is the only method capable of accurately quantifying PFPrA, by employing either the PFPrA IS as the optimal approach or the $^{13}\text{C}_1\text{-TFA}$ IS as a viable alternative for this specific sample matrix. We believe that optimizing the separation gradient without time constraints, and potentially experimenting ad hoc with altered column temperature, could resolve both the $^{13}\text{C}_2\text{-TFA}$ IS and PFPrA interferences, allowing for accurate quantitation of C2–C6 PFCAs in a single analytical run.

2.3.3 Extraction efficiency of C2–C6 PFCAs from nylon filters

Recently, the extraction efficiency of TFA (400 ng spike) from our nylon PAS ($n = 3$) was determined using extraction solvents containing 0–3 mM NaOH in water. The most efficient extraction solvent was determined to be 3 mM NaOH at 4 °C, yielding TFA recoveries of $83 \pm 2\%$ (Vanhouwaert et al., 2025). In my thesis work, additional extraction efficiency experiments were conducted for the C2–C6 PFCAs at two environmentally relevant levels that are more representative of the quantities obtained in our extracts, a ‘high’ spike of 20 ng C3–C6 PFCAs and a ‘low’ spike of 4 ng TFA, 1 ng PFPrA and 0.5 ng PFBA, PFPeA and PFHxA. In the high concentration spike and recovery experiments, the PFPrA IS was utilized to accurately quantify PFPrA. Due to the TFA contamination in the PFPrA IS described in Section 2.3.2.1, TFA was not included in the analysis.

The 20 ng spike yielded quantitative recoveries, ranging from 82–112%, for C3–C6 PFCAs at all (1–4 mM) NaOH concentrations (Table 2.4). As expected, in the absence of a competing ion (OH^-), the PFCAs recoveries were not quantitative, all below 10%. No noticeable trend was observed as a function of increasing hydroxide concentration, as seen with TFA in prior work (Vanhouwaert et al., 2025).

Table 2.4 %Recoveries of 20 ng of C3–C6 PFCAs spiked in method blanks extracted with solvents of varying NaOH concentrations ($n = 3$). The notation RT describes the extraction solvent and samples which were at room temperature.

	0 mM	1 mM ($n = 2$)*	2 mM	3 mM	3 mM (RT)	4 mM
PFPrA	6.8 ± 2.7	101 ± 0.4	103 ± 6	102 ± 4	112 ± 18	100 ± 6
PFBA	3.6 ± 1.2	98 ± 2.4	89 ± 5	82 ± 1	105 ± 5	95 ± 6
PFPeA	2.1 ± 0.8	99 ± 0.3	100 ± 3	100 ± 4	100 ± 5	101 ± 3
PFHxA	1.8 ± 0.3	105 ± 0.2	98 ± 4	101 ± 3	105 ± 7	103 ± 3

*Calculated by omitting outlier spiked method blank #2.

In the low concentration experiments, most method blanks, as well as more than one third of solvent blanks (i.e. new extraction solvents) were contaminated with PFPrA, and to a lesser extent, TFA. It appears that the extraction solvents leached TFA and PFPrA from the PP bottles in which they were stored prior to the analysis. This is because contamination was only observed in the blank extraction solvents stored in PP bottles after their use in preparing our spiked experiments; and not in the spiked solvents which were stored in HDPE bottles. A study carried out around the

same time as this work in our lab found that commercially available PP tubing immersed in water can leach detectable quantities of PFPrA from the container polymer even after sequential water extractions (Joudan et al., 2024), which was in contrast to nonfluorinated HDPE containers, for which aqueous extractions yielded no detectable PFAS (Vitale et al., 2022). It would seem that leaching of TFA and PFPrA is happening inconsistently from some of our laboratory products made from PP (Joudan et al., 2024), but not all containers and is a confounding source of random error for these analytes that warrants further study. We have yet to observe this issue with Falcon™ tubes and our IC-MS vials, which means that they may be held to a higher manufacturing and/or transport cleanliness standard compared with tubing and bottles.

Due to the contamination of the blank extraction solvents described above, TFA and PFPrA recoveries from the low concentration spike were not blank subtracted (Table 2.5). The contamination was only observed in the blank extraction solvents which were stored in PP bottles, meaning that the samples extracted with the spiked solvents were not subjected to the same contamination. The blank subtracted recoveries can be found in Appendix A, Table S2.11. The blank subtracted recoveries of TFA were similar to those presented here, with average recoveries using 3 mM or 4 mM NaOH ranging from $71 \pm 14\%$ to $74 \pm 3\%$, while the blank subtracted PFPrA recoveries exhibited high variability, with average recoveries ranging from 20 ± 53 to $78 \pm 57\%$.

Table 2.5 % Recoveries of 4 ng TFA, 1 ng PFPrA, 0.5 ng C4–C6 PFCAs spiked in method blanks extracted with solvents of varying NaOH concentrations (n = 3). The notation RT describes the extraction solvent and samples which were stored at room temperature. TFA and PFPrA recoveries were not blank corrected, while C4–C6 were blank corrected.

	0 mM	1 mM	2 mM	3 mM	3 mM (RT)	4 mM
TFA	11 ± 2	79 ± 11	78 ± 6	74 ± 13	76 ± 8	75 ± 3
PFPrA	56 ± 34	150 ± 68	100 ± 19	87 ± 15	97 ± 18	96 ± 33
PFBA	-	106 ± 23	131 ± 13	136 ± 26	114 ± 19	115 ± 19
PFPeA	-	89 ± 8	107 ± 4	129 ± 57	102 ± 2	104 ± 7
PFHxA	-	104 ± 10	130 ± 33	106 ± 5	99 ± 2	104 ± 3

Due to the spike concentrations in the low range being closer to the method detection limits (Table S2.12), the errors between triplicate measurements were expectedly higher than for the 20 ng spike. In addition, the recovered masses for PFPrA, PFBA, and PFPeA were all lower than their respective method LOQs at the time of the experiment, which was atypical. This, combined with the blank contamination described above, led to lower confidence in these results. Even so,

quantitative C2–C6 PFCA average recoveries were observed in 76% of the triplicates extracted with 1–4 mM NaOH in water. Although the recovery of the 4 ng TFA spike was 9% lower than the 400 ng spike, the % recovery of TFA extracted with 3 mM NaOH at 4 °C was not statistically different ($p > 0.05$), and both recoveries can be considered quantitative.

The phenomenon in which cold temperatures increase extraction efficiency, observed by Vanhauwaert (2024) with TFA was not seen in this study. We previously reported a 10% increase in TFA extraction efficiency at 4 °C compared with room temperature. In the current work, where we conducted more replicates of this initial experiment, extraction at a lower temperature did not have a significant effect ($p > 0.05$, Welch t-test, Equation S2.1, Table S2.13) on PFCA recoveries. A comparison of C2–C6 PFCA recoveries obtained using the 3 mM NaOH solvent at 4 °C and room temperature were not statistically different, with one exception: the 20 ng PFBA spike at room temperature resulted in significantly higher ($p < 0.05$, Table S2.13) recoveries compared with the same solvent at 4 °C. In this case, the higher room temperature extraction resulted in a PFBA recovery of $105 \pm 5\%$, a value 23% higher than observed at 4 °C, counter to our prior results. Both of the 20 ng and 0.5 ng spikes show high variability (54% difference) between PFBA recoveries even when using the same extraction solvent (3 mM NaOH at 4 °C). The observed variability could be attributed to an insufficient number of replicates tested at analyte concentrations approaching the method detection limits.

The 20 ng spike yielded quantitative recoveries for C3–C6 PFCAs using extraction solvents containing 1–4 mM of NaOH. The low concentration spike yielded quantitative recoveries for C4–C6 PFCAs using 3 mM NaOH at room temperature or 4 mM NaOH at 4 °C. The elevated recoveries ($>125\%$) and variability ($>25\%$) observed for PFBA and PFPeA when extracted with 3 mM NaOH at 4 °C could be attributed to an insufficient number of replicates tested at low analyte concentrations. Contamination of all blank extraction solvents led to lower confidence in TFA and PFPrA recoveries. Regardless, when extracting with 3 mM NaOH, TFA average recoveries were 71 and 74% with and without blank subtracting, respectively, which we consider quantitative. Greater differences were observed for recoveries of PFPrA, with quantitative recoveries only obtained by omission of the blank subtraction step, which for the 3 mM NaOH extraction increased the average recovery by 37%. Overall, the C2–C6 PFCA recoveries using either the 3 or 4 mM NaOH extraction solvent at 4 °C or room temperature were generally quantitative when

contamination issues from labware were not present. To maintain consistency with our prior research and ensure data comparability, we continued to use 3 mM NaOH at 4 °C as the nylon filter extraction methodology. Finally, in order to present conservative values of atmospheric PFCAs throughout this work, recovery corrections were not applied to calculations of atmospheric mixing ratios, meaning that actual values may be higher than those reported.

2.3.4 Inspection of overlying PP filters

Prior to our inspection of the overlying PP filters from PAS deployed in the field for any detectable amounts of C2–C6 PFCAs, spike and recovery experiments were conducted on clean PP filters to determine whether C2–C6 PFCA extraction efficiencies from this alternative material are quantitative. Blank subtracted recoveries of C2–C6 PFCAs were quantitative for the high concentration spike, with averages ranging from 100–109%, as were those of TFA, PFPeA, and PFHxA for the low concentration spike, ranging from 107–108% (Table 2.6). Blank subtracted recoveries at the low spike concentration were not quantitative for PFPrA ($135 \pm 9\%$) and PFBA ($35 \pm 19\%$). The elevated PFPrA recovery may be attributable to the low spike concentration, though the exact cause remains uncertain. The low PFBA recovery resulted from contamination in one of three method blanks (1.3 times higher than the spike mass), therefore, it was excluded from the low concentration blank subtraction, although this approach also yielded non-quantitative results, reported here.

Table 2.6 %Recoveries of 20 ng C2–C6 PFCAs (high) and 4 ng TFA, 1 ng PFPrA, and 0.5 ng PFBA, PFPeA, and PFHxA (low) from PP filters using 3 mM NaOH extraction solvent at 4°C.

	High concentration spike	Low concentration spike
TFA	100 ± 1	108 ± 9
PFPrA	100 ± 6	135 ± 9
PFBA	109 ± 32	141 ± 19
PFPeA	106 ± 2	107 ± 1
PFHxA	100 ± 7	107 ± 3

In the atmosphere, PFCAs exist in the gas and particle (aerosol) phases. Partitioning between gas and particle phases is influenced by factors such as relative humidity (RH), water pH, and the physical properties of PFCAs (Tao et al., 2023). Under typical environmental conditions, ultrashort- and short-chain PFCAs will largely be in the gas phase, with limited partitioning to particles. Our nylon PAS are designed to sample the gas-phase fraction only, with the overlying

PP filter intended to prevent particulate matter from reaching the nylon filter (Place et al., 2018). The uptake rate of PFCAs_(g) to the nylon filter can be negatively biased by the adsorption of gas-phase PFCAs in moisture or particulate matter on the PP filter surface. Partitioning of gas-phase PFCAs into dry particles is expected to be negligible, though adsorption to water can be substantial (Arp & Goss, 2009). Particle-bound PFCAs present in aerosols may also adsorb to the overlying PP filter, though this mechanism would not bias our gas-phase measurements.

The existence of the potential negative bias due to adsorption of gas-phase PFCAs on PP filters was investigated in PAS deployed at Pearson International Airport (Table 2.7). PFPeA was not detected in the PP filter extracts, and PFHxA was not detected in either PP or nylon filter extracts and will not be discussed further.

Table 2.7 Average C2–C5 PFCA quantities (ng) measured in nylon and respective PP filters from PAS deployed at Pearson International Airport. Relatively high levels in PP filters compared to their respective nylon filters are shown in **bold**.

PFCA	Filter	Nov. – Jan.	Nov. – Mar.	Jan. – Mar.	Mar. – May
TFA	PP	<0.12	<0.12	<0.12	<0.12
	Nylon	0.33	3.76	2.69	7.62
PFPrA	PP	<0.45	0.70	<0.45	<0.45
	Nylon	0.68	1.64	1.93	41.98
PFBA	PP	1.36	1.90	0.66	1.76
	Nylon	1.95	2.76	1.02	1.50

Compared with extracts from their respective field blank PP filters, TFA quantities were lower in all 13 PP filter extracts analyzed. Negligible amounts (< LOD) of PFPrA were measured on most PP filters (10 of 13), however, average PFPrA quantities on triplicate PP filters deployed November to March reached 42% of the mass measured on the nylon filters. Upon closer inspection, only one out of 13 PP filters showed detectable levels of PFPrA, comprising 62% of the mass on the respective nylon filter. This result accounts for less than 8% of all measurements and is most likely attributable to random error rather than systematic bias. Therefore, we can confidently conclude that the PP filters do not exhibit negative bias due to PFPrA adsorption by either mechanism.

Polypropylene filters were found to contain relatively high levels of PFBA, with average amounts during each sampling period ranging from 65–118% of the PFBA measured on the corresponding nylon filters. It is worth noting that the 20 ng spike and recovery experiment resulted in a high standard deviation between triplicate PFBA recoveries (32%), while those for the remaining

PFCAs were under 7%. High PFBA quantities of 0.64 ng (equivalent to 34–96% of the mass on the PP filters) were measured in one PP filter method blank, while PFBA was largely undetected in nylon method blanks. It is unclear whether the PFBA present on the PP filters was a result of contamination during washing or PFBA was collected from the atmosphere during field deployment.

Another possibility is that the measured PFBA was particle-bound in the atmosphere and collected on the PP filters as intended, preventing particulate matter from reaching the nylon filter. Across all four sampling periods, the amount of PFBA measured on individual PP filters ranged from 50 to 166% of the PFBA mass on their respective nylon filters. Within each sampling period, varying levels of PFBA were measured on PP filters with averages ranging from 65 to 106% of the PFBA mass on respective nylon filters, and relative standard deviations (RSDs) ranging from 3–65%. For replicate samplers deployed under identical meteorological conditions (i.e., the same temperature and relative humidity), losses of PFBA_(g) due to partitioning into water on the PP filter surface would be expected to be comparable. Only one of four sets of triplicate PAS fits these conditions, with a PFBA fraction of $65 \pm 2\%$ measured on the PP filters, which can just as reasonably result from a consistent interception, retention, and extraction of particles from this one deployment. Overall, the fraction of PFBA measured on PP filters relative to nylon filters in the majority of PAS (77%) displayed large variability, suggesting that adsorption of atmospheric aerosols containing PFBA, rather than aqueous partitioning of gas-phase PFBA, was the dominant source, as intended by the PAS design. Similar behavior has previously been documented for HNO₃ using an earlier version of our nylon passive air sampler equipped with PTFE overlying filters (Place et al., 2018).

The findings show that our nylon PAS measurements are likely not biased by air-water partitioning of gas-phase TFA, PFPrA, and PFPeA on the surface of the overlying PP filters. Relatively high PFBA levels were measured on all PP filters yet the associated variation is more consistent with the collection of particulate PFBA, rather than collection of gas-phase PFBA to water on the filter surface. The results are largely expected as the PP filters are meant to block particles while allowing gas-phase PFCAs to pass through. These observations increase our confidence in the quantitation of PFCAs collected on the nylon filters.

2.3.5 Calibration of PFBA and revisiting TFA using atmospheric chamber

Our nylon PAS were calibrated for PFBA by placing them into an atmospheric chamber containing gas-phase PFBA, which was quantified by an Na_2CO_3 -coated annular denuder at the outflow. This extension of our prior TFA calibration work was undertaken to compare an experimentally derived PFBA uptake rate to that predicted from our measured TFA uptake rate and Fuller's Law. In doing so we can discern whether the predicted uptake rates for C3–C6 PFCAs can be used to accurately determine atmospheric mixing ratios without having to conduct additional extensive chamber experiments.

The PFBA calibration experiment lasted four days, during which four sets of triplicate PAS and four denuders were used to create the linear uptake curve (Figure 2.9).

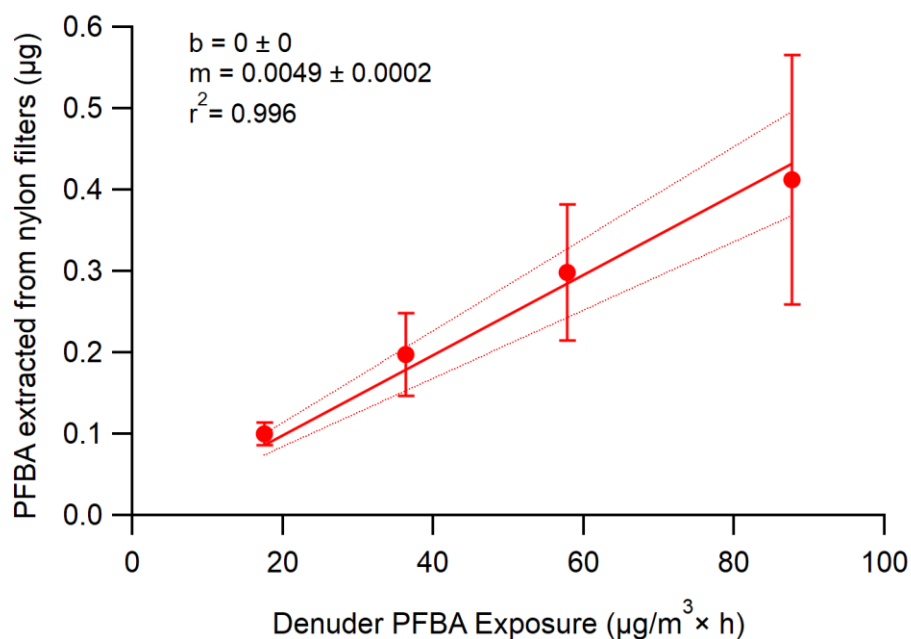


Figure 2.9 Chamber calibration for PFBA using the least-squares linear regression. The error in the regression slope represents one standard deviation. Dotted lines represent the bands of the linear regression at a 95% confidence interval. The mean measurement of triplicate PAS has an associated standard deviation represented with the error bars. The annular denuder measurement determines the mass of PFBA collected and is determined from the volume of air sampled and the PAS exposure time.

With regard to the extraction efficiency of PFBA from the nylon filters (Section 2.3.3), differing values were measured for the high (20 ng) and low (0.5 ng) concentration spikes: $82 \pm 1\%$ and 136

$\pm 26\%$, respectively, thus the extraction efficiency of PFBA was assumed to be $\sim 100\%$ and no correction was applied to the PFBA amount measured on the nylon filters. In prior work, Vanhauwaert et al. (2025) explored the necessity of including a y-intercept in the calibration and determined that if the denuder blank and the PAS field blank did not have a detectable analyte signal, the origin can be assigned as a known point on the uptake rate curve (Figure 2.9). The linear least square regression from Figure 2.9 has a coefficient of determination (r^2) of 0.996, indicating a strong linear fit. The linearity of the calibration curve demonstrates that the PAS did not near saturation, as was the case in our prior experiments.

The relative error between PAS replicates started at 14%, increasing to a maximum of 37% as the experiment progressed. These errors are fairly consistent with previously reported variability in nylon PAS chamber calibrations: 2–30% for TFA (Vanhauwaert et al., 2025), and 0–16% for HNO_3 (Bytnerowicz et al., 2005). It is worth noting that this experiment was one of the first conducted and further practice utilizing the chamber would likely lower the error between replicates as was observed in prior chamber experiments, where the highest errors ($\sim 30\%$) were observed in the samples collected during the earliest chamber experiments (Vanhauwaert, 2024). Uncertainty in the x-axis can be estimated from the relative standard deviation (4–14%) reported for annular denuder measurements of HNO_3 ($n = 4\text{--}8$) (Vanhauwaert et al., 2025). The x-axis uncertainty is, at most, comparable to that of the y-axis and, at best, minimal. This supports the use of linear regression, which assumes that uncertainty in the x-axis is negligible relative to that of the y-axis.

The linear uptake rate for $\text{PFBA}_{(g)}$, calculated by taking the inverse of the slope of the uptake rate curve is $203 \pm 7 \frac{\text{PFBA}_{(g)} (ng \cdot m^{-3}) \cdot t(h)}{\text{PFBA}_{(filter)}(ng)}$, where the error represents one standard deviation of the slope estimate (Figure 2.9). This measured value differs by a factor of 1.26 from the predicted uptake rate for PFBA (161 ± 17), determined using the measured TFA uptake rate, $113 \pm 12 \frac{\text{TFA} (ng \cdot m^{-3}) \cdot t(h)}{\text{TFA}_{(filter)}(ng)}$ and Fuller's Law (Vanhauwaert et al., 2025). Although a significant difference ($p < 0.05$, Welch t-test, Table S2.14) exists between the measured and predicted PFBA uptake rates, it is worth noting that if the extraction efficiency is actually 82%, as observed in my 20 ng PFBA spike and recoveries (Section 2.3.3), the resulting PFBA uptake rate is 167 ± 5 , which is only 4% higher than the predicted value. To reduce the uncertainty in chamber calibrations, future studies

should use additional replicates per time point, include more calibration points in the regression slope, and apply a mass-relevant spike and recovery value after improving the statistics for PFBA.

Despite PFBA concentrations in the chamber being much higher than ambient, the ~95 pptv mixing ratio used in these experiments is still considered ultra-trace in the atmosphere. The measured uptake rate has a linear response regardless of PFBA concentration, allowing for its extension into lower, environmentally relevant concentrations. Calibrating at higher levels than found in the atmosphere has been done repeatedly in prior reports, and field-based intercomparisons for $\text{HNO}_{3(g)}$ which have given good results, with Place et al. (2018) obtaining a field-derived $\text{HNO}_{3(g)}$ uptake rate nearly identical to that calculated from chamber-derived data.

As this represents the first calibration of nylon passive air samplers for PFBA, direct comparisons with other studies cannot be made. The close agreement between the predicted and measured uptake rates for PFBA demonstrates that Fuller's Law provides a good prediction for the uptake rate of PFBA based on a calibrated TFA uptake rate, increasing our confidence in the accuracy of our reported gas-phase C2–C6 PFCAs atmospheric concentrations. Compared with the predicted PFBA uptake rate, obtained using Fuller's Law and estimated from gas-phase diffusion parameters, the rate determined using the chamber is the superior measurement as it was derived utilizing a primary gas-phase standard and corrected for both extraction efficiency and wall interactions of PFBA. This change in the linear uptake rate from 161 ± 17 to $203 \pm 7 \frac{\text{PFBA}_{(g)} (\text{ng} \cdot \text{m}^{-3}) \cdot t(\text{h})}{\text{PFBA}_{(\text{filter})} (\text{ng})}$ results in a systematic offset of calculated PFBA mixing ratios by a factor of 1.26, turning for example a PFBA mixing ratio of 10 ± 3 ppqv determined theoretically into 13 ± 4 ppqv when using the chamber calibration value.

A second confirmation of the results from our initial work was also possible to obtain here, as residual $\text{TFA}_{(g)}$ was observed from the permeation oven system and consequently it was continuously present in the chamber PAS and denuder measurements. This allowed for the calculation of its linear uptake rate in parallel to that of PFBA. These experiments were conducted at an average $\text{TFA}_{(g)}$ mixing ratio of 14.6 ± 2.7 pptv (equivalent to $0.67 \pm 0.12 \mu\text{g}/\text{m}^3$; Figure 2.10), a factor of 9.2 to 26 lower than our previous TFA chamber experiments (Vanhouwaert et al., 2025).

We followed the same correction as has been used previously here, where TFA extracted from the nylon filters was corrected for the determined 83% extraction efficiency.

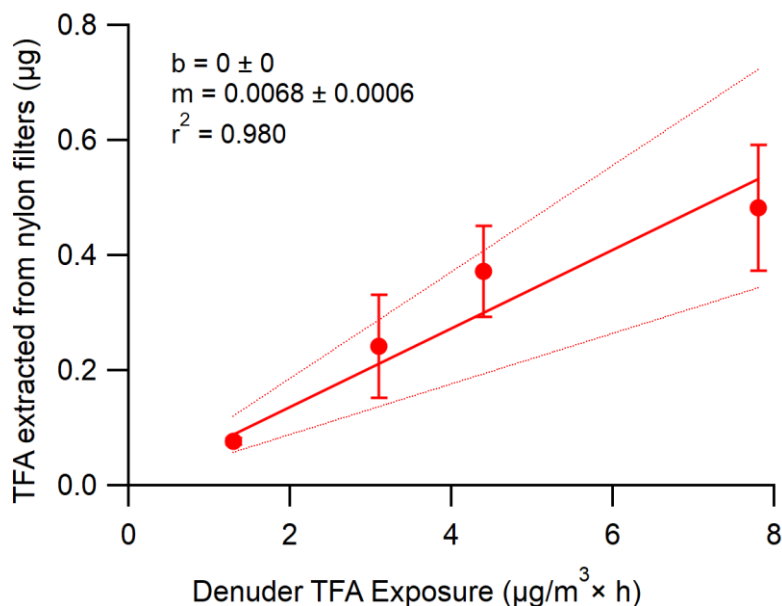


Figure 2.10 Linear uptake rate for TFA. The error in the regression slope represents one standard deviation. Dotted lines represent the confidence bands of the linear regression at a 95% confidence interval. The mean measurement of triplicate PAS has an associated standard deviation represented with the error bars. The annular denuder measurement determines the mass of PFBA collected and is determined from the volume of air sampled and the PAS exposure time. The TFA mass extracted from the nylon filters was corrected for TFA's 83% extraction efficiency.

The coefficient of determination (r^2) was 0.980, indicating a maintained linear relationship. Taking the inverse of the slope, the linear uptake rate of $\text{TFA}_{(\text{g})}$ was determined to be 146 ± 12

$\frac{\text{TFA}_{(\text{g})} (\text{ng} \cdot \text{m}^{-3}) \cdot t(\text{h})}{\text{TFA}_{(\text{filter})} (\text{ng})}$. This measured TFA uptake rate is 1.29 times higher than previously determined

by Vanhauwaert et al. (2025) using this same chamber setup, $113 \pm 12 \frac{\text{TFA} (\text{ng} \cdot \text{m}^{-3}) \cdot t(\text{h})}{\text{TFA}_{(\text{filter})} (\text{ng})}$, and 1.25

times lower than the predicted uptake rate, $182 \pm 68 \frac{\text{TFA} (\text{ng} \cdot \text{m}^{-3}) \cdot t(\text{h})}{\text{TFA}_{(\text{filter})} (\text{ng})}$ based on $\text{HNO}_{3(\text{g})}$ calibrations

and Fuller's Law (Carmichael, 2022). Although a significant difference ($p < 0.05$, Table S2.15)

exists between the two measured $\text{TFA}_{(\text{g})}$ uptake rates, our measured $\text{TFA}_{(\text{g})}$ uptake rate was not significantly different ($p > 0.05$) from the $\text{HNO}_{3(\text{g})}$ -based predicted rate. The relative difference

between the two measured TFA uptake rates is 25%, similar to the overall uncertainty of these samplers, which can be considered good agreement, increasing our confidence in the accuracy of

the previously measured TFA_(g) uptake rate. The prior uptake rate was determined using a more robust methodology with 14 triplicate PAS across a wider range of TFA exposures in the chamber and is our preferred uptake rate value at this time.

The slight inconsistencies are likely due to the challenge of quantifying at very low TFA mixing ratios, and the small number of calibration points for the current measurement where the highest value is dictating much of the slope from the regression. There is inherent increased variability when working at lower concentrations and this is compounded by sampling with fewer data points. Second, it is plausible that at lower concentrations the extraction efficiency of TFA was less than 83%, as evidenced by recoveries of 74 +/- 13% and 75 +/- 3% observed for 4 ng TFA spikes using 3 and 4 mM NaOH for extraction, respectively (Section 2.3.3). Correcting for an extraction efficiency of 75% instead of 83% would reduce the measured uptake rate to 132 ± 10 , lowering the relative difference between measurements from 25% to 16%.

Here, we obtained a TFA uptake rate that was within a factor of 1.3 of a previous measurement made using an identical enclosed chamber setup, at concentrations 9.2 to 26 times lower and with only 4 data points. This close agreement between the two measured TFA uptake rates increases our confidence in our measured PFBA uptake rate even further, as well as its necessary extension to the lower PFBA concentrations typically found in atmospheric samples. Based on these results, we use our two most robust chamber-derived TFA and PFBA linear uptake rate measurements, 113 ± 12 and 203 ± 7 , respectively, for calculation of atmospheric mixing ratios. For PFPrA, PFPeA and PFHxA, we will continue to use the predicted rates based on our prior TFA chamber calibration and Fuller's Law (Section 2.2.8.1).

2.3.6 Duration of PAS deployment and potential sampling bias

Once the PAS are deployed, PFCAs and common atmospheric acids such as HNO₃, hydrogen chloride (HCl), sulfuric acid (H₂SO₄), and other organic acids can compete for sorption sites on the nylon filter. Globally, PFCAs are found at ultra-trace levels in the atmosphere, while other acids are much more abundant, particularly in urban and polluted areas, such as Pearson International Airport (the largest and busiest airport in Canada). Ambient measurements of HNO₃ (Zbieranowski & Aherne, 2012) and HCl (Tao et al., 2022) in large cities can be up to four orders of magnitude higher than the most abundant PFCA, TFA. Over longer deployment periods, accumulation of acids on the filter may displace already-sorbed PFCAs or block available sorption

sites, leading to an underestimation of PFCA concentrations. This potential loss of target analytes over time due to saturation of, or competition over sorption sites on the nylon filter by other atmospheric acids would create a negative systematic sampling bias, which would increase over time. An investigation into the existence of this sampling bias was conducted on triplicate sets of nylon PAS deployed for different sampling durations at Toronto Pearson International Airport in the winter of 2024. Two sets of triplicate PAS were deployed in November 2023, with one set removed and replaced in January 2024, with the overlapping temporal experiment terminating in March 2024.

Time-weighted C2–C6 PFCA concentrations (ppqv) measured in PAS deployed at Pearson International Airport from November to January and January to March were summed and compared to concentrations measured in PAS deployed for the entire sampling period (November to March) (Figure 2.11).

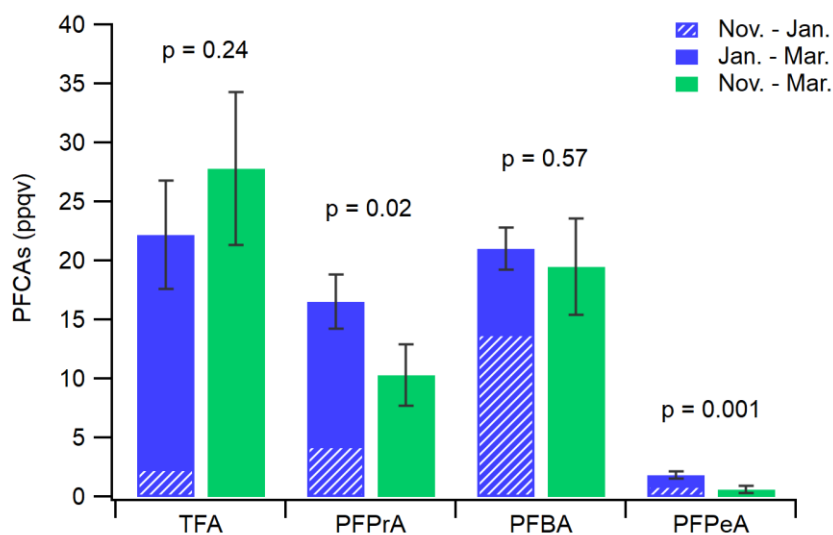


Figure 2.11 C2–C5 PFCA atmospheric concentrations (ppqv) measured at Pearson International Airport. PFHxA was not detected in samples and was omitted from this comparison. Sums of time-averaged PFCA concentrations measured in PAS deployed from November 3, 2023 to January 19, 2024 ($n = 2$) and PAS deployed January 19 to March 8, 2024 ($n = 3$), are shown in blue, with the Nov. – Jan. contribution depicted with diagonal lines; error bars represent the time-weighted propagated error for the sum of PFCA concentrations measured. PFCA measurements from PAS deployed November 3, 2023 to March 8, 2024 ($n = 3$) are shown in green; error bars represent standard deviation between triplicate measurements. The average temperature during the entire sampling period was 1.5 ± 4.7 °C.

No significant differences ($p > 0.05$, Welch t-test, Table S2.16) were observed for TFA or PFBA mixing ratios measured at Pearson International Airport across the two sampling durations. This suggests that our nylon PAS do not experience TFA or PFBA sampling bias across different sampling durations. Conversely, the PFPrA and PFPeA atmospheric mixing ratios were significantly lower ($p < 0.05$, Welch t-test) over the six-month sampling period by factors of ~ 2 and ~ 3 , respectively.

Atmospheric concentrations of PFPrA and PFPeA were lower in the PAS which sampled for a longer duration, and while it may be possible that bias results from the longer deployment duration, we have more evidence that potential analytical challenges for these analytes explain the observations (Figure 2.11). Compared with the six-month measurements, PFPrA mixing ratios determined using two consecutive 3-month measurements are higher by a factor of 1.6. This can be considered good agreement for PFPrA, the only analyte quantified using a substitute internal standard, $^{13}\text{C}_2$ -TFA, instead of its own mass labelled IS (Section 2.3.2). Quantifying PFPrA during this analysis was particularly problematic and unreliable due to the co-elution of the aforementioned isobaric interferent with $^{13}\text{C}_2$ -TFA (Section 2.3.1). The analytical challenges involved in the measurement of PFPrA result in considerable uncertainty at this time and cannot be ruled out for the observed differences across sampling durations at this time.

Mixing ratios of PFPeA determined from the sum of PAS deployed over the two shorter sampling periods were 2.8 times higher than those measured from November to March. In the atmosphere, PFPeA is present at ultra trace levels, with average mixing ratios during this sampling period ranging from 0.6–2.2 ppqv. To put this in perspective, the highest PFPeA mass measured on replicate nylon filters during the campaign was 3 times lower than the 0.5 ng spiked during the low concentration extraction efficiency experiments (Section 2.3.3). At these low concentrations, very small absolute analyte loss may occur due to minor differences in extraction efficiency and increased relative error. The observed differences in PFPrA and PFPeA measurements are likely attributable to current analytical limitations or low atmospheric concentrations, respectively, and while sampling bias may occur, there is no direct evidence of this. Further experiments with more PAS replicates could help to improve comparisons in the future.

Comparison of C2–C5 PFCA atmospheric mixing ratios at Pearson International Airport over a six-month and two consecutive three-month PAS deployments yielded contrasting results.

Measurements of TFA and PFBA were similar across the two sampling periods, with no significant differences observed suggesting that all PFCAs should be free from competitive processes during chemisorption on the nylon filters under these field conditions. Analytical determination challenges still exist in this method for PFPrA and PFPeA. Despite this, the differences in PFPrA and PFPeA mixing ratios were within factors of 2 and 3, respectively, which for the former having a persistent list of analytical QA/QC issues noted in nearly every section above, and the latter being present at or below single digit ppqv mixing ratios means these are entirely acceptable levels of uncertainty. We suggest conducting a second sampling bias experiment with more replicates per period in the summer when PFCA concentrations are higher, followed by analysis using best IS options in an optimized separation method with no interferences, in order to get more complete insight into field-based or sample handling-based losses, with the potential for correction. Overall, these observations increase our confidence in the utility of nylon PAS measurements over different sampling durations, but we do recommend that test deployments be conducted prior to study periods to ensure sampler integrity, as well as the use of as many replicates as are technically and analytically feasible.

2.3.7 Passive air sampling at a wastewater treatment plant: intercomparison between nylon PAS and SIP PAS and observed temporal trends

An intercomparison between two passive sampler methods, nylon PAS and SIP PAS, was conducted to evaluate the accuracy, reliability, and comparability of measurements of ultrashort- and short-chain (C2–C6) PFCAs in the atmosphere. As neither method has been externally validated for these compounds, comparing PFCA air concentrations determined by both samplers under the same environmental conditions provides an important assessment of method performance. Agreement between the two methods would increase confidence in the representativeness of the measurements, while discrepancies may identify limitations related to uptake rates, environmental influences, or analytical uncertainties thereby improving data interpretation and guiding further method optimization.

Nylon PAS and SIP PAS were co-deployed at a WWTP in the GTA, providing an opportunity to improve understanding of whole-air composition in WWTP air emissions based on SIP PAS measurements, while evaluating the suitability of both passive sampling approaches for measuring

atmospheric C2–C6 PFCAs, assuming these compounds predominantly reside in the gas phase. Nylon PAS operate exclusively in the kinetic sampling regime, as adsorption is limited by the number of available sorption sites and equilibrium with ambient air concentrations is not reached. In contrast, SIP PAS partition coefficients were derived assuming that analytes approach equilibrium between the sorbent and air. These fundamental differences in sampling behaviour may contribute to differences in measured concentrations. Given that nylon PAS were calibrated using controlled gas-phase exposures for TFA and PFBA, they are expected to provide a more robust measurement approach.

2.3.7.1 Intercomparison between nylon and SIP PAS C2–C6 PFCA atmospheric measurements

The principal PFCA measured by SIP PAS at all three sites was PFPrA, with air concentrations of 2380 ± 1344 pg/m³ (29% of the Σ PFCAs) at the primary clarifier, 1417 ± 646 pg/m³ (17%) between aeration tanks and 1373 ± 421 pg/m³ (17%) at the reference site (Table 2.8). For nylon PAS, TFA was the principal compound, with air concentrations of 1492 ± 156 pg/m³ (29% of the Σ PFCAs) measured between aeration tanks, 1469 ± 69 pg/m³ (28%) at the primary clarifier, and 846 ± 94 pg/m³ (16%) at the reference site.

Table 2.8 Atmospheric concentrations (pg/m³) of C2–C6 PFCAs measured at three sites within the WWTP using nylon PAS (n = 3) and SIP PAS (n = 2). Nylon PAS were deployed for one to two weeks for a combined sampling duration of one month, values displayed are sums of time weighted averages of C2–C6 PFCAs levels. SIP PAS values displayed are averages of duplicate samplers deployed May 25 – July 27, 2023. Relative errors (%) for SIP PAS and relative standard deviations (%) for nylon PAS are provided.

PFCA	Reference Site		Primary Clarifier		Aeration Tank	
	Nylon	SIP	Nylon	SIP	Nylon	SIP
TFA	846 (11)	447 (77)	1469 (5)	832 (57)	1492 (10)	957 (36)
PFPrA	211 (18)	1373 (31)	294 (51)	2380 (56)	195 (54)	1417 (46)
PFBA	124 (7)	44.4 (33)	187 (3)	328 (107)	179 (4)	138 (98)
PFPeA	33.6 (0.7)	4.8 (16)	49.2 (7)	52.6 (104)	94.9 (7)	50.9 (109)
PFHxA	<16.6	6.6 (21)	<16.6	38.4 (77)	86.6 (8)	54.9 (0.3)
ΣPFCAs	1215 (9)	1876 (36)	1999 (16)	3631 (80)	2048 (17)	2617 (58)

Enrichment ratios (ER) were calculated as average air concentrations at the WWTP (primary clarifier and/or aeration tank) divided by average air concentrations at the reference site (Table 2.9). The nylon PAS measurements show a significant increase ($p < 0.05$, Welch t-test, Table S2.17 in Appendix A) for individual C2, C4, and C5 PFCAs at the primary clarifier, with ERs of 1.5–1.7. Similarly, nylon PAS measurements of all PFCAs except PFPrA increased between aeration tanks,

with ERs of 1.4–2.8, although the increase is only significant ($p < 0.05$) for PFPeA. The results strongly suggest that the WWTP is an emission source for not just $> C_4$ PFCAs_(g), but also the ultrashort homologues. Similarly, my analysis of these analytes in the SIP disk extracts found ERs of 1.7–11 for individual C₂–C₆ PFCAs at the primary clarifier and 2.1–11 for C₂, C₄–C₆ PFCAs at the aeration tank. Likely due to the large variability between duplicate SIP PAS, the differences between on-site and off-site measurements were not significant ($p > 0.05$, Table S2.17) for any analytes. Interestingly, neither passive sampler method showed on-site enrichment of PFPrA between the aeration tanks. The highest enrichment ratios were observed for SIP PAS measurements of PFPeA (11) at both sampling sites, followed by PFHxA (8.3) between aeration tanks, and PFBA (7.4) at the primary clarifier.

Table 2.9 Enrichment ratios at two WWTP sampling sites: the primary clarifier and between aeration tanks to those at the reference site, for nylon and SIP PAS.

	Primary Clarifier		Between Aeration Tanks	
	Nylon	SIP	Nylon	SIP
TFA	1.7	1.9	1.8	2.1
PFPrA	1.4	1.7	0.9	1.0
PFBA	1.5	7.4	1.4	3.1
PFPeA	1.5	11	2.8	11
PFHxA	-	5.8	-	8.3
ΣPFCAs	1.6	1.9	1.7	1.4

Nylon PAS displayed much lower ERs on average, with the highest observed for PFPeA (2.8) between aeration tanks, followed by TFA between aeration tanks (1.8) and at the primary clarifier (1.7). The ERs > 1 observed for most PFCAs at both on-site locations indicate that C₂–C₆ PFCAs present in wastewater are emitted to the atmosphere. There are two pathways by which PFAS can be released from water to air: volatilization and aerosol ejection. In water, PFCAs are generally present in their dissociated (ionized) form but they can be protonated and volatilize, or the ionized form can be ejected as an aerosol, which is likely the dominant pathway for less volatile chemicals with high water solubility, such as PFCAs and PFSAAs (Ahrens et al., 2011; Shoeib et al., 2016).

Our observations support this theory, due to the much higher enrichment ratios obtained from SIP PAS measurements, particularly for the bigger and less volatile C₄–C₆ PFCAs which are most likely to undergo aerosol ejection (Tao et al., 2023). This finding suggests that a considerable amount of C₄–C₆ PFCAs are emitted from the WWTP in the particle phase as aerosols.

Interestingly, higher ERs were observed for PFBA at the primary clarifier, which has a calm water surface, compared to the aeration tanks, where the process of aeration creates turbulence and bubbling, enhancing both volatilization and aerosol ejection (Ahrens et al., 2011). Any PFCA emitted as an aerosol would not be measured by nylon PAS, as they are designed to only sample gas-phase acids through selective chemisorption to the nylon filter, with the overlying polypropylene (PP) filter blocking particles from reaching the nylon filter (Place et al., 2018). On the other hand, SIP PAS are capable of measuring particle-bound analytes as both gas- and particle-phases can permeate into the sorbent allowing for measurement of whole air concentrations (Shoeib et al., 2008). Consequently, we expect concentrations of individual analytes measured by SIP PAS to be equal to or greater than those measured by nylon PAS.

This is assuming that the PFCA concentrations in wastewater influent remained at similar levels during the second month of sampling (i.e. within a factor of 2 of the first month), after the nylon PAS were collected. Any changes in the wastewater PFAS concentrations during the second month of SIP PAS sampling would affect the comparability between samplers. Another important assumption is made by the SIP PAS methodology, which treats all molecules like neutral compounds than can reversibly partition into the sorbent. While this is true for neutral semivolatile organic compounds like PCBs, ultrashort- and short-chain PFCAs are ionizable strong acids which do not undergo K_{OA} -driven partitioning, having the ability to fully dissociate after partitioning (Tao et al., 2023).

The expected pattern is observed when comparing average concentrations of the aggregated Σ PFCAs, with SIP measurements higher than nylon PAS, by factors ranging from 1.3–1.8 at each site and 1.5 times higher Σ PFCAs measured during entire sampling campaign (Table S2.18). However, the observed trend is driven entirely by the high PFPrA concentrations measured by SIP PAS. When excluded from calculations, the opposite trend emerges with nylon PAS measuring 1.4–2.0 times higher Σ PFCAs concentrations and not meeting the expectation that these should always be less than or equal to the SIP when sampling only the gas phase. These results suggest that substantial differences exist between the measurement and/or quantification of all PFAAs by the two methods. To illustrate these differences, concentrations of individual C2–C4 PFCAs measured by nylon and SIP PAS were compared (Figure 2.12).

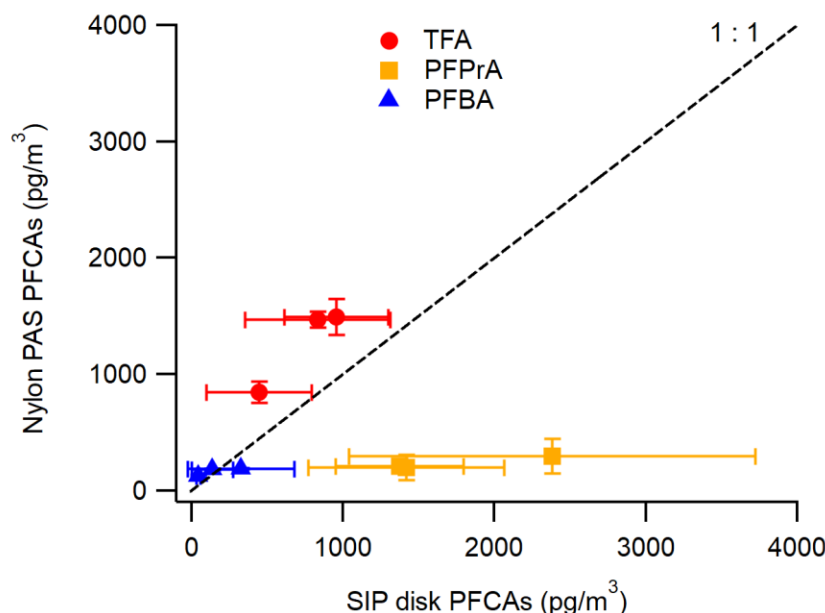


Figure 2.12 Comparison of C2–C4 PFCAs measurements using nylon and SIP PAS from the three process sites within a WWTP. Horizontal error bars represent the relative error between duplicate SIP PAS measurements collected over two months. Vertical error bars represent the time-weighted propagated error for the sum of nylon PAS concentrations from the entire month. The dashed line represents equal concentrations measured by the two samplers; the points situated above and below the line represent higher and lower analyte concentrations, respectively, measured by the nylon PAS compared with SIP PAS.

The results show that average TFA concentrations are systematically higher in nylon PAS measurements, yet within a factor of 2, while PFPrA averages are systematically lower by a factor of 7 (Table S2.18). Regarding the nylon PAS, the use of a substitute internal standard is likely to underestimate the amount of PFPrA (Section 2.3.2), however, values would still be expected to be comparable, within a factor of 4. The main drivers behind the observed inconsistencies are likely the mismatched sampling durations, the large variability between SIP duplicates, and the estimated K_{SIP-A} values. Due to the short sampling durations for the nylon PAS, PFHxA was not detected at the reference site or primary clarifier and these concentrations cannot be compared. Average concentrations of PFBA and PFPeA within a factor of 2 were observed at the primary clarifier and aeration tank, as well as for PFHxA at the aeration tank (Table S2.18).

Concentrations of C2–C6 PFCAs at the reference site were compared with those typically measured in urban areas. Due to the proximity of the reference site to the WWTP (within 200 m), levels at reference site are expected to be similar or slightly elevated to those previously reported in urban areas (Ahrens et al., 2011). To our knowledge, this study is the first to measure TFA and PFPrA in air using SIP PAS, so comparison can only be made with other methods of measuring ultrashort-chain PFCAs in air. Nylon PAS TFA levels at the reference site fell in the range of typical levels measured in Toronto, from a relatively elevated site like York University ($1020 \pm 61 \text{ pg/m}^3$) to a residential area within 25 km ($532 \pm 32 \text{ pg/m}^3$) during similar seasons (Vanhauwaert et al., 2025). Similarly, nylon PAS measurements of TFA at the reference site were within the range of summer diffusion denuder measurements in Beijing, China (~ 800 to $\sim 3400 \text{ pg/m}^3$), albeit much closer to the lower end (Wu et al., 2014). Conversely, reference site measurements of TFA by SIP PAS were below the lowest reported levels from either of these locations, while within the WWTP, TFA levels were lower than but similar to those reported at York University.

Nylon PAS measurements of TFA within the WWTP were approximately 1.4 times higher than reported at York University, again consistent with this facility being a substantial atmospheric source of TFA. Our nylon PAS measurements of TFA on-site closely aligned with but were slightly lower than those determined in Beijing, China where average summer TFA levels of $2080 \pm 589 \text{ pg/m}^3$ were measured from 2013 to 2016 (Zhang et al., 2018). The SIP PAS levels at the WWTP fell outside this range, with on-site TFA averages lower by factors of 2.2 to 2.5. Higher ambient TFA concentrations have been measured utilizing chemical ionization mass spectrometry (CIMS) with acetate ionization a few km away from York University, in winter (median $\sim 2100 \text{ pg/m}^3$) and summer (median $\sim 2640 \text{ pg/m}^3$) (Young et al., 2024). While the CIMS measurements are higher than were measured using either passive sampler method, they are still within a factor of 2 of nylon PAS average TFA levels on-site, but a factor of 3 higher than the SIP PAS measurements. We have higher confidence in nylon PAS measurements as sampling rates have been derived from controlled calibrations, while SIP PAS sampling rates rely on assumptions regarding analyte partitioning behaviour (See Section 2.3.7.2). Taken together the results suggest that air concentrations of TFA at the WWTP are systematically underestimated by SIP PAS.

Nylon and SIP PAS measurements of PFPrA at the WWTP cannot be directly compared to past reported measurements, as those quantified PFPrA using the PFBA internal standard, which we have demonstrated can significantly underestimate PFPrA levels (Section 2.3.2). In my analysis of nylon filters deployed at two urban locations in Montreal, Quebec (Chapter 4, Section 4.3), concentrations of PFPrA, quantified using $^{13}\text{C}_1$ -PFPrA, ranged from 121 ± 27 to 293 ± 60 pg/m^3 . Average nylon PAS measurements of PFPrA at all three WWTP sites fall within this range. Those determined by SIP PAS were 5 to 11 times higher at the reference site and aeration tanks and 8 to 19 times higher at the primary clarifier. There are several possibilities which may explain the elevated PFPrA concentrations measured by SIP PAS. It is possible for the concentration of PFPrA in the influent, and consequently the atmospheric emissions from the WWTP, to have increased after the nylon PAS were collected. Another possibility is for the $K_{\text{SIP-A}}$ of PFPrA to be higher than the proxy used in the calculations of air concentrations. Due to the inversely proportional relationship between $K_{\text{SIP-A}}$ and air concentration, if $K_{\text{SIP-A}}$ for PFPrA was actually higher than the value used, the resulting PFPrA air concentrations would be lower and closer to those measured by nylon PAS. That being said, elevated PFPrA levels as high or higher have been measured in other locations, the source of which remains unclear. Ambient winter CIMS measurements of PFPrA in Toronto reached a maximum of 2940 pg/m^3 , and it is likely for summer measurements to be even higher, as observed for C2, C4 and C5 PFCAs (Young et al., 2024). In my nylon PAS measurements at another PFAS point source, Pearson International Airport, extremely elevated PFPrA concentrations (4127 ± 1521 pg/m^3) approximately 18 times higher than in winter were observed during the spring (March to May) (Chapter 3, Section 3.3.2). These airport measurements demonstrate that elevated PFPrA levels equal to or greater than those measured at the WWTP using SIP PAS are feasible. The longer sampling duration of the SIP PAS introduces inherent uncertainties; therefore, it is possible that wastewater influent containing higher PFPrA concentrations reached the WWTP after the nylon PAS had been removed.

Statistically, no significant differences ($p > 0.05$, Welch t-test, Table S2.19) were found between C2–C6 PFCA concentrations measured by the two methods at either on-site location, but these results arise due to the high variability determined from duplicate SIP PAS. These were found to have relative errors for individual C2–C6 PFCAs ranging from 0.3–109% at the WWTP (Table 2.8) and warrant further discussion with respect to the chemical identity of the target analytes and design of the SIP sampling methodology.

2.3.7.2 Assessing the variability between replicate and average measurements of C2–C6 PFCAs using nylon and SIP PAS

The SIP PAS are frequently deployed as single samplers ($n = 1$) at a multitude of sites to form a large sampling network (Saini et al., 2023; Wania & Shunthirasingham, 2020). Consequently, there have not been many studies detailing the variation between replicate SIPs. The variability in replicate PUF PAS has been investigated for several polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs) at a semi-rural site, with RSDs for 5 replicates ranging from 2–29% for PAHs and 3–56% for POPs (Melymuk et al., 2021). The PUF PAS errors were lower for some analytes and similar to those obtained for SIP PAS in the current study, when applied to PFCAs. In a wider global intercomparison encompassing 14 laboratories, Melymuk et al. (2021) found much higher variability between replicates, with reported POPs masses spanning 3 orders of magnitude.

There remain a number of underexplored drivers of sampling inconsistency throughout the SIP method with respect to PFCAs in particular, but also more generally as a method. One driver of the lower standard deviations from the work of Melymuk et al. (2021) will be the additional replicates, but high RSDs persisted so clearly other issues are at play. When sampling away from point sources, they were also less likely to be impacted by atmospheric heterogeneity and would obtain more consistent results, unlike the potential for such situations in an intense emission location like our WWTP. For a partitioning-based sampler, the target analytes in the prior work being neutral semi-volatile organic compounds (SVOCs) would accumulate by the designed sampler mechanism of partitioning, rather than potentially being impacted by both partitioning and ionization in the case of PFCAs. Lastly, methods targeting ultrashort PFCAs are only realizing the necessary analytical requirements for high quality determinations and may need further improvement. We consider each of the issues in order to reflect on remaining gaps for improved comparability between atmospheric determinations of PFCAs.

Sampling at or near a point source is inherently prone to error between replicates because PFAS are being released or formed on site, especially by the primary clarifiers and aeration tanks, and may not be uniformly distributed in the air. In the current study, site specific relative errors between duplicate SIP PAS were 36%, 80%, and 58% at the reference site, primary clarifier, and aeration tank, respectively. In 2009, Ahrens et al. (2011) deployed two SIP PAS at each of the three sites

within this WWTP, but did not treat them as duplicates. Upon treatment of the two SIP PAS as duplicates, similar variability is observed, with relative errors for individual C4–C6 PFCAs ranging from 7.1 to 117% at the WWTP, and site specific average relative errors for Σ C4–C6 PFCAs of 38%, 67%, and 17% at the reference site, primary clarifier, and aeration tank, respectively (Ahrens et al., 2011). The slightly higher variability observed with the SIP PAS in the current study are likely due to differences in the analytical and extraction methods, for instance the addition of a lower mass of surrogate standards prior to extraction. Passive sampling of particles is subject to a higher degree of variability compared with sampling of gases only (Wania & Shunthirasingham, 2020). The dispersion of particles in the air is less uniform than that of gases and is highly dependent on the particle sizes as well as wind direction and speed (Seinfeld & Pandis, 2006). Slight changes in wind direction and speed can transport for example a large burst of particles or none at all towards the samplers, substantially affecting the amount of particles that reach each of the duplicate SIP disks. Conversely, the nylon PAS show much less variability in WWTP measurements, even when limited to triplicates, compared to the duplicate SIP PAS. Nylon PAS RSDs ranged from 0.7–11% for C2, C4–C6 PFCAs, and 18–54% for PFPrA. Gases mix quickly and uniformly in the air, becoming homogeneous within seconds to minutes after emission and providing more stable PAS measurements, even at an active point source. Particles experience much longer and more variable mixing times, from a few minutes to not becoming homogeneous with the surrounding air (Zhu et al., 2024). The closer the SIP PAS are to the emission source, the higher the variability will be. Due to the long mixing times and the continuous emissions from the WWTP, duplicate SIP PAS may sample separate air parcels, each with different aerosol compositions.

Much of the variation observed between the two methods is likely rooted in the assumptions made by SIP PAS with respect to sampling of ionizable compounds. SIP PAS are equilibrium samplers, which aim for analyte concentrations in the sorbent to reach equilibrium relative to air, a collection strategy based on the behaviour of neutral molecules (Shoeib & Harner, 2002). This methodology is likely to be flawed when applied to ultrashort- and short-chain PFCAs, which are ionizable strong acids that can irreversibly dissociate after partitioning (Tao et al., 2023).

The observed variation between nylon and SIP PAS measurements of TFA and PFPrA can likely be attributed to differences in calibration and methodological procedures. Nylon PAS were

calibrated for the uptake of TFA and PFBA using controlled doses in an atmospheric chamber, and the uptake rates of the remaining PFCAs were estimated using Fuller's Law based on the robust calibration conducted for TFA. The SIP-air partition coefficients ($K_{\text{SIP-A}}$) for C4–C6 PFCAs were determined experimentally through a year-long study which compared SIP PAS measurements to those from a high-volume active air sampler (Ahrens et al., 2013). However, $K_{\text{SIP-A}}$ for TFA and PFPrA were never obtained and instead the equivalent air volumes (V_{air}) of TFA and PFPrA were estimated to be equivalent to that of PFPeA, which may have artificially lowered or enhanced their air concentrations. Due to the proportional relationship between V_{air} and $K_{\text{SIP-A}}$, if $K_{\text{SIP-A}}$ for TFA was actually lower than that for PFPeA, the resulting TFA air concentrations would be higher and closer to those measured by nylon PAS. Each PFCA exhibits a different SIP-air partition coefficient, which must be experimentally derived via calibration or uptake studies.

The nylon PAS atmospheric concentrations were not recovery corrected, as previous spike and recovery testing has shown our extraction method is capable of producing quantitative recoveries of C2–C6 PFCAs (Section 2.3.3). The SIP PAS atmospheric concentrations of C4–C6 PFCAs were recovery corrected, however, those for TFA and PFPrA were not. The ultrashort-chain PFAS LC-MS/MS analysis method is relatively new; with this analysis being one of the first instances of their inclusion into the method. Due to this, the WWTP SIP samples were not spiked with the ultrashort-chain PFCA mass labelled surrogate standards prior to extraction. Recoveries of ultrashort-chain PFCAs, PFSAs, and their mass-labelled IS spiked in blank SIP disks ($n = 4$) prior to extraction (Table S2.20) show quantitative recoveries for all analytes except TFA ($169 \pm 18\%$), although the amount of analyte recovered is likely to change in the presence of the remainder of the atmospheric matrix in field-deployed samples. Owing to the multiple evaporation steps and solvent exchanges, the SIP disk extraction method could result in substantial analyte loss, which, if not tracked using a surrogate standard, can greatly under-estimate analyte levels in the original sample. Widespread and sample-dependent recoveries of short- and long-chain PFCAs and PFSAs from SIP disks, ranging from $47 \pm 21\%$ to $138 \pm 49\%$, have been previously reported (Saini et al., 2023). The lower end of this range could readily bring SIP PAS measurements of TFA into agreement with those of the nylon PAS, potentially helping to explain the lower abundances of TFA quantified by SIP PAS in this intercomparison. These results illustrate the importance of replicate measurements or development of methods that demonstrate high levels of precision, particularly at sites known to be point sources of PFAS, such as WWTPs.

To increase the comparability between nylon and SIP PAS in future studies, we recommend implementing the following procedural changes. First, matching the sampling duration exactly. For example, the same two-month long deployment with both sampler types in close proximity to each other will allow for direct comparison and eliminate any errors based on real exposure differences. An added benefit of a longer deployment would be improved detection limits for the nylon PAS in the intercomparison. Second, more sampling sites, as well as replicates for SIP PAS would lower the variability between sampler types and between SIP replicates. Third, and most important, changes to the SIP PAS analytical procedure would resolve the inconsistencies observed for the ultrashort-chain PFCAs. Experimentally derived SIP-air partition coefficients for TFA and PFPrA and the use of surrogate standards to track extraction efficiency would undoubtedly improve the calculation of their equivalent air volumes and air concentrations. The inclusion of the mass-labelled TFA and PFPrA IS prior to extraction would greatly improve the accuracy of measurements, accounting for any analyte loss. With these proposed revisions, nylon PAS gas-phase measurements should be less than or equal to SIP PAS whole-air measurements, consistent with our original study design, with the remaining difference representing the atmospheric burden of particulate PFCAs. Last, to minimize any interlaboratory variability, nylon filter and SIP disk extracts should be analyzed via the same LC-MS/MS system with a mixed mode analytical column, as has been recently accomplished by our group's collaboration with SCIEX and Phenomenex for the separation and analysis of ultrashort-, short-, and long-chain PFCAs and PFSAAs (Lee, Butt, et al., 2025; Lee, Roberts, et al., 2025).

2.3.7.3 Trends in SIP PAS concentrations of C4–C6 PFCA and PFOS measured at WWTP 14 years apart

In 2009, SIP PAS measurements at this WWTP demonstrated that the plant was a source of atmospheric PFAS, with higher PFOS and C4–C8 PFCAs measured at sites within the WWTP compared to a nearby upwind reference site (Ahrens et al., 2011). To elucidate any potential trends in PFAS usage and emissions at the WWTP over time, the 2009 measurements were compared with those obtained 14 years later. Overall, higher average concentrations of short-chain (C4–C7) PFCAs were measured in 2023, with the sum of C4–C7 PFCAs higher by a factor of 5.5 at the primary clarifier and 1.4 between aeration tanks compared with 2009 (Table 2.10).

Table 2.10 Comparison between average C4–C13 PFCAs and C8 PFSA (PFOS) atmospheric concentrations (pg/m³) measured at three sites (primary clarifier, aeration tank, and a reference site) within a WWTP in 2009 (n = 2) and 2023 (n = 2), using SIP PAS, with relative errors (%) provided for each duplicate measurement. For each site, concentrations higher by a factor of 3 or more with respect to past or future measurements are displayed in **bold** font.

	Reference site		Primary clarifier		Aeration tank	
	2009	2023	2009	2023	2009	2023
PFBA	64.5 (42)	44.4 (33)	55.2 (43)	328 (107)	108 (7.1)	138 (98)
PFPeA	0.82 (18)	4.78 (16)	4.84 (42)	52.6 (104)	15.1 (30)	50.9 (109)
PFHxA	6.49 (54)	6.60 (21)	16.4 (117)	38.4 (77)	35.7 (15)	54.9 (0.3)
PFHpA	2.37 (27)	5.20 (140)	3.30 (120)	17.1 (157)	15.2 (1.3)	5.48 (86)
PFOA	3.49 (29)	4.33 (23)	7.00 (99)	8.65 (50)	21.2 (28)	9.43 (70)
PFNA	1.41 (43)	1.73 (16)	2.76 (55)	3.05 (98)	1.10 (120)	2.44 (9.4)
PFDA	1.35 (116)	1.07 (116)	1.67 (136)	2.80 (93)	3.54 (24)	1.94 (7.1)
PFUnDA	<0.04	0.73 (48)	5.83 (197)	1.56 (113)	<0.04	1.67 (39)
PFDoDA	0.59 (137)	<0.05	0.40 (158)	<0.05	0.50 (21)	<0.05
PFTeDA	<0.28	<0.09	<0.28	<0.09	<0.28	<0.09
PFOS	14.2 (134)	4.14 (42)	120 (95)	10.8 (24)	126 (1.6)	14.5 (70)

Concentrations of C4–C6 PFCA were higher in 2023, though only slightly for PFHxA (1.5–2.3 times on site). PFBA concentrations were 5 times higher at the primary clarifier, but at similar levels (1.2 times higher) between aeration tanks. PFPeA levels were higher at all three sites, by factors of 6, 9, and 3 at the reference site, primary clarifier, and between aeration tanks, respectively. Average concentrations of PFOS, the only PFSA measured in 2009, were lower in 2023, by a factor of 8 at the primary clarifier and 9 between aeration tanks. A similar, although not as pronounced decrease, was observed for PFHpA and PFOA between aeration tanks, with 2023 measurements lower by factors of 3 and 2, respectively. Similar concentrations of C6, C9, and C10 PFCAs as in 2009 were measured in this study, with all measurements within a factor of 2 at all sites. Compared with 2009 measurements, levels of C11 PFCA (PFUnDA) were 2 times lower in 2023 at the primary clarifier, but higher at the reference site and aeration tanks. The concentrations of C12 (PFDoDA) and C14 PFCAs (PFTeDA) at the WWTP appear to be lower during the 2023 sampling period, as neither was detected in any samples.

The results from both analyses suggest that the WWTP is a point source of PFOS and C4–C10 PFCAs to the atmosphere, with enrichment ratios greater than 1.0 observed for the majority of analytes at both sites. However, likely due to the large variability between duplicates observed during both campaigns, the on-site enrichment was only found to be significant ($p < 0.05$, Welch t-test) for PFPeA, PFHpA, and PFOS in 2009, and for PFHxA at the aeration tank in 2023. Similarly, 2023 measurements were not significantly different compared with those from 2009 ($p > 0.05$, Welch t-test, Table S2.21) for the majority of analytes (75%), with the exception of PFPeA which increased significantly ($p < 0.05$) at two sites and PFOS which decreased significantly ($p < 0.05$) at the aeration tank. Surprisingly, PFOS was the only long chain PFAA to display a clear decrease in WWTP concentrations over the 14-year gap. Prior influent and effluent measurements from other Canadian WWTPs displayed a decrease over time in levels of long-chain PFCAs and PFSAs, likely attributable to regulations imposed on their production and use (Gewurtz et al., 2024).

Similar temporal differences for short-chain PFCAs and PFOS were observed in wastewater effluent samples from six San Francisco WWTPs in which C4–C6 PFCA average concentrations increased by 150–220% from 2009 to 2014, while PFOS decreased by 47% (Houtz et al., 2016). The observed increase over time in concentrations of short-chain PFCAs may reflect the increase in production and use of short-chain PFAS as replacement compounds for restricted and phased-out long-chain PFAS (Janousek et al., 2019). Due to the multitude of short-chain fluorinated alternatives used in industry, the levels of short-chain PFCAs and PFSAs have increased in various environmental media. For instance, in WWTP effluent the increase over time in PFBA and PFHxA concentrations has been attributed to the increase in production of C6 fluorotelomer compounds, which can transform to C4–C7 PFCAs in the presence of aerobic bacteria present in aeration tanks (Houtz et al., 2016; Lee et al., 2010). This biodegradation of commercial fluorinated compounds may explain the observed increase in C4–C6 PFCA concentrations from 2009 to 2023 in the current study.

2.3.7.4 Implications

Passive air sampling of ultrashort- and short-chain PFCAs was conducted at a WWTP in the GTA, providing the first intercomparison between nylon PAS and SIP PAS. The development of a novel UPLC-MS/MS analytical method targeting ultrashort-chain PFCAs and PFSA s facilitated the analysis of TFA and PFPrA in SIP PAS extracts, addressing a critical gap in the literature. On-site enrichment demonstrated the WWTP to be a source of ultrashort- and short-chain PFCAs to the atmosphere, indicating that wastewater processes transfer PFCAs from the aqueous phase into air, contributing to local atmospheric burdens. The apparent increase over time in short-chain PFCAs coupled with the decrease in PFOS suggests that the shift towards the use of short-chain fluorinated alternatives is reflected in wastewater and consequently in atmospheric emissions originating from WWTPs. TFA and PFPrA dominated WWTP measurements by both sampler types, illustrating the importance of their inclusion in these types of analyses. Higher on-site enrichment of short-chain PFCAs measured by SIP PAS compared to nylon PAS suggest that a considerable amount of C4–C6 PFCAs are emitted from the WWTP in the particle phase as aerosols (Tao et al., 2023). This provides valuable insight into the wastewater to air transfer of PFCAs which could have important implications on their atmospheric transport and deposition.

Nylon PAS represent the superior passive sampler method for measuring gas-phase TFA and PFPrA in air. The robust calibration, selectivity towards gas-phase acids and low replicate variability afforded by nylon PAS instills confidence in the quantitation of gas-phase PFCAs. On the other hand, SIP PAS provide a more complete representation of whole air composition and are capable of measuring PFSA s and neutral PFAS compounds but have higher variability and greater methodological uncertainty for ionizable compounds. For an improvement in the calculation of air concentrations, we strongly recommend that field-derived SIP-air partition coefficients be derived for TFA and PFPrA and the abundances be recovery corrected using their respective mass-labelled internal standards. Our observations underscore the need for further measurements of ultrashort-chain PFCAs at suspected point sources and highlight the importance of these types of intercomparisons, both for method validation and enhancing our knowledge of the sources and behaviour of PFCAs.

2.4 Conclusion

Analytical and field associated method quality control and quality assurance parameters for our group's nylon PAS were optimized. The shift from the mass-labelled internal standard $^{13}\text{C}_1\text{-TFA}$ to $^{13}\text{C}_2\text{-TFA}$ in the nylon PAS method reduced overlap of isotopic peaks naturally present in native TFA, thereby improving accuracy. Isobaric interferences with TFA and its, $^{13}\text{C}_2\text{-TFA}$, were resolved by employing a longer eluent gradient. An unintended consequence of the longer gradient separation, which we believe can be resolved with further gradient modification, was the co-elution of PFPrA with sulfate, resulting in substantial ion suppression for PFPrA, preventing quantitation. Accurate quantitation of PFPrA can be achieved with our short gradient method, using the mass-labelled PFPrA IS as the optimal analytical approach or the $^{13}\text{C}_1\text{-TFA}$ IS as a suitable alternative, which was demonstrated to yield PFPrA concentrations not statistically different to those obtained using the PFPrA IS. An extraction method for C2–C6 PFCAs from both nylon and polypropylene filters was validated at two environmentally relevant concentrations. The recoveries of 20 ng of C2–C6 PFCAs using the 3 mM NaOH extraction solvent at 4 °C were quantitative for both filter types. The 4 ng TFA, 1 ng PFPrA, and 0.5 ng C4–C6 PFCAs spike yielded largely quantitative recoveries for both filter types when contamination issues were not present. Polypropylene filters from nylon PAS deployed at Pearson International Airport showed that our nylon PAS measurements are likely not biased by uptake of gas-phase C2–C6 PFCAs to the surface of the PP filters, increasing our confidence in the measurement of gas phase PFCAs on the nylon filters.

Our nylon PAS were successfully calibrated for PFBA, obtaining a linear uptake rate of $203 \pm 7 \frac{\text{PFBA}_{(g)} (\text{ng}\cdot\text{m}^{-3})\cdot\text{t}(\text{h})}{\text{PFBA}_{(\text{filter})}(\text{ng})}$, a value 1.26 times higher than the predicted uptake rate for PFBA (161 ± 17),

calculated using previously chamber-derived TFA uptake rate of $113 \pm 12 \frac{\text{TFA} (\text{ng}\cdot\text{m}^{-3})\cdot\text{t}(\text{h})}{\text{TFA}_{(\text{filter})}(\text{ng})}$ and

Fuller's Law. While conducting the PFBA calibration, residual TFA contamination inside the permeation oven allowed for the simultaneous measurement of the TFA linear uptake rate onto the nylon PAS. The TFA linear uptake rate was determined to be $146 \pm 12 \frac{\text{TFA} (\text{ng}\cdot\text{m}^{-3})\cdot\text{t}(\text{h})}{\text{TFA}_{(\text{filter})}(\text{ng})}$, a value

1.29 times higher than previously measured by Vanhauwaert et al. (2025). The strong agreement between our measured linear uptake rates for TFA and PFBA with previously measured and predicted values strengthens our confidence in the determination of atmospheric mixing ratios.

The occurrence of systematic sampling bias due to time dependent losses of analytes on the nylon filters across different sampling durations was investigated. No sign of sampling bias was observed for TFA and PFBA, and only minimal and acceptable differences were seen for PFPrA and PFPeA, increasing our confidence in passive sampler measurements over different time scales. A novel intercomparison of nylon PAS and SIP PAS was conducted at a wastewater treatment plant (WWTP). Elevated C2–C6 PFCA concentrations were measured using nylon PAS and SIP PAS within the WWTP compared to an off-site reference, suggesting that the WWTP is a point source of ultrashort- and short-chain PFCAs. With the exception of PFPrA, average concentrations of individual PFCAs measured by the two passive samplers at the two on-site locations were within a factor of 2, which can be considered good agreement seeing as some variability between the two methods is to be expected. Inter-method comparability can be improved with the use of mass-labelled internal standards for recovery correction and field-derived partition coefficients for TFA and PFPrA in the SIP PAS method, as well as the quantitation of PFPrA against its own mass-labelled internal standard in the nylon PAS method. The QA/QC parameters optimized in this chapter provide an improved and validated extraction and analysis method for the atmospheric measurement of C2–C6 PFCAs using nylon PAS.

2.5 References

- Ahrens, L., Harner, T., Shoeib, M., Koblizkova, M., & Reiner, E. J. (2013). Characterization of two passive air samplers for per- and polyfluoroalkyl substances. *Environmental Science and Technology*, 47(24), 14024–14033. <https://doi.org/10.1021/es4048945>
- Ahrens, L., Harner, T., Shoeib, M., Lane, D. A., & Murphy, J. G. (2012). Improved characterization of gas-particle partitioning for per- and polyfluoroalkyl substances in the atmosphere using annular diffusion denuder samplers. *Environmental Science and Technology*, 46(13), 7199–7206. <https://doi.org/10.1021/es300898s>
- Ahrens, L., Shoeib, M., Harner, T., Lee, S. C., Guo, R., & Reiner, E. J. (2011). Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environmental Science and Technology*, 45(19), 8098–8105. <https://doi.org/10.1021/es1036173>
- Arp, H. P. H., & Goss, K. U. (2009). Gas/particle partitioning behavior of perfluorocarboxylic acids with terrestrial aerosols. *Environmental Science and Technology*, 43(22), 8542–8547. <https://doi.org/10.1021/es901864s>
- Arp, H. P. H., Gredelj, A., Glüge, J., Scheringer, M., & Cousins, I. T. (2024). The Global Threat from the Irreversible Accumulation of Trifluoroacetic Acid (TFA). *Environmental Science and Technology*, 58(45), 19925–19935. <https://doi.org/10.1021/acs.est.4c06189>
- Bangma, J., Barry, K. M., Fisher, C. M., Genualdi, S., Guillette, T. C., Huset, C. A., McCord, J., Ng, B., Place, B. J., Reiner, J. L., Robuck, A., & Rodowa, A. E. (2024). PFAS ghosts: How to identify, evaluate, and exorcise new and existing analytical interference. *Analytical and Bioanalytical Chemistry*, 416(8), 1777–1785. <https://doi.org/10.1007/s00216-024-05125-y>
- Bjornsdotter, M. K., Yeung, L. W. Y., Karrman, A., & Jogsten, I. E. (2020). Challenges in the analytical determination of ultra-short-chain perfluoroalkyl acids and implications for environmental and human health. *Anal. Bioanal. Chem*, 412(20), 4785–4796. <https://doi.org/10.1007/s00216-020-02692-8>
- Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., Voogt, P. D., Jensen, A. A., Kannan, K., Mabury, S. A., & van Leeuwen, S. P. J. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management*, 7(4), 513–541. <https://doi.org/10.1002/ieam.258>
- Bytnerowicz, A., Padgett, P. E., Arbaugh, M. J., Parker, D. R., & Jones, D. P. (2001). Passive sampler for measurements of atmospheric nitric acid vapor (HNO₃) concentrations. *TheScientificWorldJournal*, 1, 815–822. <https://doi.org/10.1100/tsw.2001.323>
- Bytnerowicz, A., Sanz, M. J., Arbaugh, M. J., Padgett, P. E., Jones, D. P., & Davila, A. (2005). Passive sampler for monitoring ambient nitric acid (HNO₃) and nitrous acid (HNO₂) concentrations. *Atmospheric Environment*, 39(14), 2655–2660. <https://doi.org/10.1016/j.atmosenv.2005.01.018>
- Carmichael, L. (2022). *Determining the sampling rates for a new nylon passive sampler to estimate the atmospheric concentrations of nitric acid and perfluoroalkyl acids pollutants* [Master's Thesis, York University]. <http://hdl.handle.net/10315/40980>

- Cheng, L., Teagle, S., Enders, J. R., Weed, R. A., Nichols, H. B., Knappe, D. R. U., & Hoppin, J. A. (2025). Historical Blood Serum Samples from Wilmington, North Carolina: The Importance of Ultrashort-Chain Per- and Polyfluoroalkyl Substances. *Environmental Science & Technology*. <https://doi.org/10.1021/acs.est.5c08146>
- Clouthier, J., Vandenboer, T., & Young, C. (2026). Direct-inject suppressed ion chromatography-mass spectrometry method with online preconcentration for short- and ultra short-chain perfluoroalkyl carboxylic acids in fresh water. *Analytical Methods*. <https://doi.org/10.1039/D5AY02105G>
- Crilley, L. R., Lao, M., Salehpoor, L., & VandenBoer, T. C. (2023). Emerging investigator series: An instrument to measure and speciate the total reactive nitrogen budget indoors: Description and field measurements. *Environmental Science: Processes and Impacts*, 25(3), 389–404. <https://doi.org/10.1039/d2em00446a>
- Fenton, S. E., Ducatman, A., Boobis, A., DeWitt, J. C., Lau, C., Ng, C., Smith, J. S., & Roberts, S. M. (2021). Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environmental Toxicology and Chemistry*, 40(3), 606–630. <https://doi.org/10.1002/etc.4890>
- Freeling, F., & Bjornsdotter, M. K. (2023). Assessing the environmental occurrence of the anthropogenic contaminant trifluoroacetic acid (TFA). *Current Opinion in Green and Sustainable Chemistry*, 41(100807). <https://doi.org/10.1016/j.cogsc.2023.100807>
- Fuller, E. N., Schettler, P. D., & Giddings, J. C. (1966). *A New Method for Prediction of Binary Gas-Phase Diffusion Coefficients*. 58(5), 18–27. <https://doi.org/10.1021/ie50677a007>
- Furey, A., Moriarty, M., Bane, V., Kinsella, B., & Lehane, M. (2013). Ion suppression; A critical review on causes, evaluation, prevention and applications. *Talanta*, 115, 104–122. <https://doi.org/10.1016/j.talanta.2013.03.048>
- Gallo, B., Berrueta, L. A., Gallo, / B, & Vicente, / F. (1995). A review of solid phase extraction: Basic principles and new developments Cite this paper A Review of Solid Phase Extraction: Basic Principles and New Developments. *Chromatographia*, 40, 474–483. <https://doi.org/10.1007/BF02269916>
- Gewurtz, S. B., Auyeung, A. S., De Silva, A. O., Teslic, S., & Smyth, S. A. (2024). Per- and polyfluoroalkyl substances (PFAS) in Canadian municipal wastewater and biosolids: Recent patterns and time trends 2009 to 2021. *Science of the Total Environment*, 912. <https://doi.org/10.1016/j.scitotenv.2023.168638>
- Gorecki, T., & Namiesnik, J. (2002). Passive sampling. *Trends Anal. Chem.*, 21(4), 276–291. [https://doi.org/10.1016/S0165-9936\(02\)00407-7](https://doi.org/10.1016/S0165-9936(02)00407-7)
- Gu, W., Cheng, P., & Tang, M. (2018). Compilation and evaluation of gas phase diffusion coefficients of halogenated organic compounds. *Royal Society Open Science*, 5(7). <https://doi.org/10.1098/rsos.171936>
- Harner, T. (2021). *2021 V10 Template for Calculating PUF and SIP Disk Sample Air Volumes April 28*. https://www.researchgate.net/publication/351495899_2021_v10_Template_for_calculating_PUF_and_SIP_disk_sample_air_volumes_April28

- Historical Data—Climate—Environment and Climate Change Canada*. (2025).
https://climate.weather.gc.ca/historical_data/search_historic_data_e.html
- Houtz, E. F., Sutton, R., Park, J. S., & Sedlak, M. (2016). Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Research*, 95, 142–149. <https://doi.org/10.1016/j.watres.2016.02.055>
- Jacob, D. J. (1999). *Introduction to Atmospheric Chemistry*. Princeton University Press.
- Jahnke, A., & Berger, U. (2009). Trace analysis of per- and polyfluorinated alkyl substances in various matrices-How do current methods perform? *Journal of Chromatography A*, 1216(3), 410–421. <https://doi.org/10.1016/j.chroma.2008.08.098>
- Janda, J., Nödler, K., Brauch, H. J., Zwiener, C., & Lange, F. T. (2019). Robust trace analysis of polar (C2-C8) perfluorinated carboxylic acids by liquid chromatography-tandem mass spectrometry: Method development and application to surface water, groundwater and drinking water. *Environmental Science and Pollution Research*, 26(8), 7326–7336. <https://doi.org/10.1007/s11356-018-1731-x>
- Janousek, R. M., Mayer, J., & Knepper, T. P. (2019). Is the phase-out of long-chain PFASs measurable as fingerprint in a defined area? Comparison of global PFAS concentrations and a monitoring study performed in Hesse, Germany from 2014 to 2018. *TrAC - Trends in Analytical Chemistry*, 120. <https://doi.org/10.1016/j.trac.2019.01.017>
- Jia, S., Marques Dos Santos, M., Li, C., & Snyder, S. A. (2022). Recent advances in mass spectrometry analytical techniques for per- and polyfluoroalkyl substances (PFAS). *Analytical and Bioanalytical Chemistry*, 414(9), 2795–2807. <https://doi.org/10.1007/s00216-022-03905-y>
- Joudan, S., De Silva, A. O., & Young, C. J. (2021). Insufficient evidence for the existence of natural trifluoroacetic acid. *Environ. Sci.: Processes Impacts*, 23, 1641–1649. <https://doi.org/10.1039/d1em00306b>
- Joudan, S., Gauthier, J., Mabury, S. A., & Young, C. J. (2024). Aqueous Leaching of Ultrashort-Chain PFAS from (Fluoro)polymers: Targeted and Nontargeted Analysis. *Environmental Science and Technology Letters*, 11(3), 237–242. <https://doi.org/10.1021/acs.estlett.3c00797>
- Karášková, P., Codling, G., Melymuk, L., & Klánová, J. (2018). A critical assessment of passive air samplers for per- and polyfluoroalkyl substances. *Atmospheric Environment*, 185, 186–195. <https://doi.org/10.1016/j.atmosenv.2018.05.030>
- Khalid, N. K., Le Calvez, M., Lemire, M., Dinh, Q. T., Fontaine, J., Lair, S., & Sauvé, S. (2024). Occurrence of 80 per and polyfluorinated alkyl substances (PFAS) in muscle and liver tissues of marine mammals of the St. Lawrence Estuary and Gulf, Quebec, Canada. *Frontiers in Environmental Chemistry*, 5. <https://doi.org/10.3389/fenvc.2024.1403728>
- Lao, M., R. Crilley, L., Salehpour, L., C. Furlani, T., Bourgeois, I., Andrew Neuman, J., W. Rollins, A., R. Veres, P., A. Washenfelder, R., C. Womack, C., J. Young, C., & C. Vandenboer, T. (2020). A portable, robust, stable, and tunable calibration source for gas-phase nitrous acid (HONO). *Atmospheric Measurement Techniques*, 13(11), 5873–5890. <https://doi.org/10.5194/amt-13-5873-2020>

- Lee, H., Butt, C. M., Lodge, S., Ye, R., Nistorescu, I., Young, C., & VandenBoer, T. (2025). *Quantitation of ultrashort- and short-chain PFAS in beverages by a direct injection LC-MS/MS method*. SCIEX. <https://sciex.com/tech-notes/food-beverage/food-and-beverage/quantitation-of-ultrashort-and-short-chain-pfas-in-beverages-by-a-direct-injection-lc-ms-ms-method>
- Lee, H., Deon, J., & Mabury, S. A. (2010). Biodegradation of polyfluoroalkyl phosphates as a source of perfluorinated acids to the environment. *Environmental Science and Technology*, 44(9), 3305–3310. <https://doi.org/10.1021/es9028183>
- Lee, H., Roberts, S., Butt, C. M., Lodge, S., Ye, R., Young, C., & VandenBoer, T. (2025). *Simultaneous quantitation of ultrashort-, short- and long-chain PFAS in water by a single direct injection LC-MS/MS method*. SCIEX. <https://sciex.com/tech-notes/environmental-industrial/water-and-soil/simultaneous-quantitation-of-ultrashort-short-and-long-chain-pfas-in-water-by-a-single-direct-injection-lc-ms-ms-method>
- Martin, J. W., Mabury, S. A., Wong, C. S., Noventa, F., Solomon, K. R., Alaee, M., & Muir, D. C. G. (2003). Airborne haloacetic acids. *Environmental Science and Technology*, 37(13), 2889–2897. <https://doi.org/10.1021/es026345u>
- Melymuk, L., Nizzetto, P. B., Harner, T., White, K. B., Wang, X., Tominaga, M. Y., He, J., Li, J., Ma, J., Ma, W. L., Aristizábal, B. H., Dryer, A., Jiménez, B., Muñoz-Arnanz, J., Odabasi, M., Dumanoglu, Y., Yaman, B., Graf, C., Sweetman, A., & Klánová, J. (2021). Global intercomparison of polyurethane foam passive air samplers evaluating sources of variability in SVOC measurements. *Environmental Science and Policy*, 125, 1–9. <https://doi.org/10.1016/j.envsci.2021.08.003>
- Michalski, R. (2016). Principles and Applications of Ion Chromatography. In R. Michalski (Ed.), *Application of IC-MS and IC-ICP-MS in Environmental Research* (1st ed., pp. 1–46). Wiley. <https://doi.org/10.1002/9781119085362.ch1>
- Padgett, P. E., Bytnerowicz, A., Dawson, P. J., Riechers, G. H., & Fitz, D. R. (2004). Design, Evaluation and Application of a Continuously Stirred Tank Reactor System for Use in Nitric Acid Air Pollutant Studies. *Water, Air, and Soil Pollution*, 151(1–4), 35–51. <https://doi.org/10.1023/B:WATE.00000009890.74470.fa>
- Persaud, D., Joudan, S., VandenBoer, T. C., & Young, C. J. (2026). Atmospheric Removal of Trifluoroacetic Acid by Dry and Wet Deposition: A Multiyear Analysis in Toronto. *Environmental Science & Technology Letters*, 13(2), 261–267. <https://doi.org/10.1021/acs.estlett.5c01100>
- Pickard, H. M., Criscitiello, A. S., Persaud, D., Spencer, C., Muir, D. C. G., Lehnher, I., Sharp, M. J., De Silva, A. O., & Young, C. J. (2020). Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations. *Geophysical Research Letters*, 47(10). <https://doi.org/10.1029/2020GL087535>
- Pickard, H. M., Criscitiello, A. S., Spencer, C., Sharp, M. J., Muir, D. C. G., De Silva, A. O., & Young, C. J. (2018). Continuous non-marine inputs of per- and polyfluoroalkyl substances to the High Arctic: A multi-decadal temporal record. *Atmospheric Chemistry and Physics*, 18(7), 5045–5058. <https://doi.org/10.5194/acp-18-5045-2018>

- Place, B. K., Quilty, A. T., Di Lorenzo, R. A., Ziegler, S. E., & VandenBoer, T. C. (2017). Quantitation of 11 alkylamines in atmospheric samples: Separating structural isomers by ion chromatography. *Atmospheric Measurement Techniques*, *10*(3), 1061–1078. <https://doi.org/10.5194/amt-10-1061-2017>
- Place, B. K., Young, C. J., Ziegler, S. E., Edwards, K. A., Salehpoor, L., & VandenBoer, T. C. (2018). Passive sampling capabilities for ultra-trace quantitation of atmospheric nitric acid (HNO₃) in remote environments. *Atmospheric Environment*, *191*, 360–369. <https://doi.org/10.1016/j.atmosenv.2018.08.030>
- Röhrh, A., & Lammel, G. (2002). Determination of malic acid and other C₄ dicarboxylic acids in atmospheric aerosol samples. *Chemosphere*, *46*(8), 1195–1199. [https://doi.org/10.1016/S0045-6535\(01\)00243-0](https://doi.org/10.1016/S0045-6535(01)00243-0)
- Saini, A., Chinnadurai, S., Schuster, J. K., Eng, A., & Harner, T. (2023). Per- and polyfluoroalkyl substances and volatile methyl siloxanes in global air: Spatial and temporal trends. *Environmental Pollution*, *323*. <https://doi.org/10.1016/j.envpol.2023.121291>
- Seinfeld, J. H., & Pandis, S. N. (2006). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (3rd ed.). John Wiley & Sons Inc.
- Shoeib, M., & Harner, T. (2002). Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environmental Science and Technology*, *36*(19), 4142–4151. <https://doi.org/10.1021/es020635t>
- Shoeib, M., Harner, T., Sum, C. L., Lane, D., & Zhu, J. (2008). Sorbent-impregnated polyurethane foam disk for passive air sampling of volatile fluorinated chemicals. *Analytical Chemistry*, *80*(3), 675–682. <https://doi.org/10.1021/ac701830s>
- Shoeib, M., Schuster, J., Rauert, C., Su, K., Smyth, S. A., & Harner, T. (2016). Emission of poly and perfluoroalkyl substances, UV-filters and siloxanes to air from wastewater treatment plants. *Environmental Pollution*, *218*, 595–604. <https://doi.org/10.1016/j.envpol.2016.07.043>
- Taniyasu, S., Kannan, K., Yeung, L. W. Y., Kwok, K. Y., Lam, P. K. S., & Yamashita, N. (2008). Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C₂–C₄) in precipitation by liquid chromatography-tandem mass spectrometry: Comparison to patterns of long-chain perfluorinated acids (C₅–C₁₈). *Analytica Chimica Acta*, *619*(2), 221–230. <https://doi.org/10.1016/j.aca.2008.04.064>
- Tao, Y., VandenBoer, T. C., Veres, P. R., Warneke, C., de Gouw, J. A., Weber, R. J., Markovic, M. Z., Zhao, Y., Baker, K. R., Kelly, J. T., Murphy, J. G., Young, C. J., & Roberts, J. M. (2022). Hydrogen Chloride (HCl) at Ground Sites During CalNex 2010 and Insight Into Its Thermodynamic Properties. *Journal of Geophysical Research: Atmospheres*, *127*(9). <https://doi.org/10.1029/2021JD036062>
- Tao, Y., VandenBoer, T. C., Ye, R. X., & Young, C. J. (2023). Exploring controls on perfluorocarboxylic acid (PFCA) gas-particle partitioning using a model with observational constraints. *Environmental Science: Processes and Impacts*, *25*(2), 264–276. <https://doi.org/10.1039/d2em00261b>

- Thackray, C. P., Selin, N. E., & Young, C. J. (2020). A global atmospheric chemistry model for the fate and transport of PFCAs and their precursors. *Environmental Science: Processes and Impacts*, 22(2), 285–293. <https://doi.org/10.1039/c9em00326f>
- VandenBoer, T. C., Markovic, M. Z., Petroff, A., Czar, M. F., Borduas, N., & Murphy, J. G. (2012). Ion chromatographic separation and quantitation of alkyl methylamines and ethylamines in atmospheric gas and particulate matter using preconcentration and suppressed conductivity detection. *Journal of Chromatography A*, 1252, 74–83. <https://doi.org/10.1016/j.chroma.2012.06.062>
- Vanhouwaert, E. (2024). *A passive air sampling technique for ultra-trace quantitation of perfluoroalkyl carboxylic acids* [Master's Thesis, York University]. <https://hdl.handle.net/10315/42427>
- Vanhouwaert, E., Carmichael, L., Nistorescu, I., Crilley, L., Shunthirasingham, C., Hung, H., Young, C., & Vandenboer, T. C. (2025). Selective ultra-trace atmospheric passive sampling of gaseous perfluoroalkyl carboxylic acids. *Environmental Science: Processes & Impacts*. <https://doi.org/10.1039/d5em00297d>
- Vitale, R. J., Acker, J. K., & Somerville, S. E. (2022). An assessment of the potential for leaching of per- and polyfluoroalkyl substances from fluorinated and non-fluorinated high-density polyethylene containers. *Environmental Advances*, 9. <https://doi.org/10.1016/j.envadv.2022.100309>
- Wang, Y., Liu, M., Vo Duy, S., Munoz, G., Sauv  , S., & Liu, J. (2024). Fast analysis of short-chain and ultra-short-chain fluorinated organics in water by on-line extraction coupled to HPLC-HRMS. *Science of the Total Environment*, 943. <https://doi.org/10.1016/j.scitotenv.2024.173682>
- Wang, Z., Cousins, I. T., Scheringer, M., & Hungerb  hler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSA) and their potential precursors. *Environment International*, 60, 242–248. <https://doi.org/10.1016/j.envint.2013.08.021>
- Wang, Z., Dewitt, J. C., Higgins, C. P., & Cousins, I. T. (2017). A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environmental Science and Technology*, 51(5), 2508–2518. <https://doi.org/10.1021/acs.est.6b04806>
- Wania, F., & Shunthirasingham, C. (2020). Passive air sampling for semi-volatile organic chemicals. *Environmental Science: Processes and Impacts*, 22(10), 1925–2002. <https://doi.org/10.1039/d0em00194e>
- Wong, F., Shoeib, M., Katsoyiannis, A., Eckhardt, S., Stohl, A., Bohlin-Nizzetto, P., Li, H., Fellin, P., Su, Y., & Hung, H. (2018). Assessing temporal trends and source regions of per- and polyfluoroalkyl substances (PFASs) in air under the Arctic Monitoring and Assessment Programme (AMAP). *Atmospheric Environment*, 172, 65–73. <https://doi.org/10.1016/j.atmosenv.2017.10.028>
- Wu, J., Martin, J. W., Zhai, Z., Lu, K., Li, L., Fang, X., Jin, H., Hu, J., & Zhang, J. (2014). Airborne trifluoroacetic acid and its fraction from the degradation of HFC-134a in Beijing, China. *Environmental Science and Technology*, 48(7), 3675–3681. <https://doi.org/10.1021/es4050264>

- Ye, R. X., Di Lorenzo, R. A., Clouthier, J. T., Young, C. J., & VandenBoer, T. C. (2023). A Rapid Derivatization for Quantitation of Perfluorinated Carboxylic Acids from Aqueous Matrices by Gas Chromatography-Mass Spectrometry. *Analytical Chemistry*, 95(19), 7648–7655. <https://doi.org/10.1021/acs.analchem.3c00593>
- Young, C. J., Joudan, S., Tao, Y., Wentzell, J. J. B., & Liggio, J. (2024). High Time Resolution Ambient Observations of Gas-Phase Perfluoroalkyl Carboxylic Acids: Implications for Atmospheric Sources. *Environmental Science and Technology Letters*, 11(12), 1348–1354. <https://doi.org/10.1021/acs.estlett.4c00897>
- Young, C. J., & Mabury, S. A. (2010). Atmospheric perfluorinated acid precursors: Chemistry, occurrence, and impacts. *Reviews of Environmental Contamination and Toxicology*, 208, 1–109. https://doi.org/10.1007/978-1-4419-6880-7_1
- Young, C. J., & VandenBoer, T. C. (2023, October). PFAS: Unraveling the analytical challenges: Separations and selectivity for measurements of atmospheric PFAS. *Separation Science*. <https://www.sepscience.com/separations-and-selectivity-for-measurements-of-atmospheric-pfas-7951>
- Zbieranowski, A. L., & Aherne, J. (2012). Ambient concentrations of atmospheric ammonia, nitrogen dioxide and nitric acid across a rural-urban-agricultural transect in southern Ontario, Canada. *Atmospheric Environment*, 62, 481–491. <https://doi.org/10.1016/j.atmosenv.2012.08.040>
- Zhang, B., Zhai, Z., & Zhang, J. (2018). Distribution of trifluoroacetic acid in gas and particulate phases in Beijing from 2013 to 2016. *Science of the Total Environment*, 634, 471–477. <https://doi.org/10.1016/j.scitotenv.2018.03.384>
- Zheng, G., Eick, S. M., & Salamova, A. (2023). Elevated Levels of Ultrashort- and Short-Chain Perfluoroalkyl Acids in US Homes and People. *Environmental Science and Technology*, 57(42), 15782–15793. <https://doi.org/10.1021/acs.est.2c06715>
- Zhu, F.-J., Wang, L.-F., Qu, L.-Z., Ma, W.-L., Ren, G.-B., Li, B.-H., & Ma, X.-D. (2024). Modelling the dynamic gas/particle partitioning process of semi-volatile organic compounds emitted from point sources: Quantitative analysis and impact assessment. *Science of The Total Environment*, 933, 172935. <https://doi.org/10.1016/j.scitotenv.2024.172935>
- Zou, J., Zhao, M., Chan, S. A., Song, Y., Yan, S., & Song, W. (2024). Rapid and simultaneous determination of ultrashort-, short- and long- chain perfluoroalkyl substances by a novel liquid chromatography mass spectrometry method. *Journal of Chromatography A*, 1734. <https://doi.org/10.1016/j.chroma.2024.465324>

Chapter 3. Nylon passive air sampler measurement of gas-phase C2–C6 PFCAs in the Greater Toronto Area

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IN prepared, with TCV editing the chapter/manuscript.

CJY and TCV conceptualized the work and acquired the funding. CJY and TCV provided the resources to support this work.

IN performed all experiments and analyses under the guidance of TCV.

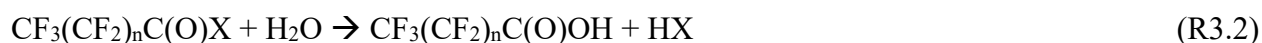
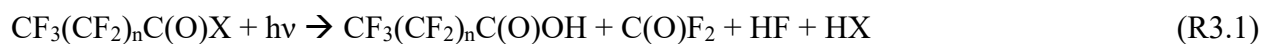
For the SWAPIT and Pearson International Airport (YYZ) campaigns, HH and CS were associated with funding to support the participation of IN and helped with project design and logistics. SWAPIT sample deployment and collection was conducted by DP. Sampler deployment and collection at Pearson International Airport and surrounding sites was conducted by the research team of RR, DP, AK, and IN due to security clearances and various adjacent site access required.

3.1 Introduction

3.1.1 Sources and formation of PFCAs in the atmosphere

Perfluoroalkyl carboxylic acids (PFCAs), a group of per- and polyfluoroalkyl substances (PFAS), are persistent anthropogenic compounds that have been widely detected in environmental media such as air (Young et al., 2024) and precipitation (Persaud et al., 2026; Scott et al., 2006), as well as in wildlife (Khalid et al., 2024) and humans (Fenton et al., 2021). Due to their unique properties, such as chemical stability, surface tension lowering, and ability to create stable foams, PFCAs have been widely used in the manufacture of a variety of products such as aqueous film forming foam (AFFF), polyurethane, inks, lubricants, gasoline, and water repellents for leather, paper and fabric for more than 60 years (Prevedouros et al., 2006). In the past, long-chain ($\geq C7$) perfluoroalkyl acids (PFAAs), in particular perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) were favoured in industry. The discovery of their bioaccumulative and harmful nature in mammals (e.g. in rats, PFOA increased the incidence of cancers and caused weight loss, liver enlargement and changes in lipid metabolism) led to restrictions on their production and use (Fenton et al., 2021; Janousek et al., 2019; Lindstrom et al., 2011). Consequently, manufacturers turned to the use of ultrashort-chain ($C2, C3$) and short-chain ($C4-C6$) PFAS as substitutes (Janousek et al., 2019; Z. Wang et al., 2013, 2017). Recently, it has been shown that short-chain PFAS can be just as persistent and even more mobile in the environment (Janousek et al., 2019).

In addition to their direct release into the environment from their manufacture and industrial use, PFCAs can be formed indirectly from the environmental degradation of PFAS commercial products that are emitted from point sources such as chemical and material production facilities, wastewater treatment plants, landfills, airports and military bases (Andrews et al., 2021). Many PFAS products such as hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) and fluorotelomer compounds can undergo atmospheric oxidation to form intermediates such as acyl halides or perfluoroacyl peroxy radicals (Young & Mabury, 2010). The intermediates can undergo photolysis (R3.1), hydrolysis (R3.2), or reactions with hydroperoxyl radicals (R3.3) to form PFCAs as terminal products.





Ultrashort- and short-chain PFCAs, in particular trifluoroacetic acid (TFA), can be formed from many more PFAS compounds compared to the longer chain PFCAs (Young & Mabury, 2010). For example, HFO-1234yf, used as a refrigerant in automobile air conditioners (A/C) degrades in the atmosphere to TFA in almost 100% yield (Luecken et al., 2010). Although refrigerants may leak at any time including when the A/C unit and/or engine are off due to permeation through hoses and diffusion through fittings and seals, (Siegl et al., 2002) as well as due to accidents, strikes by road debris, and component failures (Y. Zhang et al., 2017), losses are expected to be higher in summer when both the engine and A/C unit are on.

The atmospheric lifetimes of PFCA precursors vary widely, from as little as 4 – 16 days for HFO-1234yf and 10 – 20 days for fluorotelomer alcohols (FTOHs), to 14 years for HFC-134a (World Meteorological Organization, 2022; Young & Mabury, 2010). PFCAs are expected to have short atmospheric lifetimes, on the order of a few days, depositing back to the surface through wet and dry deposition (Persaud et al., 2026; Pickard et al., 2020; Young et al., 2024). Due to their short lifetimes, atmospheric emissions of PFCAs and short-lived precursors are expected to be elevated near PFAS point sources compared to the surrounding areas. On the other hand, volatile precursor PFAS with longer lifetimes are likely to undergo long-range atmospheric transport and form PFCAs as terminal degradation products far from where they were emitted (Pickard et al., 2018, 2020; Thackray et al., 2020; Wong et al., 2018). The types of PFAS products used in commercial applications influence both the range and spatial distribution of PFCAs in the atmosphere.

3.1.2 Airports as point sources of PFAS

Airports have been demonstrated to be point sources of PFAS contamination to their surroundings, particularly to soil and groundwater (M. Liu et al., 2022; Nunes et al., 2011), and surface water and fish (Awad et al., 2011; Carrizo et al., 2023; J. Liu et al., 2023). Historically, PFAS contamination at airports has been attributed to the use of AFFF to prevent and fight fires in emergencies, as well as for routine firefighting training or due to spills (Milley et al., 2018). For instance, Toronto Pearson International Airport was the site of several substantial AFFF releases in the early 2000s, with large spills and applications discharging more than 60,000 L of AFFF into the surrounding environment.

In the past, AFFF mixtures contained PFOS but after restrictions on the manufacture and use of long-chain PFAS were implemented, fluorotelomer-based AFFF mixtures became widely adopted (Place & Field, 2012; Prevedouros et al., 2006). Current formulations of AFFF contain volatile neutral fluorosurfactants which can be released into the atmosphere at each use (Mattila et al., 2024). The 6:2 FTOH is one of the major degradation products of fluorotelomer-based AFFF mixtures (D'Agostino & Mabury, 2017). The 6:2 FTOH can itself undergo biotransformation or atmospheric oxidation to form the C2–C6 PFCAs (Just et al., 2022; Sture et al., 2026; Young & Mabury, 2010).

Numerous studies have examined the impacts of AFFF to the aqueous environment, driven by its widespread use, the inclusion of PFOS in its past formulations, and documented contamination of nearby surface waters following major release events (Awad et al., 2011; Carrizo et al., 2023; Koch et al., 2021; Milley et al., 2018; Nunes et al., 2011; Ruyle et al., 2023; Sture et al., 2026). Comparatively, the release of volatile PFAS to the atmosphere from AFFF use is understudied. Investigations of the volatile headspace above AFFF revealed the presence of C5–C15 PFCAs and fluorotelomer compounds (e.g. 4:2, 6:2, 10:2 FTOHs) (Mattila et al., 2024; Roth et al., 2020). In a study by Ye et al. (2024) untargeted total organic fluorine measurements showed that the majority (99.8%) of AFFF volatile emissions were unknown compounds, which would be unaccounted for during targeted analysis.

The extensive use of AFFF at airports is likely to have caused legacy contamination, with precursor compounds expected to persist long-term (M. Liu et al., 2022). Our limited understanding of the fluorinated organic compounds released into the atmosphere following AFFF use underscores the importance of investigating atmospheric degradation products associated with its use at airports. Furthermore, during routine operations such as aircraft de-icing, cleaning, and fueling, airports may use other PFAS-containing commercial products, possibly resulting in additional atmospheric emissions. The contributions of legacy and contemporary volatile emission sources at airports remain largely uncharacterized, particularly for the ultrashort-chain PFCAs.

3.1.3 Indoor environments as point sources of PFAS

Indoor air quality is a major concern for human health, as Canadians and Americans typically spend ~90% of their time indoors (Klepeis et al., 2001). Indoors, exposure to PFCAs can occur through drinking water, diet, ingestion of dust, and inhalation of air (Eichler & Little, 2020).

Recently, ultrashort-chain PFCAs have been measured in drinking water (Neuwald et al., 2022; Zheng et al., 2023), food and beverages (Hawley et al., 2025; Lee et al., 2025), food contact materials (Schwartz-Narbonne et al., 2023), and dust (Zheng et al., 2023). To our knowledge, our research group is the first to measure ultrashort-chain PFCAs in indoor air using passive samplers (Vanhauwaert, 2024). Some studies have conducted passive air sampling indoors, with most utilizing SIP PAS, but these focused on neutral PFAS such as FTOHs, fluorotelomer acrylates (FTACs), perfluoroalkane sulfonamides (FOSAs), perfluoroalkane sulfonamidoethanols (FOSEs), and long-chain PFCAs (with a couple of studies including C4–C6 PFCAs) (Goosey & Harrad, 2012; Heydebreck et al., 2016; Morales-McDevitt et al., 2021; Shoeib et al., 2011; Winkens et al., 2017). Ultrashort- and short-chain PFCAs are non-volatile ionizable compounds which are difficult to measure indoors using SIP PAS due to the much lower air turbulence and sampling rates (Wania & Shunthirasingham, 2020). In one of the few studies to include ultrashort-chain PFCAs in their analysis, Zheng et al. (2023) investigated the occurrence of C2–C7 PFCAs in indoor dust, drinking water, and human serum. They observed that TFA was the dominant PFAA in dust, water and serum samples, with PFPrA the second most abundant, illustrating the need for further indoor sampling, with a focus on ultrashort-chain PFCAs.

3.1.4 Need for atmospheric measurements of ultrashort- and short-chain PFCAs

Atmospheric measurements can be done indirectly via wet and total deposition. Deposition measurements of ultrashort-chain PFCAs have previously been conducted in Toronto and other North American locations (Persaud et al., 2026; Scott et al., 2006). Scott et al. (2006) detected TFA in 100% of precipitation samples, with concentrations one to two orders of magnitude higher than the other PFCAs. Deposition measurements are useful in elucidating deposition fluxes; however they cannot provide information on gas and particle phase concentrations due to the simultaneous collection of both gaseous and particulate matter. Direct measurements of PFCAs in the atmosphere have been conducted utilizing active and passive sampling techniques. While active air sampling techniques utilizing a low- or high-volume active air sampler (LV-AAS or HV-AAS) can measure both gas and particle phases, they are subject to sampling artifacts, are expensive and high maintenance (Ahrens et al., 2012; Tao et al., 2023). Passive air sampling utilizing polyurethane foam (PUF) or sorbent-impregnated polyurethane foam (SIP) disks to measure persistent organic pollutants has been conducted on a global scale (Genualdi et al., 2010; Saini et al., 2023), however some limitations exist, such as difficult sample preparation and use of

estimated sampling rates for PFCAs. In addition, due in large part to their inability to be retained on typical reversed phase liquid chromatography columns, LV- or HV-AAS or SIP disk samples have not yet been analyzed for ultrashort-chain PFCAs.

Recently ultrashort- and short-chain PFCAs were measured in various locations across Canada in freshwater (Clouthier et al., 2026) and in air using our nylon passive air samplers (PAS) paired with analysis by ion chromatography-mass spectrometry (IC-MS) (Vanhauwaert et al., 2025). Mixing ratios of TFA were substantially higher (11 to 200 ppqv) than the other PFCAs (0.2 to 26.4 ppqv) at all locations, with mixing ratios decreasing with increasing chain length. Our past nylon PAS measurements aimed to compare C2–C6 PFCA mixing ratios at urban and remote locations and elucidate seasonal trends. There is still a need for atmospheric measurements of PFCAs at suspected point sources, such as airports, as well as in indoor environments. Our nylon PAS are particularly well suited for large scale multi-location monitoring campaigns due to their compact size, low cost, and low maintenance design.

3.1.5 Objectives

The objective of this work is the atmospheric measurement of C2–C6 PFCAs in various locations across the Greater Toronto Area (GTA) utilizing our custom-built nylon PAS, described in Chapter 2. First, sampling was undertaken at three urban locations spread throughout the GTA as part of the Study of Winter Air Pollution in Toronto (SWAPIT) campaign. Next, at Pearson International Airport and three neighboring sites, sampling was conducted to study aircraft and airport-derived PFCA emissions compared to the surrounding urban environment. Last, sampling was conducted in four indoor locations, including two chemistry laboratories and two offices.

3.2 Methods

3.2.1 Materials and Chemicals

Sodium carbonate (Na_2CO_3 , $\geq 99.5\%$, ACS reagent grade), glycerol ($>99\%$), and sodium hydroxide (NaOH) solution (49–51% in water) were purchased from Sigma Aldrich (ON, Canada). Methanol (MeOH, Optima LC-MS) was obtained from Fisher Chemical (ON, Canada) and used for IC-MS analysis. Methanol (HPLC grade, $\geq 99.9\%$) was obtained from Sigma Aldrich (ON, Canada) and used for rinsing glassware. The sodium salts of TFA ($>98\%$) and perfluoropropanoic acid (PFPrA, $>99\%$) were obtained from Sigma Aldrich; sodium salts of perfluorobutanoic acid (PFBA, $>98\%$), perfluoropentanoic acid (PFPeA, purity not reported) and perfluorohexanoic acid (PFHxA, $>98\%$) were obtained from Synquest (FL, US). Individual 1000 $\mu\text{g/mL}$ stock solutions of each sodium salt PFCA were prepared in ultrapure Milli-Q water ($18.2 \text{ M}\Omega\cdot\text{cm}$ at 25°C , Direct 8; EMD Millipore), and subsequently combined and diluted to prepare working stock solutions.

Mass-labelled $^{13}\text{C}_1$ -TFA (T786038) and $^{13}\text{C}_1$ -PFPrA were purchased from Toronto Research Chemicals (ON, Canada) and dissolved separately in MeOH to 50 mg/mL . Mass-labelled $^{13}\text{C}_2$ -TFA-sodium salt (99%, 50 $\mu\text{g/mL}$ in MeOH) was purchased from Cambridge Isotope Laboratories, Inc. Mass-labelled $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_3$ -PFPeA, and $^{13}\text{C}_2$ -PFHxA were obtained as individual 50 $\mu\text{g/mL}$ in MeOH solutions from Wellington Laboratories (ON, Canada; MPFBA, M3PFPeA, and MPFHxA). Subsets of these compounds were combined and diluted with Milli-Q water into one solution for use as internal standards (IS) for IC-MS analysis.

3.2.2 Preparation, deployment, and analysis of nylon passive air samplers

Preparation of our nylon PAS is described in Chapter 2, Section 2.2.2. Briefly, nylon filters were cleaned using a Na_2CO_3 solution, followed by Milli-Q water and dried prior to PAS assembly, after which they were stored in Ziploc[®] bags in the freezer. Sampling locations are detailed in Section 3.2.3. The PAS are deployed in triplicate to reduce random error by providing the minimum assessment of measurement precision, while also representing a practical balance with the labour required for assembly, deployment, and analysis. To deploy, each PAS was taken out of the Ziploc[®] bag, the lid removed, and the PAS attached via hook and loop fasteners to the inside of a weatherproof cap. Gas-phase acids, including PFCAs_(g), pass through the overlying polypropylene (PP) filter via diffusion, followed by chemisorption to the nylon filter. The field blank was exposed to the air at each site for ~ 10 s. For collection, each PAS was detached from the weatherproof cap,

and they were capped and stored in Ziploc[®] bags in the freezer. Before extraction, each nylon filter was placed in a Falcon[™] tube. Extraction and IC-MS analysis of nylon filters is described in detail in Section 2.2.4.1. Briefly, 3 mM NaOH in Milli-Q water (3 or 4 mL) was added to each Falcon[™] tube containing a nylon filter, after which they were sonicated for ~15 min, and stored in the fridge for 12–24 hours prior to filter removal. The sample extracts were analyzed for the C2–C6 PFCA_{S(g)} via ion chromatography-mass spectrometry (IC-MS). Due to an isobaric interference with ¹³C₂-TFA, most samples were analyzed twice: for C3–C6 PFCA_S using an anion-selective concentrator column and a short gradient separation, and for TFA using a loop and a longer gradient.

The operating parameters for IC-MS analysis of C2–C6 PFCA_S are summarized in Section 2.2.4.1, Table 2.1. Ten-point calibration standards were prepared for C2–C6 PFCA_S in Milli-Q water, ranging from 0.01–10 ng/mL. For analysis of any standards, blanks, or samples, 800 µL of the solution was transferred to a 1 mL polypropylene IC-MS vial (Agilent, PN: 5182-0567), internal standard (IS) (100 µL) was added, and the solution was vortexed. To correct for matrix effects and instrument fluctuations, the peak areas of each PFCA were normalized against its corresponding mass-labelled internal standard, except for PFPrA, for which the ¹³C₁-PFPrA, ¹³C₁-TFA or ¹³C₂-TFA IS were used, depending on availability. Details on data analysis can be found in Section 2.2.8.1. Briefly, the data was blank corrected using the normalized concentrations of each site-specific field blank, with the following exception. The instrument and method limits of detection (iLOD and mLOD) were calculated as three times the standard deviation of the peak area signals in the solvent blanks (n = 3) or method blanks (n = 3), respectively. Solvent blanks were 800 µL Milli-Q water + 100 µL IS and method blanks used nylon filters extracted with 3 or 4 mL of 3 mM NaOH instead of water.

The average PFCA mass on each filter was converted to atmospheric concentrations using the linear uptake rate of each PFCA onto the nylon filter (Equation 2.2 in Section 2.2.8.1). The values for the measured TFA and PFBA uptake rates and the predicted PFPrA, PFPeA and PFHxA uptake rates onto the nylon filters can be found in Section 2.2.8.1, Table 2.3. The mass loadings in ng/m³ were transformed into mixing ratios in parts-per-trillion (pptv) or parts-per-quadrillion (ppqv) by volume (Equation 2.3 in Section 2.2.8.1). Average temperature at each site was determined from daily meteorological data measured by the nearest weather station for the specific time periods

corresponding to each sampler deployment (*Historical Data - Climate - Environment and Climate Change Canada, 2025*).

3.2.3 Sampling Locations

Air measurements of gas-phase C2–C6 PFCAs were conducted utilizing nylon PAS at three sites within the GTA as part of the Study of Winter Air Pollution in Toronto (SWAPIT) campaign (Section 3.2.3.1), at Pearson International Airport and three surrounding sites (Section 3.2.3.2) and at four indoor locations within the GTA (Section 3.2.3.3). Deployment dates and sampling durations are summarized in Table 3.1.

Table 3.1 PAS replicates (n), deployment dates, and sampling durations at sites in the GTA as part of SWAPIT, at Pearson International Airport, and at four indoor sites.

Locations	n	Date deployed	Date retrieved	Sampling time (d)	Sampling time (h)
SWAPIT					
High Park, Toronto, ON	3	2024-01-29	2024-03-08	38.9	933
Evergreen Brickworks Toronto, ON	3	2024-01-29	2024-03-11	41.9	1005
University of Toronto, Scarborough Campus Scarborough, ON	3	2024-02-12	2024-03-11	27.9	670
Pearson International Airport					
On airport grounds ‘Nov. – Jan.’	2	2023-11-03	2024-01-19	77.0	1848
On airport grounds ‘Nov. – Mar.’	3	2023-11-03	2024-03-08	126.0	3024
On airport grounds ‘Jan. – Mar.’	3	2024-01-19	2024-03-08	49.0	1176
On airport grounds ‘Mar. – May’	5	2024-03-19	2024-05-17	58.9	1414
Site 1 - York University Toronto, ON	3	2023-11-29	2024-05-27	180.3	4326
Site 2 - Brampton, ON	3	2023-11-29	2024-05-27	179.7	4314
Reference site - Toronto, ON	3	2023-12-05	2024-05-29	176.2	4229
Indoor					
Lab 1	3	2025-01-27	2025-04-28	90.7	2177
Lab 2	3	2025-01-27	2025-04-28	90.7	2177
Office 1	3	2025-01-27	2025-04-28	90.7	2177
Office 2	3	2025-01-27	2025-04-28	90.6	2174

3.2.3.1 Study of Winter Air Pollution in Toronto (SWAPIT)

In the winter of 2024, triplicate nylon PAS were deployed in three urban areas spread across the Greater Toronto Area (GTA), as part of the SWAPIT campaign, a 6-week research initiative led by Environment and Climate Change Canada (Figure 3.1). Sampling was carried out from January to March 2024 in High Park, one of Toronto's largest parks, situated approx. 9 km west of downtown Toronto; at Evergreen Brickworks, a former brick factory near a major highway; and at the University of Toronto Scarborough Campus (UTSC), which is located more than 20 km northwest of downtown Toronto.



Figure 3.1 Sampling locations in Greater Toronto Area as part of the Study of Winter Air Pollution in Toronto (SWAPIT) campaign. Nylon PAS ($n = 3$) were deployed at High Park, Evergreen Brickworks, and University of Toronto Scarborough Campus (UTSC) from January to March 2024. Map was generated using OpenStreetMap data, available under the Open Database License (<https://www.openstreetmap.org/copyright>).

3.2.3.2 Pearson International Airport

Multiple sets of triplicate nylon PAS were deployed at Pearson International Airport, a suspected PFAS-contaminated site based on historic use of AFFF and other performance chemicals and materials, for two to six months each, from November 2023 to May 2024 (Figure 3.2). Additional PAS ($n = 3$) were deployed at two sites underneath possible airplane landing routes on approach

to the airport, to isolate PFAS associated and/or deposited from their operating in the boundary layer prior to landing, and at a nearby reference site free of these intensive airport operations.

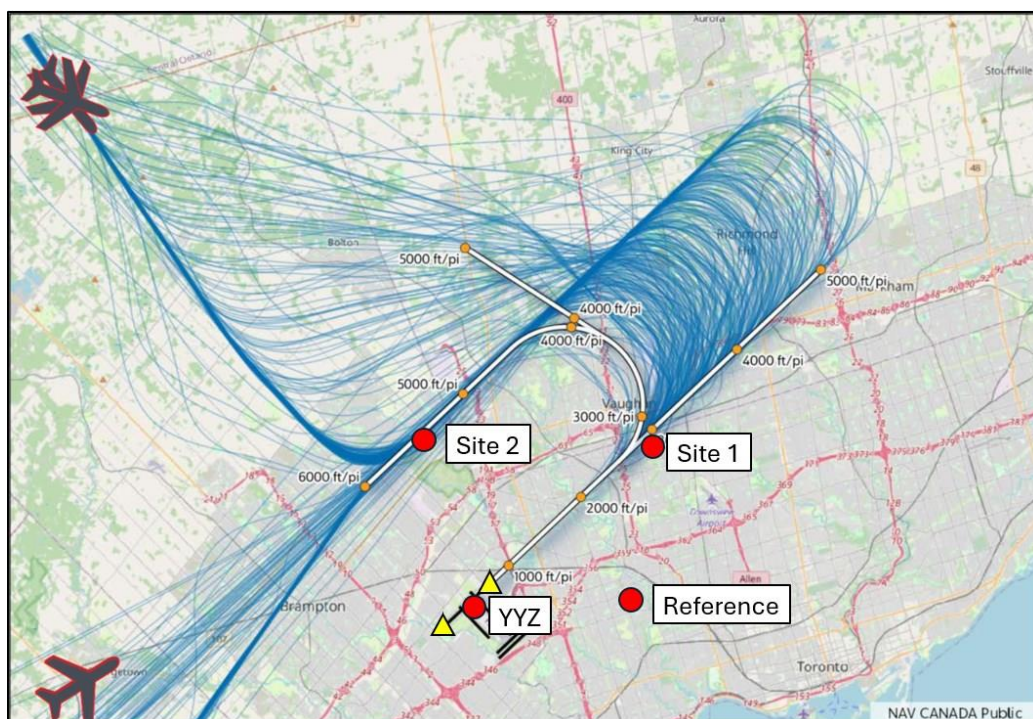


Figure 3.2 Map of possible airplane landing routes (blue lines) upon approach to runway 23 at Pearson International Airport (Nav Canada, 2021). Nylon PAS were deployed at the airport (YYZ) and at three surrounding sites (red circles) to make a transect along plane landing paths. At Site 1 (York University) plane altitude above sea level is approximately 900 m (3000 ft), at Site 2 planes are at an altitude of approximately 1500 – 1800 m (5000 – 6000 ft); A third site was chosen as a reference site, away from the plane landing paths. Yellow triangles represent planned sampling sites where PAS were lost.

At the start of the campaign, two additional sampling locations, within 100 m of airport grounds, were attempted (Figure 3.2). Unfortunately, both sets of triplicate nylon PAS deployed at these sites in November were missing at the end of the six-month sampling period, likely due to human interference. One site was positioned directly beneath airplane landing paths at an elevation below ~300 m, while the other site was located at the opposite end of the landing path, in close proximity to recently landed planes. We selected these sites to gain insight into airport and aircraft-derived PFCA sources and achieve a more comprehensive understanding of PFCA contamination at airports.

3.2.3.3 Indoor

Nylon PAS ($n = 3$) were deployed in four indoor locations: two chemistry laboratories and one academic office at York University, and one office in a residential home for approximately three months from January 27 to April 28, 2025. The following notation was used: ‘Lab 1’ refers to a chemistry lab containing a fume hood and high use of concentrated stock chemicals including PFAS, ‘Lab 2’ refers to a chemistry lab without a fume hood and moderate chemical use including PFAS at much lower concentrations, ‘Office 1’ refers to an occupied office in a university research building, and ‘Office 2’ refers to an office in a private residence.

3.3 Results and Discussion

3.3.1 Determination of C2–C4 PFCA levels in Toronto during the 2024 SWAPIT campaign

In the winter of 2024, as part of the Study of Winter Air Pollution in Toronto (SWAPIT) campaign, atmospheric measurements of gas-phase PFCAs using nylon PAS were conducted at three urban locations spread across the GTA: High Park (HP, $n = 3$), Evergreen Brickworks (EB, $n = 3$), and University of Toronto Scarborough Campus (UTSC, $n = 3$). Samples from all three sites demonstrate a pattern in which the mixing ratios of PFCAs decrease with increasing chain length (Figure 3.3). This trend is consistent with previous atmospheric measurements in Toronto and at remote Canadian sites (Pickard et al., 2020; Vanhauwaert et al., 2025; Ye et al., 2023). Ultrashort-chain PFCAs, in particular TFA, have consistently been measured at higher concentrations in the atmosphere, likely due to its possible formation from many more volatile PFAS precursor compounds than the longer chain PFCAs (Young & Mabury, 2010).

The individual C2–C4 PFCA mixing ratios were similar across the three SWAPIT sampling sites, all within a factor of 2, with average levels slightly lower at UTSC (Table S3.1 in Appendix B). The lower PFCA concentrations at UTSC align with expectations based on its relatively secluded location compared to the other two sites, which we expect to isolate it from direct point sources or those of short-lived precursors. The potential distinct emission sources of PFCAs or very short-lived precursors close to each of the sites are not evident. It is possible for the proximity (within 100 m) of both a major road (Bayview Ave.) and a highway (Don Valley Pkwy) to Evergreen Brickworks to lead to higher TFA mixing ratios due to increased leaks of automobile A/C

refrigerant precursors, although these would be much more prevalent in the summer when A/C units are in use (Hu et al., 2015). In the case of High Park, one of Toronto's largest parks, located ~300 m from both a major highway (Gardiner Expy.) and Lake Ontario, PFCA levels may be influenced by the site's proximity to the lake, over which volatile PFCA precursors can be transported from industrialized areas, such as Hamilton, ON, the lakeside, or border cities of the United States.

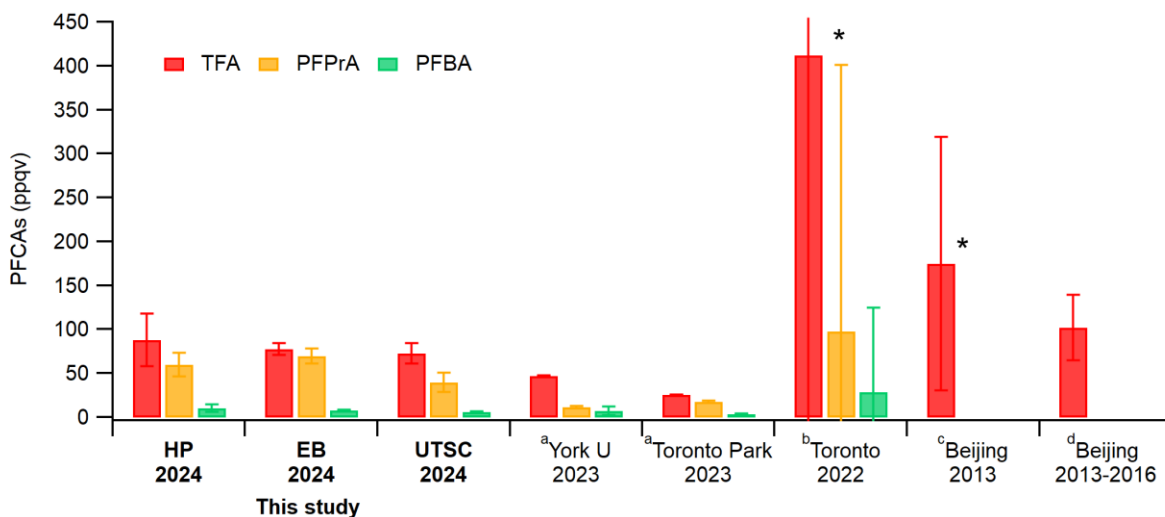


Figure 3.3 Comparison of average nylon PAS C2–C4 PFCA measurements (ppqv) at three SWAPIT sites with previous Toronto winter measurements using ^anylon PAS at York University and a park (Vanhouwaert et al., 2025), ^bCIMS (Young et al., 2024) and to ^{c,d}annular denuder measurements from Beijing, China ^c(Wu et al., 2014), ^d(B. Zhang et al., 2018). In current work, nylon PAS (n = 3) were deployed Jan. – Mar. 2024 at three Toronto locations: High Park (HP), Evergreen Brickworks (EB), and University of Toronto Scarborough Campus (UTSC), with error bars indicating one standard deviation of the mean. *PFCA abundance depicted in refs. b and c are median values, with error bars representing minimum and maximum measurements. For ref. b the TFA maximum (979 ppqv) is not shown on the graph.

Average TFA and PFBA concentrations at the three SWAPIT sites align well with nylon PAS measurements taken at York University the prior winter, all within a factor of 2 (Vanhouwaert et al., 2025). Mixing ratios of PFPrA were higher by factors ranging from 3 to 6 compared with prior measurements at York University. Still, since past PFPrA determinations used the PFBA IS for quantitation, they likely underestimated PFPrA levels, suggesting a closer agreement between actual concentrations. Surprisingly, TFA mixing ratios at all three SWAPIT sites were higher than

those measured at York University, by factors ranging from 1.5 to 1.9. Given that York University represents a site with elevated TFA concentrations with respect to the surrounding area, the higher levels of TFA measured at three sites spread out over 40 km across Toronto may be indicative of an increase in atmospheric TFA during this observation period. The apparent increase in the winter atmospheric abundance of TFA in an urban environment suggests increases in local and/or regional emissions of TFA (direct) or short-lived precursors (indirect). In the winter, both direct and indirect emission sources can become important contributors to the atmospheric abundance of PFCAs due to their slower atmospheric dispersion. The planetary boundary layer is shallower, and the air is colder and denser, so constant regional emissions are constrained in a smaller atmospheric box and are not dispersed as quickly, leading to an increase in ground-level concentrations.

A similar observation was made at York University in summer 2023 with nylon PAS measuring TFA levels almost twice as high as those measured the previous summer (Vanhouwaert et al., 2025). However, in both cases, only two data points were available so no trends could be revealed. Contrary to expectations, Persaud et al. (2026) reported no temporal increase in annual TFA atmospheric deposition during a six-year study in Toronto. They attributed the discrepancy to reduced emissions of short-lived precursors such as HFOs, hydrochlorofluoroolefins, and fluorotelomer compounds during the COVID-19 pandemic in 2020, at which time their deposition flux was significantly lower ($p < 0.05$) compared to other years. There are many complex factors involved in the release, formation and deposition of PFCAs at the city scale we currently do not understand, for which further research is needed.

Our TFA measurements closely aligned with diffusion denuder measurements from Beijing, China where average TFA concentrations of $\sim 102 \pm 37$ ppqv (514 ± 189 pg/m³) were measured across three consecutive winters from 2013 to 2016 (B. Zhang et al., 2018). Mixing ratios of C2–C4 PFCAs at the three SWAPIT sites were within the range (but lower than the median values) of ambient chemical ionization mass spectrometry (CIMS) winter measurements taken at Environment and Climate Change Canada, 4 km away from York University in 2022 (Young et al., 2024). Discrepancies between the measurements may arise from several sources, including the distinct QA/QC challenges inherent to each analytical method, as well as differences in physical or meteorological factors during sampling. The measurements were collected in different years, at different locations, and over different sampling durations – all of which could influence the results.

Variations in temperature and air mass transport over the respective sampling periods may have had a substantial impact on atmospheric PFCA abundances. For instance, positive correlations between temperature and C2–C6 PFCA concentrations were observed during the CIMS sampling. Given that the CIMS campaign sampled for almost twice as long and concluded in April, mean temperatures during this period were likely higher than those recorded during SWAPIT sampling, potentially leading to higher PFCA abundances. Inter-annual variability in measurement periods introduces an additional source of uncertainty, as air masses sampled in different years may have originated from different geographic regions. Prevailing winds drawing air from the polar north, for example, would be much less contaminated than air from the industrialized southern regions, possibly leading to differences in PFCA abundance. To better elucidate the sources of measurement discrepancy, a direct intercomparison of the nylon PAS and CIMS should be conducted simultaneously at the same location and over same sampling duration.

Overall, the nylon PAS measurements can be considered to be in agreement with past measurements when accounting for spatial and temporal variability in Toronto, measurement uncertainties, and the relatively short nylon PAS sampling durations of approximately one month. In this work, our nylon PAS proved to be well suited for measuring gas-phase C2–C4 PFCAs at multiple urban locations in Toronto, producing results consistent with previous nylon PAS measurements and integrating smoothly into a large-scale sampling campaign. To better characterize these patterns and improve understanding of seasonal variability and emission sources in urban environments, future studies should include additional sampling sites, particularly near suspected point sources, and conduct measurements in each season.

3.3.2 Distribution of C2–C5 PFCAs at Pearson International Airport and surrounding area

Our nylon PAS were deployed at Toronto Pearson International Airport, a suspected PFAS point source, to investigate aircraft- and airport-derived PFCA emissions and/or formation relative to the surrounding urban environment. To our knowledge, this study provides the first reported measurements of ultrashort-chain PFCAs in air at an airport setting. Replicate PAS were deployed on airport grounds across three consecutive deployments of two to three months each. PFHxA was not detected in any sample and is therefore excluded from further discussion. Considerable variability was observed in the PFCA distribution across the three sampling periods (Figure 3.4).

TFA and PFPrA showed increasing concentrations over time, which in the case of TFA, is consistent with its documented seasonal variability in environmental matrices (Martin et al., 2003; Vanhauwaert et al., 2025; Wu et al., 2014; Young et al., 2024). In contrast, concentrations of PFBA and PFPeA remained relatively stable throughout the three sampling periods.

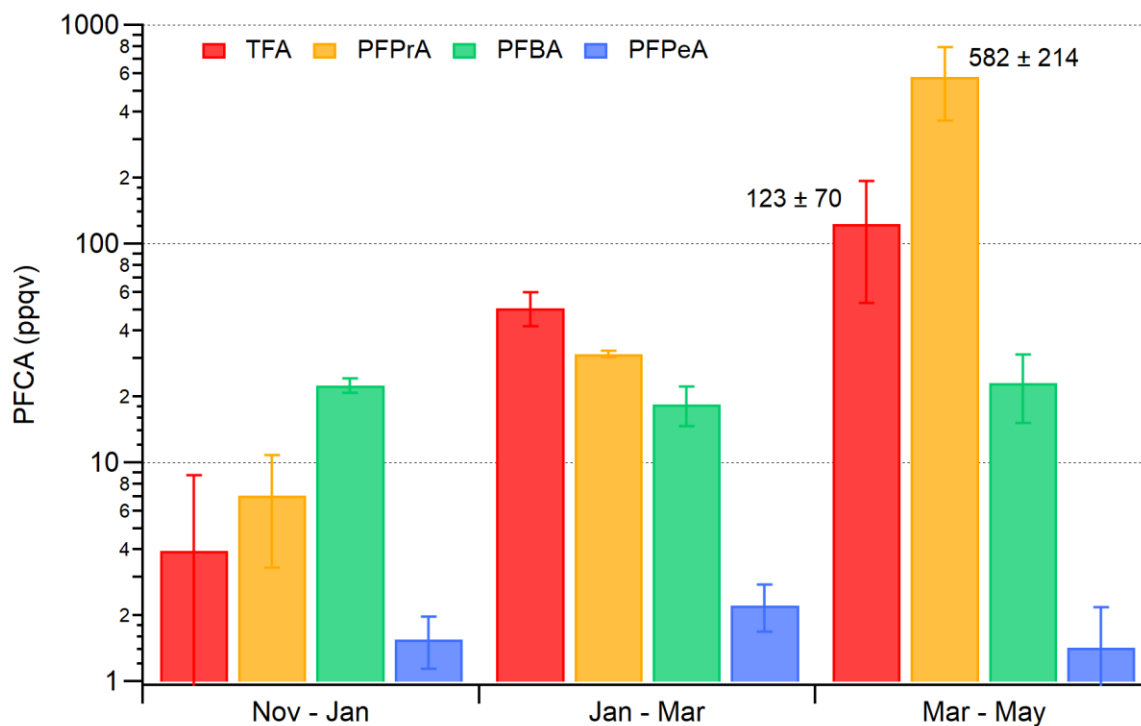


Figure 3.4 Atmospheric mixing ratios (ppqv) of C2–C5 PFCAs at Pearson International Airport, with a logarithmic ($\log_{10}$) vertical axis. Nylon PAS were deployed November to January ($n = 2$), January to March ($n = 3$) and March to May ($n = 5$). Error bars represent the relative error between duplicate measurements or one standard deviation of replicate measurements. For clarity, TFA and PFPrA mixing ratios measured from March to May are displayed.

During the first sampling period, notably low TFA and PFPrA mixing ratios were observed at the airport relative to both the subsequent sampling periods and previous nylon PAS winter measurements in Toronto (Vanhauwaert et al., 2025). As this represents the first measurements conducted between November and January, the discrepancy may reflect differences in sampling duration and/or ambient temperature during this period.

Measurements from January to March displayed the frequently observed trend of decreasing atmospheric PFCA concentrations with increasing chain length. This trend has been observed in

multiple environmental matrices including air, precipitation, and ice cores (Pickard et al., 2020; Scott et al., 2006; Vanhauwaert et al., 2025). The TFA mixing ratios at the airport were comparable to previous winter measurements obtained using nylon PAS at York University and were similar to, though slightly lower than, concentrations recorded at the SWAPIT sites. PFPrA levels were within the lower and upper limits previously measured in Toronto.

During the spring (March to May) sampling period, TFA levels remained within the ranges previously recorded in Toronto using nylon PAS in similar seasons (105 ± 6 to 200 ± 12 ppqv) (Vanhauwaert et al., 2025). PFPrA concentrations, however, were extremely elevated, 19 times higher than those measured during the preceding sampling period. These concentrations also substantially exceeded Toronto nylon PAS measurements by factors of 10 to 29 and median winter ambient CIMS measurements by a factor of 6 (Young et al., 2024). This represents the first record of highly elevated atmospheric PFPrA concentrations and suggests that the airport is a point source of gas-phase PFPrA or PFPrA-specific short-lived precursors.

The identity of the PFPrA peak and the absence of isobaric interference were confirmed through a supplemental qualitative analysis. Due to the small sample volumes remaining, a small subset of extracts were spiked with the $^{13}\text{C}_1$ -PFPrA IS and re-analyzed using the loop and longer gradient. The PFPrA peak retention times matched precisely with those of the $^{13}\text{C}_1$ -PFPrA IS with the PFPrA peaks showing no signs of irregularity such as peak shouldering.

Interestingly, in comparison to median ambient CIMS measurements taken in Toronto two winters prior, PFPrA was the only gas-phase PFCA found to be elevated at the airport (Young et al., 2024). Throughout the campaign, PFBA levels at the airport were elevated in comparison to past Toronto nylon PAS measurements, by factors of 2 to 8, yet remained comparable to median ambient levels measured using CIMS, within a factor of 2. The observed differences relative to previous nylon PAS measurements and the closer agreement to CIMS data likely reflect a combination of contributing factors. Meaningful direct comparisons are limited by differences in analytical methodology, sampling duration, and the timing of sample collection. Robust intercomparisons would require simultaneous measurements conducted under consistent conditions.

Nylon PAS measurements at the airport were compared to those from the surrounding area, by evaluating the weighted sum of C2–C5 PFCA mixing ratios measured at the airport (Figure 3.5). Triplicate nylon PAS were deployed from November to May at two sites (Sites 1 and 2) located

beneath airplane landing routes and at a third reference site. TFA concentrations at all sites fell within the minimum and maximum previously recorded in winter and spring in Toronto using nylon PAS (Vanhauwaert et al., 2025). TFA levels were consistent across all sites, varying by no more than a factor of 1.5, with the highest average concentrations observed at York University (Site 1). No statistically significant difference in TFA concentrations was found between the airport and the three surrounding sites ($p > 0.05$, Table S3.2 in Appendix B). Taken together, these findings indicate that, over this sampling period, the airport was not a point source of gas-phase TFA.

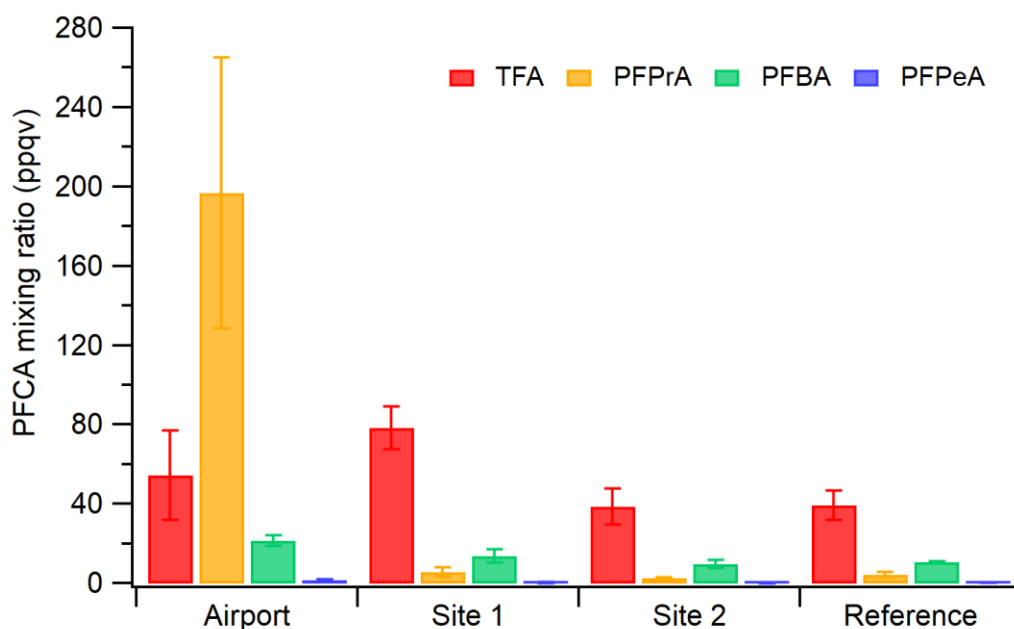


Figure 3.5 Nylon PAS measurements of C2–C5 PFCAs at Pearson International Airport and three sites in the surrounding area. All measurements were normalized to the same total sampling duration. The airport measurements displayed are the weighted sums of November to January, January to March and March to May measurements. Error bars represent one standard deviation of triplicate measurements for Sites 1, 2, and the reference, while the error bars for the airport measurements represent the propagated error for the weighted sums.

In contrast, significant differences were observed for concentrations of PFPrA ($p < 0.01$), PFBA ($p < 0.05$), and PFPeA ($p < 0.01$) at the airport compared with the three surrounding sites. PFPrA concentrations at the airport were exceptionally elevated, measuring 34 to 67 times higher than those recorded at the surrounding sites. These elevated PFPrA concentrations were present during both January to March and March to May sampling periods, with the latter making up 88% of the

total PFPrA measured during the campaign (Figure 3.4). The results strongly suggest that Pearson International Airport is a point source of gas-phase PFPrA or PFPrA precursors.

PFBA concentrations at the airport were approximately twice those measured at the surrounding sites, while PFPeA concentrations were roughly four times higher than at Site 1 and the reference site, and 13 times higher than at Site 2. Both compounds exhibited relatively stable emission profiles throughout the sampling campaign, yet remained statistically higher than the surrounding sites, suggesting a localized emission source at or near the airport. The lower concentrations observed at the reference site ~10 km to the east further suggest that the airport is a point source of PFBA and PFPeA, or their precursor compounds.

Airports are known to be PFAS point sources to their immediate surroundings, where elevated concentrations of PFCAs, PFSAs, and their precursors have been measured (M. Liu et al., 2022). In addition to the well-documented contamination of nearby water sources, wildlife, and soil (Awad et al., 2011; J. Liu et al., 2023; Nunes et al., 2011), release of volatile PFAS to the atmosphere can occur (Mattila et al., 2024). There are many possible sources of elevated gas-phase PFCA atmospheric concentrations at airports. The historical use of both PFOS-based and fluorotelomer-based AFFF at the airport has likely resulted in long-term PFAS contamination of the surrounding area. Upon application, non-volatile and ionic compounds readily partition into the aqueous environment, migrating into nearby surface waters such as rivers and creeks, affecting local wildlife, and leaching into soil, ultimately contaminating groundwater.

Many neutral AFFF components can volatilize following release and are subsequently transported into the atmosphere or partition into surface films, establishing a persistent reservoir from which on-going gas-phase emissions can occur. This behaviour has been observed for PFCAs, SVOCs, and strong acids indoors (See Section 3.3.3) (Crilley et al., 2024; C. Wang et al., 2020). Beyond AFFF, airports may employ a range of other PFAS-containing products in daily operations, which may further contribute to atmospheric PFCA loadings, either directly or indirectly. The elevated levels of gas-phase C3–C5 PFCAs observed at Pearson International Airport may reflect a combination of direct PFCA emissions, re-emission from surfaces, and atmospheric oxidation of short-lived precursors that are either emitted directly or volatilized from contaminated surface reservoirs.

The presence of a surface reservoir on airport grounds may partly account for the elevated TFA and PFPrA mixing ratios observed in the spring. Gas-phase re-emissions from contaminated surfaces are likely to increase with rising spring temperatures, consistent with behaviour documented for SVOCs (Wang C 2020). However, given that TFA levels remain comparable to past measurements at other Toronto locations and are not significantly different from the three surrounding sites, a TFA point source at the airport appears unlikely. The elevated spring TFA concentrations are therefore more plausibly attributed to TFA's seasonal dependence (Young et al. and Wu et al.).

The same reasoning does not readily apply to PFPrA. Unlike TFA, PFPrA has not previously exhibited a clear seasonal pattern, yet spring concentrations at the airport represent some of the highest ever recorded, 19 times higher than those observed during the preceding sampling period. One possible explanation is that PFPrA displays site-specific seasonality at the airport, driven by enhanced re-emission of gas-phase PFPrA or its precursors from contaminated surfaces with rising temperatures, rather than by increased rates of atmospheric oxidation, as seen with TFA.

Alternatively, direct emissions of PFPrA or indirect emissions of its short-lived precursors may be episodic in nature, linked to specific airport operations and largely independent of temperature or seasonal variability.

Emissions of PFBA and PFPeA remained relatively stable across all three sampling periods, suggesting emission sources distinct from those of PFPrA. Two plausible explanations exist for the consistency in PFBA and PFPeA emissions. First, historical AFFF use may have broadly contaminated surfaces with fluorotelomer compounds, which are now slowly volatilizing and undergoing atmospheric oxidation to yield PFBA and PFPeA. Alternatively, other PFAS- or fluorotelomer-containing products in continuous use at the airport may be releasing gas-phase PFBA and PFPeA or volatile precursors which similarly oxidize to form these compounds. While PFPrA could also be formed through this pathway, the substantially elevated spring concentrations indicate the presence of at least one additional source. The behavior of PFPrA appears to diverge from that of other ultrashort- and short-chain PFCAs. Notably, PFPrA was the only PFCA to display neither a diurnal pattern of elevated daytime concentrations nor a correlation with ozone in prior CIMS measurements (Young et al., 2024). These distinctions suggest that the emission sources of PFPrA and its precursors are more complex than those of the longer-chained

homologues. Further measurements are necessary to fully understand the sources, behaviour, and distribution of PFCAs in the atmosphere.

Likely due to the small sample size, no conclusion could be drawn as to whether the PFCA emissions at the airport originated from routine airport operations or from landing aircraft. The C2–C5 PFCA concentrations at Site 2, where airplanes are at an elevation of ~1600 m, were similar to, and slightly lower than those at the reference site. Although at Site 1, where airplanes are at an elevation of ~900 m, the mixing ratios of C2–C5 PFCAs were higher than at the other two sites, the difference was only found to be significant for TFA ($p < 0.01$, Table S3.3). The higher TFA levels at Site 1, York University, are not surprising as this represents a location where elevated PFCA concentrations have previously been observed, in comparison with the surrounding area (Vanhouwaert et al., 2025). Currently, we do not have any evidence to determine whether atmospheric PFCA concentrations at York University are influenced by airplanes or other elevated emission sources in the region. To facilitate source identification, future studies are strongly encouraged to incorporate sampling sites in close proximity to active aircraft during and immediately after landing.

As evidenced by the elevated PFPrA concentrations in the spring, it appears that emissions at the airport are not continuous year-round, so conducting additional sampling spanning all four seasons may help in the determination of emission sources. The small size and user-friendly design of nylon PAS allowed for simultaneous sampling at several sites in Toronto, including their novel deployment at an international airport, highlighting the utility and versatility of passive air samplers.

3.3.3 Measurement of C2–C6 PFCAs at four indoor locations

Indoor measurements of C2–C6 PFCAs were performed in two laboratories and a university building office (Office 1), as well as in an office in a residential home (Office 2) (Figure 3.6). The current measurements provide average PFCA concentrations over the course of three months at each indoor location. The first laboratory (Lab 1) represents a high PFAS use research laboratory, where high concentrations of PFCAs have been and continue to be used in the preparation of analytical standards, and where several experiments utilizing high concentration PFCA permeation

tubes are conducted. Lab 2 represents an instrumental lab, where only low concentrations of PFCAs are used to prepare working solutions and standards.

As expected, the highest concentrations of total and individual gas-phase C2–C6 PFCAs were measured in Lab 1. Extreme and significant differences ($p < 0.01$, Table S3.4 in Appendix B) were observed in the measurements of TFA, PFPrA, and PFPeA in the two labs, with Lab 1 mixing ratios higher by factors of 48, 184, and 157, respectively. Although the difference between PFHxA concentrations was significant ($p < 0.01$), the levels in Lab 1 were only higher by a factor of 4. Despite periodical use of a highly concentrated PFBA permeation tube in a chamber experiment, PFBA concentrations in Lab 1 were only higher by factors of 2, 3, and 5 compared with Lab 2, Office 1, and Office 2, respectively. At the 99% confidence level, the differences in PFBA concentrations in Lab 1 were only found to be statistically significant ($p < 0.01$, Table S3.4) in comparison to Office 2.

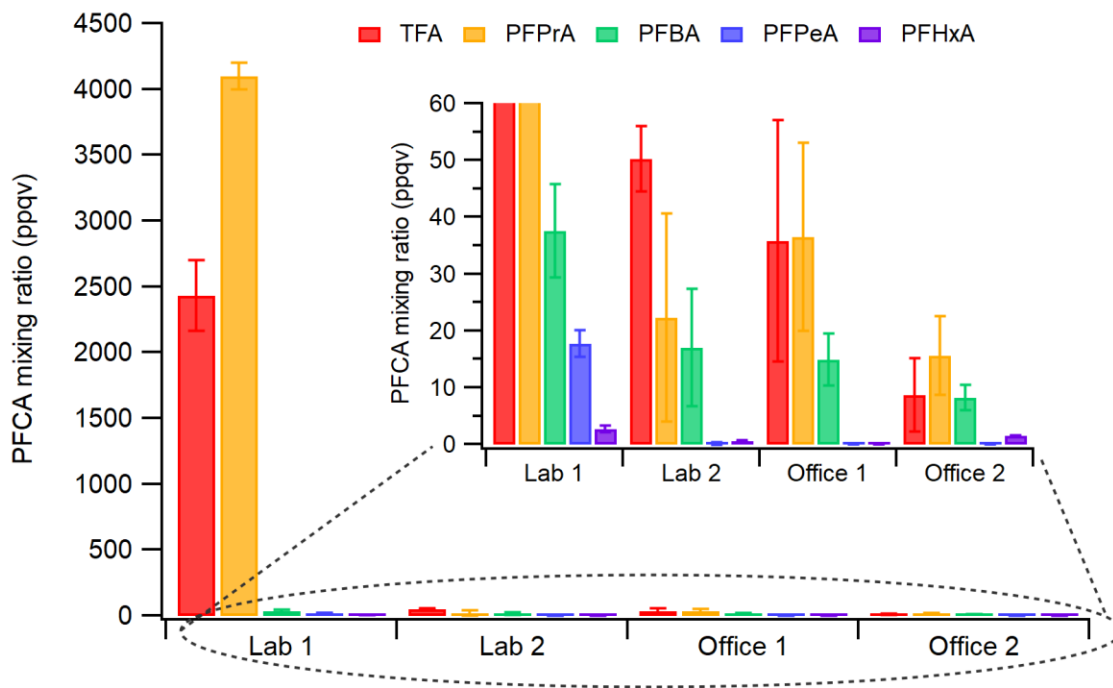


Figure 3.6 Nylon PAS ($n = 3$) measurements of C2–C6 PFCAs in air at four indoor locations from January to April 2025. Error bars represent one standard deviation of triplicate measurements. Lab 1 represents a lab with a fume hood, where high concentrations of PFAS are routinely used, while Lab 2 represents a lab where low concentrations of PFAS are periodically used. Office 1 is a shared office in a university building, and Office 2 is an office in a private residence.

High RSDs (26–173%) were observed for the majority (75%) of PFCAs at all indoor locations except Lab 1, where average RSDs for C2–C6 PFCAs were $14 \pm 8\%$. The relatively low variation between triplicates deployed in Lab 1 may be due to the uniform air mixing caused by the higher air exchange rate typical of laboratories with fume hoods. In addition, the PFCA mixing ratios in the other three locations were much closer to the method detection limits (Table S3.6), so the variability between replicates is expected to increase.

Current TFA measurements in Lab 1 were within the range of prior nylon PAS measurements (2 – 10 pptv) at this location, while PFPrA mixing ratios were ~ 4 times higher (Vanhouwaert, 2024). However, prior nylon PAS measurements utilized the PFBA IS for quantitation, which likely led to an underestimation of PFPrA levels (see Chapter 2 Section 2.3.2). As a result, the apparent discrepancy is likely to be smaller, resulting in a closer agreement between measurements. The PFPrA levels in Lab 1 (4.1 ± 0.1 pptv) were the highest recorded in Toronto, considering all prior measurements, both indoors and outdoors. Mixing ratios of PFPrA in Lab 1 were 7 times higher than the extremely elevated PFPrA levels recorded at Pearson International Airport the prior spring (Section 3.3.2). With such high concentrations measured indoors, air exchange to the outdoors represents a weak source of gas-phase PFCAs to the outdoor environment. Both indoor-to-outdoor and outdoor-to-indoor air transport can occur via concentration gradients, through the air exchange system, open windows and doors and cracks in the walls (Abbatt & Wang, 2020).

The similarity of TFA concentrations in Lab 1 with prior measurements suggests that the elevated TFA (and likely PFPrA) levels are due to a constant and steady emission source in the lab, rather than several point sources such as use of PFCA standards or permeation tubes (Vanhouwaert, 2024). Since this contamination appears to be ongoing, it is likely that these compounds are being re-emitted at a relatively steady rate from surfaces onto which they previously adsorbed. All indoor spaces have a very high surface-area-to-volume ratio, providing much more area for potential adsorption of PFCAs and condensed-phase area into which PFCAs can partition, creating surface reservoirs (Abbatt & Wang, 2020; Crilley et al., 2024). This adsorption behaviour has been shown to occur for TFA and PFBA to the atmospheric chamber walls and permeation oven tubing in Chapter 2, Section 2.3.5, and has also been previously reported by Wang et al. (2020) for other acidic compounds, which were found in higher abundance on surfaces than in the gas phase indoors. The findings suggest that TFA and PFPrA can accumulate in research laboratories from

prolonged use and release of high-concentration PFAS stock solutions, potentially leading to long-term contamination of surfaces and indoor air.

Although C2–C6 PFCA mixing ratios were higher in Lab 1 compared with the other three indoor locations, only TFA and PFPrA levels were found to be elevated compared with outdoor ambient CIMS measurements (Young et al., 2024). Concentrations of C2–C6 PFCAs measured in Lab 2 and both offices were comparable to outdoor nylon PAS measurements.

The levels of C2–C4 PFCAs in Lab 2 were similar to those measured in Office 1, within a factor of 1.7. The slightly higher (1.6 times) PFPrA levels observed in Office 1 were surprising, considering the lack of PFCA standard usage in this space. Nevertheless, no statistical differences ($p > 0.05$, Table S3.5) were found between concentrations of C2–C4 PFCAs at the two locations. Concentrations of TFA, PFPrA, and PFBA in the home office were lower than those measured in the York University office by factors of 4, 2, and 2, respectively; however, the differences were not significant ($p > 0.05$). This trend is consistent with expectations, as PFCA concentrations at York University are typically elevated relative to the surrounding area. Due to the poor detection frequency of PFPeA and PFHxA at the two office sites, the results will not be compared here and are instead reported in Appendix B, Table S3.1. As the PFCA concentrations at all indoor locations except Lab 1 were the same or lower than measured outdoors we cannot determine whether indoor or outdoor sources are dominant.

Indoors, the formation of PFCAs from precursor compounds such as FTOHs is likely not a major source. Due to the lack of sunlight, atmospheric oxidants like hydroxyl radicals are not present at high concentrations indoors, slowing down the oxidation of precursor compounds. Indoor sources of gas-phase PFCAs are likely attributed to their direct gas-phase emission and re-emission from surfaces, and since there are few gas-phase emission sources in offices or homes, gas-phase air concentrations are likely to be lower than in the condensed phase (e.g. in dust). While not a perfect comparison due to the mismatched units, C2–C4 PFCAs were found in much lower levels in indoor air (single digit ppqv to pptv) than were previously determined in dust (single to triple digit ng/g; ppb) in U.S. homes (Zheng et al., 2023). It is also possible for PFCAs to be transported from outdoors, but since PFCAs are strong acids, they will readily adsorb to surfaces, likely partitioning into the condensed phase on surface films (Crilley et al., 2024; C. Wang et al., 2020).

In a study by Shoeib et al. (2011) measuring neutral PFAS, indoor air samples were dominated by FTOHs, and total neutral PFAS concentrations were 17 times higher indoors compared with outdoors. This trend was not observed for C2–C6 PFCAs in the three indoor locations without a historical usage of stock-concentration PFAS. Overall, the findings suggest that indoor environments such as instrumental laboratories, academic offices and home offices may be weak sources of gas-phase ultrashort- and short-chain PFCAs to the outdoor environment, with mixing ratios comparable to outdoor levels in much smaller volumes of atmosphere. TFA and PFPrA can accumulate in research labs from the sustained use of stock concentration PFAS compounds, potentially contaminating the surfaces and air long-term and providing a source of PFCAs to the outdoor environment. On a larger scale, indoor-to-outdoor transport is likely negligible compared to outdoor formation. Current HFO-1234yf emissions in the U.S., estimated at 24.53 Gg/year, are predicted to yield maximum global atmospheric TFA mixing ratios of 1.15 pptv (Z. Wang et al., 2018). In comparison, TFA emissions from Lab 1, roughly 14.3 mg/year (Equation S3.1), contribute approximately 7.06×10^{-10} ppqv of TFA to the global atmosphere, 12 to 13 orders of magnitude lower than typical outdoor levels measured by nylon PAS and 14 orders of magnitude lower than the maximum TFA expected to form in the atmosphere from annual HFO-1234yf emissions in the U.S. Even if we grossly overestimate the number of weak indoor TFA sources across Canada and the U.S. at one billion, the resulting indoor-to-outdoor TFA contribution would only be 0.71 ppqv, five orders of magnitude lower than U.S. atmospheric TFA formation from a single precursor, HFO-1234yf. Although the gas-phase TFA and PFPrA concentrations are ultra trace and exposure due to inhalation is likely to be low, there are many routes of PFCA exposure indoors and more research must be done to understand the importance of inhalation and dermal exposure of both gas- and particle-phase PFCAs indoors. Nylon PAS have demonstrated to be an unobtrusive cost-effective strategy in the measurement of gas-phase PFCAs in indoor environments.

3.4 Conclusion

In conclusion, nylon passive air sampler (PAS) measurements of gas-phase PFCAs were conducted across multiple urban locations in the Greater Toronto Area. First, sampling was conducted at three Toronto locations spanning a distance of 40 km across the city, as part of the Study of Winter Air

Pollution in Toronto (SWAPIT) campaign. Overall, C2–C4 PFCA atmospheric concentrations were comparable among the three SWAPIT sampling sites with generally lower levels observed at UTSC, the most secluded site. Our nylon PAS demonstrated to be capable of measuring air concentrations of TFA, PFPrA, and PFBA over the course of 4 to 6 weeks, producing consistent results to past measurements in Toronto. Nylon PAS proved to be well suited for multi-location sampling in an urban city, seamlessly integrating into a large research initiative involving collaborators from more than 10 academic and government research groups.

Next, sampling of gas-phase C2–C5 PFCAs was undertaken at Pearson International Airport and three sites in the surrounding area, providing the first measurements of atmospheric gas-phase TFA and PFPrA at an airport. Nylon PAS were effective in identifying differences in PFCA distribution profiles across the three sampling periods. This finding indicated that emissions of PFCAs or their short-lived precursor compounds are intermittent rather than continuous, further demonstrating the effectiveness of passive sampling in capturing episodic emission events. Highly elevated PFPrA atmospheric concentrations were observed at the airport, approximately 50 times higher in comparison to neighbouring sites, suggesting that the airport may be a point source of gas-phase PFPrA or PFPrA-specific short-lived precursors. The role of aircraft as a PFCA source at the airport remains unclear, likely owing to the limited sample size and missing PAS data from the two nearest sites.

Last, sampling was conducted at four indoor locations, including two laboratories and an academic office at York University as well as an office in a residential home. The highest recorded gas-phase PFPrA air concentrations in Toronto, 4.1 ± 0.1 pptv (equivalent to a mass loading of 27.5 ± 0.7 ng/m³) were measured in a chemistry laboratory at York University with a long history of PFAS usage. The findings suggest that TFA and PFPrA can accumulate in research labs from the sustained use of stock concentration PFAS compounds, potentially contaminating the surfaces and air long-term. Overall, the findings suggest that indoor environments such as instrumental laboratories, academic offices and home offices may be weak point sources of gas-phase ultrashort- and short-chain PFCAs to the outdoor environment. The current work demonstrates the suitability of nylon PAS in advancing our knowledge of PFCA atmospheric concentrations in urban locations, and potential point sources such as airports and indoor environments.

3.5 References

- Abbatt, J. P. D., & Wang, C. (2020). The atmospheric chemistry of indoor environments. *Environmental Science: Processes and Impacts*, 22, 25–48. <https://doi.org/10.1039/c9em00386j>
- Ahrens, L., Harner, T., Shoeib, M., Lane, D. A., & Murphy, J. G. (2012). Improved characterization of gas-particle partitioning for per- and polyfluoroalkyl substances in the atmosphere using annular diffusion denuder samplers. *Environmental Science and Technology*, 46(13), 7199–7206. <https://doi.org/10.1021/es300898s>
- Andrews, D. Q., Hayes, J., Stoiber, T., Brewer, B., Campbell, C., & Naidenko, O. V. (2021). Identification of point source dischargers of per- and polyfluoroalkyl substances in the United States. *AWWA Water Science*, 3(5). <https://doi.org/10.1002/aws2.1252>
- Awad, E., Zhang, X., Bhavsar, S. P., Petro, S., Crozier, P. W., Reiner, E. J., Fletcher, R., Tittlemier, S. A., & Braekevelt, E. (2011). Long-term environmental fate of perfluorinated compounds after accidental release at Toronto airport. *Environmental Science and Technology*, 45(19), 8081–8089. <https://doi.org/10.1021/es2001985>
- Carrizo, J. C., Munoz, G., Vo Duy, S., Liu, M., Houde, M., Amé, M. V., Liu, J., & Sauvé, S. (2023). PFAS in fish from AFFF-impacted environments: Analytical method development and field application at a Canadian international civilian airport. *Science of the Total Environment*, 879. <https://doi.org/10.1016/j.scitotenv.2023.163103>
- Clouthier, J., Vandenboer, T., & Young, C. (2026). Direct-inject suppressed ion chromatography-mass spectrometry method with online preconcentration for short- and ultra short-chain perfluoroalkyl carboxylic acids in fresh water. *Analytical Methods*. <https://doi.org/10.1039/D5AY02105G>
- Crilley, L. R., Ditto, J. C., Lao, M., Zhou, Z., Abbatt, J. P. D., Chan, A. W. H., & VandenBoer, T. C. (2024). Commercial kitchen operations produce a diverse range of gas-phase reactive nitrogen species. *Environmental Science: Processes and Impacts*. <https://doi.org/10.1039/d4em00491d>
- D’Agostino, L. A., & Mabury, S. A. (2017). Aerobic biodegradation of 2 fluorotelomer sulfonamide-based aqueous film-forming foam components produces perfluoroalkyl carboxylates. *Environmental Toxicology and Chemistry*, 36(8), 2012–2021. <https://doi.org/10.1002/etc.3750>
- Eichler, C. M. A., & Little, J. C. (2020). A framework to model exposure to per- And polyfluoroalkyl substances in indoor environments. *Environmental Science: Processes and Impacts*, 22(3), 500–511. <https://doi.org/10.1039/c9em00556k>
- Fenton, S. E., Ducatman, A., Boobis, A., DeWitt, J. C., Lau, C., Ng, C., Smith, J. S., & Roberts, S. M. (2021). Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environmental Toxicology and Chemistry*, 40(3), 606–630. <https://doi.org/10.1002/etc.4890>

- Genualdi, S., Lee, S. C., Shoeib, M., Gawor, A., Ahrens, L., & Harner, T. (2010). Global Pilot Study of Legacy and Emerging Persistent Organic Pollutants using Sorbent-Impregnated Polyurethane Foam Disk Passive Air Samplers. *Environmental Science & Technology*, 44(14), 5534–5539. <https://doi.org/10.1021/es1009696>
- Goosey, E., & Harrad, S. (2012). Perfluoroalkyl substances in UK indoor and outdoor air: Spatial and seasonal variation, and implications for human exposure. *Environment International*, 45(1), 86–90. <https://doi.org/10.1016/j.envint.2012.04.007>
- Hawley, A. S., Winne, M., & Cahill, T. M. (2025). Trifluoroacetic Acid Concentrations in Consumer Foods. *Journal of Agricultural and Food Chemistry*, 73(50), 32250–32254. <https://doi.org/10.1021/acs.jafc.5c07390>
- Heydebreck, F., Tang, J., Xie, Z., & Ebinghaus, R. (2016). Emissions of Per- and Polyfluoroalkyl Substances in a Textile Manufacturing Plant in China and Their Relevance for Workers' Exposure. *Environmental Science & Technology*, 50(19), 10386–10396. <https://doi.org/10.1021/acs.est.6b03213>
- Historical Data—Climate—Environment and Climate Change Canada*. (2025). https://climate.weather.gc.ca/historical_data/search_historic_data_e.html
- Hu, L., Montzka, S. A., Miller, J. B., Andrews, A. E., Lehman, S. J., Miller, B. R., Thoning, K., Sweeney, C., Chen, H., Godwin, D. S., Masarie, K., Bruhwiler, L., Fischer, M. L., Biraud, S. C., Torn, M. S., Mountain, M., Nehrkorn, T., Eluszkiewicz, J., Miller, S., ... Tans, P. P. (2015). U.S. emissions of HFC-134a derived for 2008–2012 from an extensive flask-air sampling network. *Journal of Geophysical Research: Atmospheres*, 120(2), 801–825. <https://doi.org/10.1002/2014JD022617>
- Janousek, R. M., Mayer, J., & Knepper, T. P. (2019). Is the phase-out of long-chain PFASs measurable as fingerprint in a defined area? Comparison of global PFAS concentrations and a monitoring study performed in Hesse, Germany from 2014 to 2018. *TrAC - Trends in Analytical Chemistry*, 120. <https://doi.org/10.1016/j.trac.2019.01.017>
- Just, H., Göckener, B., Lämmer, R., Wiedemann-Krantz, L., Stahl, T., Breuer, J., Gassmann, M., Weidemann, E., Bücking, M., & Kowalczyk, J. (2022). Degradation and Plant Transfer Rates of Seven Fluorotelomer Precursors to Perfluoroalkyl Acids and F-53B in a Soil-Plant System with Maize (*Zea mays L.*). *Journal of Agricultural and Food Chemistry*, 70(29), 8920–8930. <https://doi.org/10.1021/acs.jafc.1c06838>
- Khalid, N. K., Le Calvez, M., Lemire, M., Dinh, Q. T., Fontaine, J., Lair, S., & Sauvé, S. (2024). Occurrence of 80 per and polyfluorinated alkyl substances (PFAS) in muscle and liver tissues of marine mammals of the St. Lawrence Estuary and Gulf, Quebec, Canada. *Frontiers in Environmental Chemistry*, 5. <https://doi.org/10.3389/fenvc.2024.1403728>
- Klepeis, N. E., Nelson, W. C., Ott, W. R., Robinson, J. P., Tsang, A. M., Switzer, P., Behar, J. V., Hern, S. C., & Engelmann, W. H. (2001). The National Human Activity Pattern Survey (NHAPS): A resource for assessing exposure to environmental pollutants. *Journal of Exposure Analysis and Environmental Epidemiology*, 11, 231–252. <https://doi.org/10.1038/sj.jea.7500165>

- Koch, A., Yukioka, S., Tanaka, S., Yeung, L. W. Y., Kärrman, A., & Wang, T. (2021). Characterization of an AFFF impacted freshwater environment using total fluorine, extractable organofluorine and suspect per- and polyfluoroalkyl substance screening analysis. *Chemosphere*, 276, 130179. <https://doi.org/10.1016/j.chemosphere.2021.130179>
- Lee, H., Butt, C. M., Lodge, S., Ye, R., Nistorescu, I., Young, C., & VandenBoer, T. (2025). *Quantitation of ultrashort- and short-chain PFAS in beverages by a direct injection LC-MS/MS method*. SCIEX. <https://sciex.com/tech-notes/food-beverage/food-and-beverage/quantitation-of-ultrashort-and-short-chain-pfas-in-beverages-by-a-direct-injection-lc-ms-ms-method>
- Lindstrom, A. B., Strynar, M. J., & Libelo, E. L. (2011). Polyfluorinated compounds: Past, present, and future. *Environmental Science and Technology*, 45(19), 7954–7961. <https://doi.org/10.1021/es2011622>
- Liu, J., Zhao, Z., Li, J., Hua, X., Zhang, B., Tang, C., An, X., & Lin, T. (2023). Emerging and legacy perfluoroalkyl and polyfluoroalkyl substances (PFAS) in surface water around three international airports in China. *Chemosphere*, 344, 140360. <https://doi.org/10.1016/j.chemosphere.2023.140360>
- Liu, M., Munoz, G., Vo Duy, S., Sauvé, S., & Liu, J. (2022). Per- and Polyfluoroalkyl Substances in Contaminated Soil and Groundwater at Airports: A Canadian Case Study. *Environmental Science & Technology*, 56(2), 885–895. <https://doi.org/10.1021/acs.est.1c04798>
- Luecken, D. J., Waterland, R. L., Papasavva, S., Taddonio, K. N., Hutzell, W. T., Rugh, J. P., & Andersen, S. O. (2010). Ozone and TFA Impacts in North America from Degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), A Potential Greenhouse Gas Replacement. *Environmental Science & Technology*, 44(1), 343–348. <https://doi.org/10.1021/es902481f>
- Martin, J. W., Mabury, S. A., Wong, C. S., Noventa, F., Solomon, K. R., Alaei, M., & Muir, D. C. G. (2003). Airborne haloacetic acids. *Environmental Science and Technology*, 37(13), 2889–2897. <https://doi.org/10.1021/es026345u>
- Mattila, J. M., Krug, J. D., Roberson, W. R., Burnette, R. P., McDonald, S., Virtaranta, L., Offenberg, J. H., & Linak, W. P. (2024). Characterizing Volatile Emissions and Combustion Byproducts from Aqueous Film-Forming Foams Using Online Chemical Ionization Mass Spectrometry. *Environmental Science and Technology*, 58(8), 3942–3952. <https://doi.org/10.1021/acs.est.3c09255>
- Milley, S. A., Koch, I., Fortin, P., Archer, J., Reynolds, D., & Weber, K. P. (2018). Estimating the number of airports potentially contaminated with perfluoroalkyl and polyfluoroalkyl substances from aqueous film forming foam: A Canadian example. *Journal of Environmental Management*, 222, 122–131. <https://doi.org/10.1016/j.jenvman.2018.05.028>
- Morales-McDevitt, M. E., Becanova, J., Blum, A., Bruton, T. A., Vojta, S., Woodward, M., & Lohmann, R. (2021). The Air That We Breathe: Neutral and Volatile PFAS in Indoor Air. *Environmental Science & Technology Letters*, 8(10), 897–902. <https://doi.org/10.1021/acs.estlett.1c00481>

- Nav Canada. (2021). *Toronto Pearson Noise Management Forums Neighbourhood Table. Approach to runway 23 (today & future)* (p. 38). <https://www.torontopearson.com/-/media/project/pearson/content/community/noise-management/pdfs/2021-12-01-presentation.pdf>
- Neuwald, I. J., Hübner, D., Wiegand, H. L., Valkov, V., Borchers, U., Nödler, K., Scheurer, M., Hale, S. E., Arp, H. P. H., & Zahn, D. (2022). Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated. *Environmental Science and Technology*, 56(10), 6380–6390. <https://doi.org/10.1021/acs.est.1c07949>
- Nunes, L. M., Zhu, Y. G., Stigter, T. Y., Monteiro, J. P., & Teixeira, M. R. (2011). Environmental impacts on soil and groundwater at airports: Origin, contaminants of concern and environmental risks. *Journal of Environmental Monitoring*, 13(11), 3026–3039. <https://doi.org/10.1039/c1em10458f>
- Persaud, D., Joudan, S., VandenBoer, T. C., & Young, C. J. (2026). Atmospheric Removal of Trifluoroacetic Acid by Dry and Wet Deposition: A Multiyear Analysis in Toronto. *Environmental Science & Technology Letters*, 13(2), 261–267. <https://doi.org/10.1021/acs.estlett.5c01100>
- Pickard, H. M., Criscitiello, A. S., Persaud, D., Spencer, C., Muir, D. C. G., Lehnher, I., Sharp, M. J., De Silva, A. O., & Young, C. J. (2020). Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations. *Geophysical Research Letters*, 47(10). <https://doi.org/10.1029/2020GL087535>
- Pickard, H. M., Criscitiello, A. S., Spencer, C., Sharp, M. J., Muir, D. C. G., De Silva, A. O., & Young, C. J. (2018). Continuous non-marine inputs of per- and polyfluoroalkyl substances to the High Arctic: A multi-decadal temporal record. *Atmospheric Chemistry and Physics*, 18(7), 5045–5058. <https://doi.org/10.5194/acp-18-5045-2018>
- Place, B. J., & Field, J. A. (2012). Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams Used by the US Military. *Environmental Science & Technology*, 46(13), 7120–7127. <https://doi.org/10.1021/es301465n>
- Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). Sources, fate and transport of perfluorocarboxylates. *Environmental Science and Technology*, 40(1), 32–44. <https://doi.org/10.1021/es0512475>
- Roth, J., Abusallout, I., Hill, T., Holton, C., Thapa, U., & Hanigan, D. (2020). Release of Volatile Per- and Polyfluoroalkyl Substances from Aqueous Film-Forming Foam. *Environmental Science and Technology Letters*, 7(3), 164–170. <https://doi.org/10.1021/acs.estlett.0c00052>
- Ruyle, B. J., Thackray, C. P., Butt, C. M., LeBlanc, D. R., Tokranov, A. K., Vecitis, C. D., & Sunderland, E. M. (2023). Centurial Persistence of Forever Chemicals at Military Fire Training Sites. *Environmental Science & Technology*, 57(21), 8096–8106. <https://doi.org/10.1021/acs.est.3c00675>
- Saini, A., Chinnadurai, S., Schuster, J. K., Eng, A., & Harner, T. (2023). Per- and polyfluoroalkyl substances and volatile methyl siloxanes in global air: Spatial and temporal trends. *Environmental Pollution*, 323. <https://doi.org/10.1016/j.envpol.2023.121291>

- Schwartz-Narbonne, H., Xia, C., Shalin, A., Whitehead, H. D., Yang, D., Peaslee, G. F., Wang, Z., Wu, Y., Peng, H., Blum, A., Venier, M., & Diamond, M. L. (2023). Per- and Polyfluoroalkyl Substances in Canadian Fast Food Packaging. *Environmental Science and Technology Letters*, 10(4), 343–349. <https://doi.org/10.1021/acs.estlett.2c00926>
- Scott, B. F., Spencer, C., Mabury, S. A., & Muir, D. C. G. (2006). Poly and perfluorinated carboxylates in north American precipitation. *Environmental Science and Technology*, 40(23), 7167–7174. <https://doi.org/10.1021/es061403n>
- Seinfeld, J. H., & Pandis, S. N. (2006). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (3rd ed.). John Wiley & Sons Inc.
- Shoeib, M., Harner, T., M. Webster, G., & Lee, S. C. (2011). Indoor Sources of Poly- and Perfluorinated Compounds (PFCS) in Vancouver, Canada: Implications for Human Exposure. *Environmental Science & Technology*, 45(19), 7999–8005. <https://doi.org/10.1021/es103562v>
- Siegl, W. O., Wallington, T. J., Guenther, M. T., Henney, T., Pawlak, D., & Duffy, M. (2002). R-134a Emissions from Vehicles. *Environmental Science & Technology*, 36(4), 561–566. <https://doi.org/10.1021/es011108x>
- Sture, M., Valdersnes, S., Boitsov, S., Grosvik, B. E., & Ali, A. (2026). Source and fate of ultra-short-chain PFAS in water and biota from an AFFF impacted site. *Journal of Chromatography B*, 1268(124848). <https://doi.org/10.1016/j.jchromb.2025.124848>
- Tao, Y., VandenBoer, T. C., Ye, R. X., & Young, C. J. (2023). Exploring controls on perfluorocarboxylic acid (PFCA) gas-particle partitioning using a model with observational constraints. *Environmental Science: Processes and Impacts*, 25(2), 264–276. <https://doi.org/10.1039/d2em00261b>
- Thackray, C. P., Selin, N. E., & Young, C. J. (2020). A global atmospheric chemistry model for the fate and transport of PFCAs and their precursors. *Environmental Science: Processes and Impacts*, 22(2), 285–293. <https://doi.org/10.1039/c9em00326f>
- Trenberth, K. E., Christy, J. R., & Olson, J. G. (1987). Global atmospheric mass, surface pressure, and water vapor variations. *Journal of Geophysical Research: Atmospheres*, 92(D12), 14815–14826. <https://doi.org/10.1029/JD092iD12p14815>
- Vanhauwaert, E. (2024). *A passive air sampling technique for ultra-trace quantitation of perfluoroalkyl carboxylic acids* [Master's Thesis, York University]. <https://hdl.handle.net/10315/42427>
- Vanhauwaert, E., Carmichael, L., Nistorescu, I., Crilley, L., Shunthirasingham, C., Hung, H., Young, C., & Vandenboer, T. C. (2025). Selective ultra-trace atmospheric passive sampling of gaseous perfluoroalkyl carboxylic acids. *Environmental Science: Processes & Impacts*. <https://doi.org/10.1039/d5em00297d>
- Wang, C., Collins, D. B., Arata, C., Goldstein, A. H., Mattila, J. M., Farmer, D. K., Ampollini, L., DeCarlo, P. F., Novoselac, A., Vance, M. E., Nazaroff, W. W., & Abbatt, J. P. D. (2020). Surface reservoirs dominate dynamic gas-surface partitioning of many indoor air constituents. *Science Advances*, 6(8), eaay8973. <https://doi.org/10.1126/sciadv.aay8973>

- Wang, Z., Cousins, I. T., Scheringer, M., & Hungerbühler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFASs) and their potential precursors. *Environment International*, 60, 242–248. <https://doi.org/10.1016/j.envint.2013.08.021>
- Wang, Z., Dewitt, J. C., Higgins, C. P., & Cousins, I. T. (2017). A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environmental Science and Technology*, 51(5), 2508–2518. <https://doi.org/10.1021/acs.est.6b04806>
- Wang, Z., Wang, Y., Li, J., Henne, S., Zhang, B., Hu, J., & Zhang, J. (2018). Impacts of the Degradation of 2,3,3,3-Tetrafluoropropene into Trifluoroacetic Acid from Its Application in Automobile Air Conditioners in China, the United States, and Europe. *Environmental Science & Technology*, 52(5), 2819–2826. <https://doi.org/10.1021/acs.est.7b05960>
- Wania, F., & Shunthirasingham, C. (2020). Passive air sampling for semi-volatile organic chemicals. *Environmental Science: Processes and Impacts*, 22(10), 1925–2002. <https://doi.org/10.1039/d0em00194e>
- Winkens, K., Koponen, J., Schuster, J., Shoeib, M., Vestergren, R., Berger, U., Karvonen, A. M., Pekkanen, J., Kiviranta, H., & Cousins, I. T. (2017). Perfluoroalkyl acids and their precursors in indoor air sampled in children's bedrooms. *Environmental Pollution*, 222, 423–432. <https://doi.org/10.1016/j.envpol.2016.12.010>
- Wong, F., Shoeib, M., Katsoyiannis, A., Eckhardt, S., Stohl, A., Bohlin-Nizzetto, P., Li, H., Fellin, P., Su, Y., & Hung, H. (2018). Assessing temporal trends and source regions of per- and polyfluoroalkyl substances (PFASs) in air under the Arctic Monitoring and Assessment Programme (AMAP). *Atmospheric Environment*, 172, 65–73. <https://doi.org/10.1016/j.atmosenv.2017.10.028>
- World Meteorological Organization. (2022). *Scientific Assessment of Ozone Depletion* (No. 278; Ozone Research and Monitoring, pp. 448–483).
- Wu, J., Martin, J. W., Zhai, Z., Lu, K., Li, L., Fang, X., Jin, H., Hu, J., & Zhang, J. (2014). Airborne trifluoroacetic acid and its fraction from the degradation of HFC-134a in Beijing, China. *Environmental Science and Technology*, 48(7), 3675–3681. <https://doi.org/10.1021/es4050264>
- Ye, R. X., Di Lorenzo, R. A., Clouthier, J. T., Young, C. J., & VandenBoer, T. C. (2023). A Rapid Derivatization for Quantitation of Perfluorinated Carboxylic Acids from Aqueous Matrices by Gas Chromatography-Mass Spectrometry. *Analytical Chemistry*, 95(19), 7648–7655. <https://doi.org/10.1021/acs.analchem.3c00593>
- Ye, R. X., Furlani, T. C., Folkerson, A. P., Mabury, S. A., VandenBoer, T. C., & Young, C. J. (2024). A Method to Measure Total Gaseous Fluorine. *Environmental Science and Technology Letters*, 11(10), 1062–1067. <https://doi.org/10.1021/acs.estlett.4c00553>
- Young, C. J., Joudan, S., Tao, Y., Wentzell, J. J. B., & Liggio, J. (2024). High Time Resolution Ambient Observations of Gas-Phase Perfluoroalkyl Carboxylic Acids: Implications for Atmospheric Sources. *Environmental Science and Technology Letters*, 11(12), 1348–1354. <https://doi.org/10.1021/acs.estlett.4c00897>

- Young, C. J., & Mabury, S. A. (2010). Atmospheric perfluorinated acid precursors: Chemistry, occurrence, and impacts. *Reviews of Environmental Contamination and Toxicology*, 208, 1–109. https://doi.org/10.1007/978-1-4419-6880-7_1
- Zhang, B., Zhai, Z., & Zhang, J. (2018). Distribution of trifluoroacetic acid in gas and particulate phases in Beijing from 2013 to 2016. *Science of the Total Environment*, 634, 471–477. <https://doi.org/10.1016/j.scitotenv.2018.03.384>
- Zhang, Y., Yang, W., Huang, Z., Liu, D., Simpson, I., Blake, D. R., George, C., & Wang, X. (2017). Leakage Rates of Refrigerants CFC-12, HCFC-22, and HFC-134a from Operating Mobile Air Conditioning Systems in Guangzhou, China: Tests inside a Busy Urban Tunnel under Hot and Humid Weather Conditions. *Environmental Science & Technology Letters*, 4(11). <https://doi.org/10.1002/2014JD022617>
- Zheng, G., Eick, S. M., & Salamova, A. (2023). Elevated Levels of Ultrashort- and Short-Chain Perfluoroalkyl Acids in US Homes and People. *Environmental Science and Technology*, 57(42), 15782–15793. <https://doi.org/10.1021/acs.est.2c06715>

Chapter 4. Nylon passive air sampling network for atmospheric measurements of C2–C6 PFCAs along the St. Lawrence River and Estuary, Quebec

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IN prepared, with TCV editing the chapter.

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IN performed all experiments and analyses under the guidance of TCV.

Sampler deployment was conducted by IN, DP, HH, and C Shin. Sample collection was conducted by ABC and FB. ZL and C Shunthirasingham were associated with project logistics, support and funding.

4.1 Introduction

4.1.1 Sources, behaviour, and distribution of perfluoroalkyl carboxylic acids

Perfluoroalkyl carboxylic acids (PFCAs), a subgroup of per- and polyfluoroalkyl substances (PFAS) are persistent and highly mobile anthropogenic compounds. Due to their useful properties, they have been widely employed in industry, including in the manufacture of fluoropolymers and aqueous film forming foam (AFFF), and as water repellents for leather, paper, and textiles (Prevedouros et al., 2006). Due to the strength of the carbon-fluorine bonds, PFCAs are resistant to environmental degradation and represent the terminal atmospheric degradation products of a multitude of PFAS compounds such as fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamides (FASAs) and perfluoroalkyl sulfonamidoethanols (FASEs) (Young & Mabury, 2010). In addition to the sources mentioned, the two smallest PFCAs, trifluoroacetic acid (TFA, C2) and perfluoropropionic acid (PFPrA, C3) can be formed from the atmospheric degradation of chlorofluorocarbon (CFC) replacement compounds, hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) (Bjornsdotter et al., 2020; Joudan et al., 2021; Young & Mabury, 2010). Newer classes of compounds designed to have lower ozone depleting potential, such as hydrofluoroolefins (HFOs) and hydrochlorofluoroethers (HFEs), can degrade in the atmosphere to form TFA, PFPrA, or perfluorobutanoic acid (PFBA) (Sulbaek Andersen et al., 2026). The types of PFAS products used in commercial applications influence both the range and spatial distribution of PFCAs in the atmosphere.

Long-chain PFCAs containing eight or more carbons ($\geq C8$) such as perfluorooctanoic acid (PFOA), long favoured in industry, were recently phased out of production due to their bioaccumulative and toxic properties (Wang et al., 2013). Regulations on manufacture and use of long-chain PFCAs and their precursors has led to replacements based on PFAS compounds containing less than seven carbons ($< C7$), termed short-chain. PFCAs are expected to have short atmospheric lifetimes, on the order of a few days, depositing back to the surface through wet and dry deposition (Persaud et al., 2026; Pickard et al., 2020; Young et al., 2024). Ultrashort-chain PFCAs, containing two or three carbons (C2, C3), in particular TFA, have many more sources than longer chain PFCAs and almost no environmental sinks, leading to their indefinite accumulation in the environment (Joudan et al., 2021; Young & Mabury, 2010). For example, the two most widely used refrigerants for automobile air conditioners (A/C) since the 1990s, HFC-134a, and

2010s, HFO-1234yf, undergo atmospheric degradation to form TFA. HFC-134a produces TFA at a slow rate (~14 years) and a low yield of ~21%, while HFO-1234yf produces TFA at a faster rate (4–16 days) in almost 100% yield (Luecken et al., 2010; World Meteorological Organization, 2022). Losses are expected to be higher (e.g. 14.3% for HFC-134a) in summer when both the engine and A/C unit are on due to higher vapor pressures and increased heat stress during operation (Siegl et al., 2002). This is supported by higher atmospheric concentrations of HFC-1234yf and HFC-134a (20–52%) in summer compared with winter (Hu et al., 2015; Plant et al., 2026).

The widespread use of commercial PFAS products, and the resulting release of PFCAs precursor compounds to the environment, are likely to scale with population size due to a higher density of emission sources in urban areas relative to rural regions (Plant et al., 2026; Wang et al., 2018). Precursor compounds with relatively short lifetimes will likely undergo atmospheric degradation to PFCAs close to where they were emitted, rather than being transported over long distances. At a regional scale, where such sources dominate emissions, PFCA abundance is expected to increase with population size, as observed for legacy persistent organic pollutants (POPs) (Oh et al., 2024). Conversely, emissions of gas-phase PFCAs or their short-lived precursors from industrial or point source applications are unlikely to exhibit a clear relationship with population and are expected to be elevated near point sources compared to the surrounding areas. Some neutral volatile precursor PFAS have longer lifetimes, and undergo long-range atmospheric transport, ultimately forming PFCAs as terminal degradation products far from where they were emitted (Pickard et al., 2018, 2020; Thackray et al., 2020; Wong et al., 2018). Transport of PFCA precursors in the atmosphere is very fast, on the order of a few weeks to a year, leading to their accelerated global distribution (Young & Mabury, 2010). Due to the higher abundance and increased mobility, water-solubility, and environmental persistence of ultrashort- and short-chain PFCAs in the environment, there is increased exposure and possible health risks to humans and wildlife.

4.1.2 Utility of passive air samplers for large monitoring networks

Direct air measurements have been conducted using active air samplers (AAS), such as high volume AAS (HV-AAS) and diffusion denuders. HV-AAS sample particles before gases and are prone to breakthrough losses, leading to a misrepresentation of air composition (Young & VandenBoer, 2023). Diffusion denuders do not suffer from those sampling biases because they sample the gas phase first, however, both active sampling methods are expensive, high

maintenance, and require power, limiting the number of available sampling locations and preventing large-scale sampling endeavors. Passive air samplers (PAS) provide a low-cost power-free alternative to AAS (Wania & Shunthirasingham, 2020). Due to their compact size, as well as their ease of deployment and maintenance, PAS can be deployed across large regional sampling networks allowing for mapping of the spatial variability of atmospheric contaminants, with the possibility of tracking sources.

As part of the Government of Canada's "Whales Initiative" established in 2018, air measurements of polychlorinated biphenyls (PCBs) were conducted via a large network of styrene-divinylbenzene (XAD-2) resin-based PAS, spanning 118 unique sites in coastal regions of Quebec and British Columbia to study the impact of PCBs on two endangered Canadian whale populations (Oh et al., 2024). Sampling focused on two PCB classes, those intentionally manufactured during the mid-20th century (i.e. Aroclors) and those formed as unintentional side products from processes such as pigment sealing, silicone rubber production, incineration of waste, and e-waste dismantling (i.e. non-Aroclors). Until recently, the application of PAS to PFCA monitoring has mainly been limited to those with four or more carbons (Saini et al., 2023; Shoeib et al., 2016). There is a need for reliable and accurate large scale atmospheric measurements of ultrashort- and short-chain PFCAs, in particular TFA and PFPrA. The utility and convenience of our nylon PAS for atmospheric measurements of ultrashort- and short-chain PFCAs was recently demonstrated in urban areas of Toronto, ON, including at point sources such as a wastewater treatment plant (WWTP) and an airport (See Chapter 3) as well as in remote locations such as Saturna Island, BC and Tadoussac, QC (Vanhauwaert et al., 2025).

4.1.3 Objectives

The objective of this work is the atmospheric measurement of C2–C6 PFCAs in 14 locations along the St. Lawrence Estuary, Quebec, habitat of the endangered St. Lawrence Estuary beluga whales utilizing nylon PAS. The current round of sampling, named "Whale Initiative 2.0" targeted potential source regions where elevated levels of traditional POPs, such as PCBs, were found (Oh et al., 2024). These endeavors were undertaken to determine whether PFCAs share PCB sources, which are linked to consumer product use and population size, or whether industrial and point source emissions dominate. This large nylon PAS network will provide insights into the abundance and spatial distribution of PFCAs.

4.2 Methods

4.2.1 Materials and Chemicals

Sodium carbonate (Na_2CO_3 , $\geq 99.5\%$, ACS reagent grade), glycerol ($>99\%$), and sodium hydroxide (NaOH) solution (49-51% in water) were purchased from Sigma Aldrich (ON, Canada). Methanol (MeOH , Optima LC-MS) was obtained from Fisher Chemical (ON, Canada) and used for IC-MS analysis. Methanol (HPLC grade, $\geq 99.9\%$) was obtained from Sigma Aldrich (ON, Canada) and used for rinsing glassware. The sodium salts of TFA ($>98\%$) and PFPrA ($>99\%$) were obtained from Sigma Aldrich; sodium salts of PFBA ($>98\%$), PFPeA (purity not reported) and PFHxA ($>98\%$) were obtained from Synquest (FL, US). Individual 1000 $\mu\text{g/mL}$ stock solutions of each sodium salt PFCA were prepared in ultrapure Milli-Q water ($18.2 \text{ M}\Omega\cdot\text{cm}$ at 25°C , Direct 8; EMD Millipore), and subsequently combined and diluted to prepare working stock solutions.

Mass-labelled $^{13}\text{C}_1$ -TFA (T786038) and $^{13}\text{C}_1$ -PFPrA were purchased from Toronto Research Chemicals (ON, Canada) and dissolved separately in MeOH to 50 mg/mL . Mass-labelled $^{13}\text{C}_2$ -TFA-sodium salt (99%, 50 $\mu\text{g/mL}$ in MeOH) was purchased from Cambridge Isotope Laboratories, Inc. Mass-labelled $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_3$ -PFPeA, and $^{13}\text{C}_2$ -PFHxA were obtained as individual 50 $\mu\text{g/mL}$ in MeOH solutions from Wellington Laboratories (ON, Canada; MPFBA, M3PFPeA, and MPFHxA). Subsets of these compounds were combined and diluted with Milli-Q water into one solution for use as internal standards (IS) for IC-MS analysis.

4.2.2 Preparation, deployment, and analysis of nylon passive air samplers

Preparation of our nylon PAS is described in Chapter 2, Section 2.2.2. Briefly, the nylon filters were cleaned using a Na_2CO_3 solution, followed by Milli-Q water and dried prior to PAS assembly, after which the PAS were stored in Ziploc[®] bags in the freezer. The PAS are deployed in triplicate to reduce random error by providing the minimum assessment of measurement precision, while also representing a practical balance with the labour required for assembly, deployment, and analysis. To deploy, each PAS was taken out of the Ziploc[®] bag, the lid was removed, and the PAS was attached via hook and loop fasteners to the inside of a weatherproof cap. Gas-phase acids, including $\text{PFCAs}_{(\text{g})}$, pass through the overlying polypropylene (PP) filter via diffusion followed by chemisorption to the nylon filter. The field blank was exposed to the air at the site for ~ 10 s. For collection, each PAS was detached from the weatherproof cap, and they were capped and

stored in Ziploc[®] bags in the freezer. Before extraction, each nylon filter was placed inside a Falcon[™] tube.

Extraction and analysis of nylon filters is described in detail in Chapter 2, Section 2.2.3.1. Briefly, 3 mM NaOH in Milli-Q water (4 mL) was added to each Falcon[™] tube containing a nylon filter, after which they were sonicated for ~15 min, and stored in the fridge for 12–24 hours prior to filter removal. The sample extracts were analyzed for the C2–C6 PFCAs_(g) via ion chromatography-mass spectrometry (IC-MS). C3–C6 PFCAs were quantified using an anion-selective concentrator column with a short gradient separation method. Due to an isobaric interference with ¹³C₂-TFA, TFA was quantified separately using a loop and a longer gradient. The operating parameters for IC-MS analysis of C2–C6 PFCAs are summarized in Chapter 2, Section 2.2.3.1, Table 2.1. Ten-point calibration standards were prepared for C2–C6 PFCAs in Milli-Q water, ranging from 0.01–10 ng/mL. For analysis of any standards, blanks, or samples, 800 µL of the solution was transferred to a 1 mL polypropylene IC-MS vial (Agilent, PN: 5182-0567), internal standard (100 µL) was added, and the solution was vortexed. To correct for matrix effects and instrument fluctuations, the peak area of each PFCA was normalized against its corresponding mass-labelled internal standard.

Details on data analysis can be found in Chapter 2, Section 2.2.8.1. Briefly, the data was blank corrected using the normalized concentrations of each site-specific field blank. The values for the measured TFA and PFBA uptake rates and the predicted PFPrA, PFPeA, and PFHxA uptake rates onto the nylon filters can be found in Section 2.2.8.1, Table 2.3. The mass loadings in ng/m³ were transformed into mixing ratios in parts-per-quadrillion by volume (ppqv) (Equation 2.3 in Section 2.2.8.1). Average temperature at each site was determined from daily meteorological data measured by the nearest weather station for the specific time periods corresponding to each sampler deployment (*Historical Data - Climate - Environment and Climate Change Canada*, 2025).

4.2.3 Sampling Locations

Triplicate nylon PAS were deployed from June to October 2024 at 14 locations along the St. Lawrence River, Quebec (Figure 4.1.). With this round of sampling, we are seeking to establish whether PFCAs follow the same trends in the atmosphere as legacy POPs like PCBs, with site selection based on PCB-polluted sites from the initial Whales Initiative deployment (2019–2022)

(Oh et al., 2024). Site numbers were preserved to allow straightforward comparison of past and future sampling at these sites.

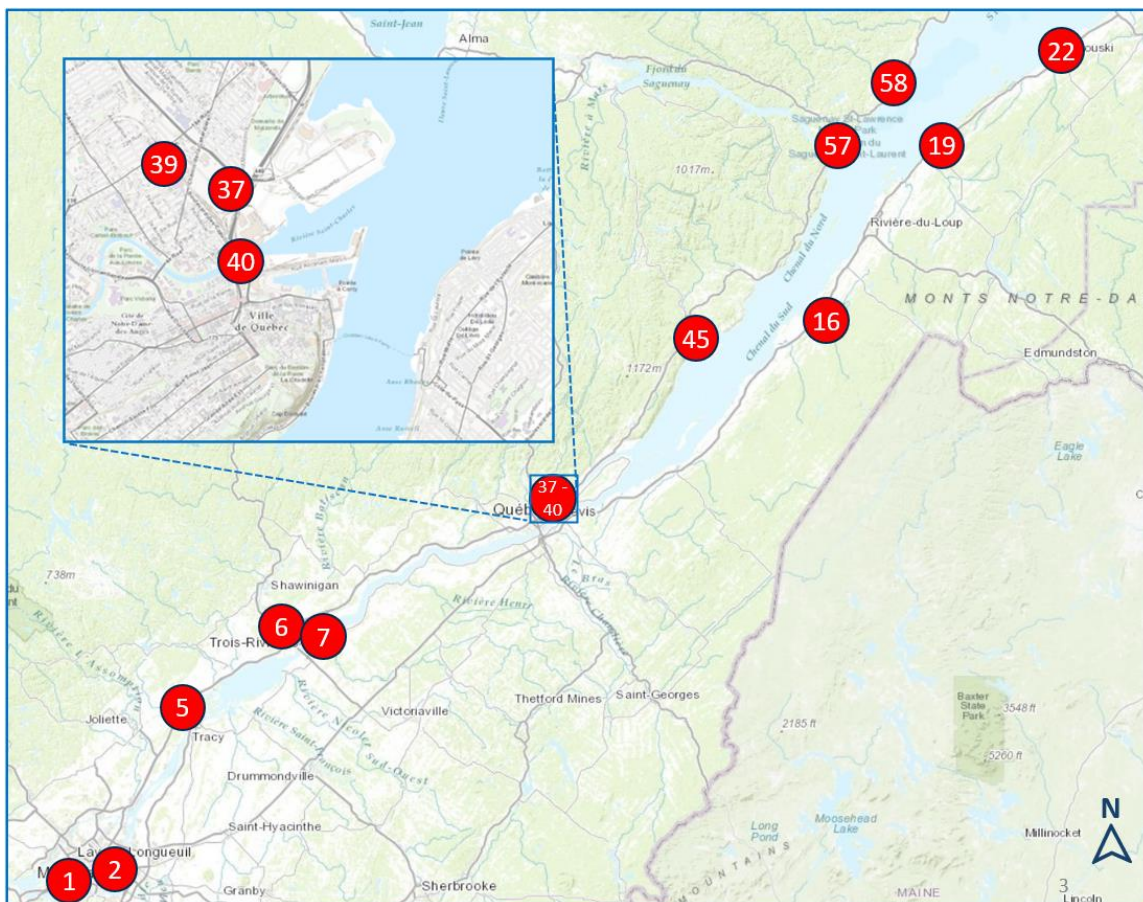


Figure 4.1 Nylon PAS sampling locations along St. Lawrence River, Quebec, where site numbers correspond to those in Oh et al. (2024). Nylon PAS ($n = 3$) were deployed for approximately four months, from June to October 2024. Map inset provides a detailed view of sampling sites in Quebec City. Maps were generated using OpenStreetMap data, available under the Open Database License (<https://www.openstreetmap.org/copyright>).

Additional deployment details including locations, latitude and longitude, and sampling durations are provided in Table 4.1. Sites were classified based on population concentration (i.e. total number of persons) and population density (i.e. number of persons per square km). For large cities, the population of the city (i.e. subdivision) was used rather than the metropolitan area, meaning that the surrounding commuter zone was not included. ‘Urban’ is defined as an area with a minimum population concentration of 1000 persons and a population density of at least 400 persons per square km; ‘Rural’ is defined as an area with a population concentration below 10,000 and a

population density below 400/km². In cases where neither classification fit, the prefix “Semi-” was added to the closest designation. Population data retrieved from Statistics Canada, 2021 Census of Population (n.d.).

Table 4.1 Deployment details for nylon PAS at 14 sites along the St. Lawrence River, Quebec from June to October 2024.

Site #	n	Location	Population	Classification	Latitude, Longitude	Date deployed (mm-dd)	Date retrieved (mm-dd)
S1	3	Montreal	1762949	Urban	45.469167, -73.800278	06-20	10-15
S2	3		1762949	Urban	45.505833, -73.543611	06-20	10-15
S5	3	Sorel-Tracy	35165	Urban	46.047778, -73.109722	06-20	10-15
S6	2	Trois Rivieres	139163	Urban	46.333056, -72.555278	06-20	10-16
S7	3		139163	Urban	46.390556, -72.382778	06-20	10-15
S37	3	Quebec City	549459	Urban	46.828611, -71.216944	06-20	10-16
S39	3		549459	Urban	46.831667, -71.227222	06-20	10-16
S40	3		549459	Urban	46.820556, -71.215000	06-19	10-16
S45	3	Baie-St-Paul	7371	Rural	47.445870, -70.48776	06-23	10-17
S16	2	Saint Pascal	3530	Rural	47.527507, -69.802977	06-19	10-15
S57	3	Tadoussac	814	Rural	48.141483, -69.697406	06-22	10-17
S58	3	Northwest of Tadoussac	1794	Rural	48.344537, -69.410674	06-22	10-17
S19	3	Trois Pistoles	3115	Semi-rural	48.129463, -69.175293	06-21	10-15
S22	3	Rimouski	48935	Semi-urban	48.590301, -68.182699	06-20	10-15

4.3 Results and Discussion

4.3.1 Absolute PFCA concentrations and comparisons with past Canadian measurements

Nylon PAS measurements of C2–C6 PFCA were conducted at 14 sites along the St. Lawrence River and Estuary in Quebec, the habitat of endangered beluga whales (Figure 4.2). PFHxA was not detected above the method limit of detection (mLOD) at any site (Appendix C, Table S4.1) and is therefore excluded from further analysis. Among all sites, the highest total C2–C5 PFCA (Σ PFCA) concentrations were observed at site 16 (S16; 917 ± 284 ppqv), followed by S40 (583 ± 101 ppqv) (Table S4.2). Concentrations at the remaining 12 sites were considerably lower, ranging from 40 ± 9 to 153 ± 14 ppqv, roughly 6 to 23 times below those observed at S16. Both TFA and PFPrA displayed a wide variability in mixing ratios across the sampling network, with TFA ranging from 29 ± 4 ppqv to 621 ± 282 ppqv, and PFPrA ranging from 5 ± 8 ppqv to 273 ± 32 ppqv.

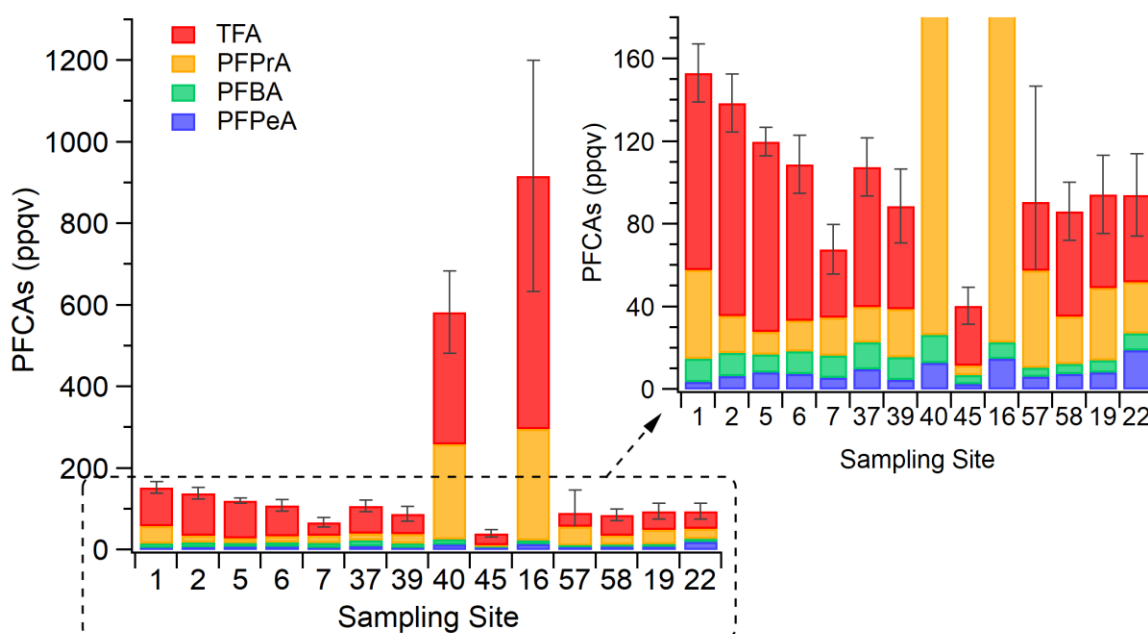


Figure 4.2 Concentration profiles of C2–C5 PFCA at 14 sampling sites along the St. Lawrence River and Estuary in Quebec. Values displayed at each site are average mixing ratios (ppqv) of triplicate nylon PAS ($n = 3$), or duplicate nylon PAS ($n = 2$; S6, S16). Error bars represent the propagated error for Σ C2–C5 PFCA. With the exception of sites within Quebec City (S37–S40), sampling sites are organized by geographical location from west to east.

This study represents the most extensive nylon PAS PFCA spatial sampling campaign conducted to date, which limits direct comparison with prior measurements. The only existing nylon PAS data from Quebec comes from measurements taken in 2022 at S57 in Tadoussac. At that site, current TFA and PFBA concentrations were consistent with 2022 values, agreeing within a factor of 1.5, whereas PFPrA and PFPeA levels were elevated by factors of 12 and 3, respectively. It should be noted that earlier PFPrA determinations were likely underestimated due to quantitation with the PFBA IS and the true agreement is likely closer than the reported values suggest (Vanhouwaert et al., 2025). Nevertheless, the mean PFCA mixing ratios and their ranges across Quebec are largely consistent with those reported at other Canadian urban and rural locations.

As expected, average TFA concentrations in Quebec were lower than those recorded in Toronto during similar seasons, and higher than year-round levels in the remote location on Saturna Island, BC. As the largest and most populated city in Canada, Toronto has many more sources of short-lived precursors, as well as additional input from long-range transport of precursors from the Greater Toronto Area (GTA) and the United States, compared with the secluded Saturna Island site and the St. Lawrence River region of Quebec. Modelling studies estimate a larger deposition of PFCAs ($< C8$) from atmospheric formation in the GTA compared with the Quebec region and Saturna Island, BC (Thackray et al., 2020; Wang et al., 2018). Differences in regional emissions and meteorological factors make the Quebec region more susceptible to long-range atmospheric transport of PFCA precursors compared with Saturna Island. This is supported by the modelled deposition of PFCAs ($< C8$), estimated to be larger in the Quebec region compared with the region around Saturna Island, BC (Thackray et al., 2020; Wang et al., 2018). PFBA mixing ratios fell within the range of previous nylon PAS measurements in Toronto and SIP PAS measurements at rural locations in Canada (Saini et al., 2023). Notably, PFPeA concentrations in Quebec were generally higher than values previously reported using either nylon or SIP PAS across Canadian sites, including Toronto, with levels ranging from comparable to approximately 6 times greater.

4.3.2 Spatial distribution of C2–C5 PFCAs along St. Lawrence River and Estuary

With this nylon PAS network, we obtained large spatial coverage, spanning nearly 600 km of coastal area in Quebec, from Montreal in the southwest to Rimouski in the northeast. TFA was the principal compound at the majority of sites (13 of 14), with PFPrA exhibiting higher averages at S57, but with RSDs greater than 100%. The majority of sampling sites (9 of 14) followed the expected trend, whereby TFA was the principal compound and PFCa mixing ratios decreased with increasing chain length (Figure 4.3, Table S4.2). This trend has been observed in past nylon PAS measurements in Toronto, ON and Tadoussac, QC (Vanhauwaert et al., 2025) and is consistent with relative abundances in deposition measurements (Pickard et al., 2020; Scott et al., 2006).

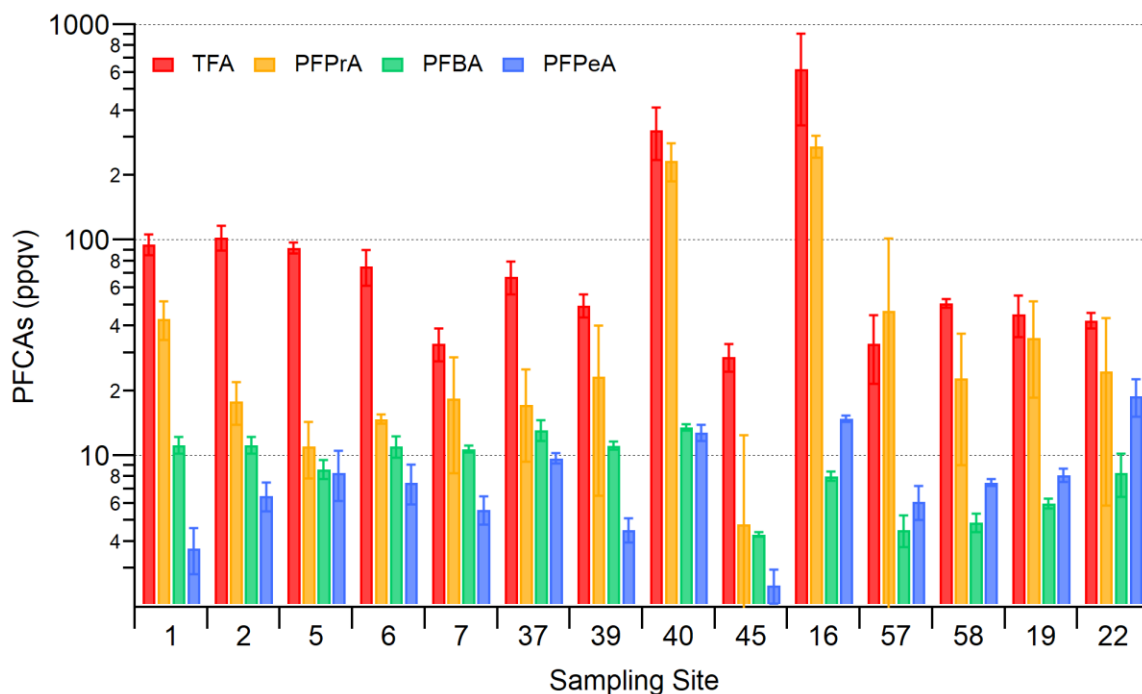


Figure 4.3 Mixing ratios of C2–C5 PFCAs (ppqv) measured using nylon PAS at 14 sites along the St. Lawrence River, Quebec from June to October 2024, with a logarithmic ($\log_{10}$) vertical axis. Error bars represent relative error between duplicate PAS or standard deviation of triplicate PAS measurements. With the exception of sites within Quebec City (S37–S40), sampling sites are organized by geographical location from west to east.

At the remaining five sampling sites, average mixing ratios of PFPeA exceeded those of PFBA. Notably, all five sites are located northeast of Quebec City, and four of the sites have a population size below 8,000. At the majority of sites (4 of 5), PFPeA concentrations were significantly higher

than PFBA (Welch t-test, $p < 0.05$) (Equation S4.1, Table S4.3). It is possible for sampling locations in this region to have a higher abundance of direct and indirect emission sources of PFPeA compared with PFBA. Another possibility is that prevailing wind patterns may transport air masses enriched with PFPeA-specific precursors from more industrialized regions like Quebec City or the U.S. In the Cl-atom-initiated oxidation of the 8:2 FTOH, Ellis et al. (2004) demonstrated that yields of individual PFCA homologues is proportional to chain length, with PFCAs containing one and two fewer carbons than the precursor dominating as homologue pairs. Similarly, the oxidation of 6:2 FTOH primarily forms PFHpA and PFHxA, while 4:2 FTOH forms PFPeA and PFBA (Thackray et al., 2020; Thackray & Selin, 2017). One possible explanation for the pattern observed across the five sites is that PFPeA is formed in greater yield than PFBA from the atmospheric oxidation of longer chain FTOHs (e.g. 6:2, 8:2, 10:2). Although this pattern has not been reported in previous nylon PAS studies, it is consistent with ambient air measurements conducted in Toronto using CIMS, where PFPeA concentrations were consistently higher than those of PFBA, across both winter and summer sampling periods (Young et al., 2024). As these sites are the closest to the habitat of the endangered St. Lawrence Estuary beluga whales, elucidation of PFCA emission sources in the area remains an important research question for future studies.

Highly elevated TFA and PFPrA concentrations were measured at S40 in Quebec City and S16 in Saint-Pascal. Compared to the average values across the remaining 12 sites, TFA mixing ratios at S40 and S16 were higher by factors of 5 and 10, respectively, while PFPrA mixing ratios were higher by factors of 10 and 12. Elevated PFPrA concentrations of 582 ± 214 ppqv were also measured that spring at Toronto Pearson International Airport (Chapter 3, Section 3.3.2). Average PFPrA levels at the airport were higher by factors of 2.5 and 2.1 compared with sites 40 and 16, respectively, though it should be noted that the airport measurements represent time-integrated values over a sampling duration half that of the Quebec sites. A key distinction exists between the two datasets: at the airport, only PFPrA was markedly elevated, whereas at both Quebec sites, TFA and PFPrA were similarly elevated. This difference in the ultrashort-chain PFCA occurrence pattern suggests that the emission sources influencing the two Quebec sites are likely distinct in nature from those associated with the airport.

The identity of the PFPrA peak and the absence of isobaric interference were assessed as follows. Samples were analyzed twice, first using the concentration column with a short gradient (quantitative method) and again using the loop with a longer gradient (qualitative method). In both analyses, the PFPrA peaks showed no signs of irregularity such as peak shouldering, and retention times matched precisely with those of the mass-labelled internal standard, $^{13}\text{C}_1$ -PFPrA. Identity was further corroborated by a confirmation ion at m/z 119 (transition m/z 163 $\rightarrow$ 119, corresponding to loss of CO_2), whose retention time matched that of the PFPrA peak.

Elevated TFA and PFPrA concentrations were observed exclusively at sites S40 and S16, with field blanks from both sites containing lower analyte masses than their corresponding samples. Notably, the field blanks at S40 and S16 contained TFA and PFPrA masses roughly 30 times higher than the average field blank masses from the remaining 12 sites. At S40 and S16, TFA masses on the field blanks represented 29% and 23% of the non-blank subtracted sample masses, respectively. The discrepancy was more pronounced for PFPrA, where field blank masses reached 56% (S40) and 53% (S16) of their corresponding sample masses prior to blank subtraction.

Because all samples were collected, transported, stored, and extracted under identical conditions, procedural contamination would be expected to affect all sites uniformly. Random, individualized contamination would produce elevated concentrations with no spatial organization. The restriction of elevated concentrations to only 2 of 14 sites, in both samples and blanks, is spatially selective and is indicative of a real environmental signal rather than contamination. A plausible explanation is that ambient TFA and PFPrA concentrations were elevated during sampler deployment due to an episodic emission event, with the field blanks capturing a snapshot of that ambient burden rather than a time-integrated accumulation. The field blanks would have recorded the initial elevated concentrations in their 10 second exposure, with that signal diluting slightly over the total integrated mass accumulated over the four-month sampler deployment.

Quebec City is the second most populated city among the sampling locations, and S40 is situated in close proximity to numerous potential PFAS emission sources, including a municipal waste incinerator, a paper mill, a fuel distributor, and a marina. Elevated TFA and PFPrA concentrations were observed at S40, but not at S37, a site located approximately 1 km away, which suggests that direct gas-phase emissions of TFA and PFPrA from a nearby point source are responsible for these elevated concentrations, rather than atmospheric degradation of short-lived precursors. Given that

the prevailing winds originate predominantly from the west, it is plausible for direct PFCA emissions in that area to only be collected by the closest PAS, thereby accounting for the spatially localized nature of the signal. Site 37 therefore appears to be unaffected by direct point source emissions, instead reflecting background urban PFCA abundance driven primarily by atmospheric formation from precursor compounds.

Site 16 is located in Saint-Pascal, a small community of approximately 3,500 residents situated roughly 170 km from Quebec City. No industrial or population-dependent PFAS sources were identified from a survey of this the area, suggesting that the elevated ultrashort-chain PFCA concentrations at this site may stem either from long-range atmospheric transport of precursor compounds or from a less obvious point source that is neither industrial nor population-dependent, such as one of agricultural origin. Point sources of PFCAs or their short-lived precursors can exist in sparsely populated rural areas; a notable example is the land application of fertilizers containing biosolids derived from WWTPs. Such biosolids have been widely shown to contain precursor compounds such as fluorotelomer compounds, FOSAs, and FOSEs, as well as C4–C14 PFCAs and C4–C11 PFSAs (Gewurtz et al., 2024; Tansel et al., 2024). At present, the available data is insufficient to distinguish between these potential source types, with both long-range precursor transport and local agricultural emissions remaining plausible explanations for the elevated concentrations observed at S16. Given that S16 yielded elevated gas-phase PFPrA concentrations comparable to those at an urban site, S40, future work should prioritize source attribution for this type of rural emission pathway.

To assess whether the elevated TFA and PFPrA concentrations observed at S40 and S16 represent statistical outliers relative to the broader dataset, a statistical analysis was conducted. Prior to choosing the appropriate statistical method for outlier identification, the distributions of individual C2–C6 PFCA concentrations were examined for normality through an assessment of their histograms (Figure S4.1) and the Shapiro-Wilk and Jarque-Bera tests (Table S4.4) (Jarque & Bera, 1987; Shapiro & Wilk, 1965; Yazici & Yolacan, 2007). With the exception of PFBA, PFCA concentrations departed significantly from normality, at the 95% confidence level. Based on this outcome, the Tukey interquartile range (IQR) method was selected and box plots were generated, illustrating the PFCA concentration distribution among all nylon PAS measurements ($n = 40$) (Figure 4.4).

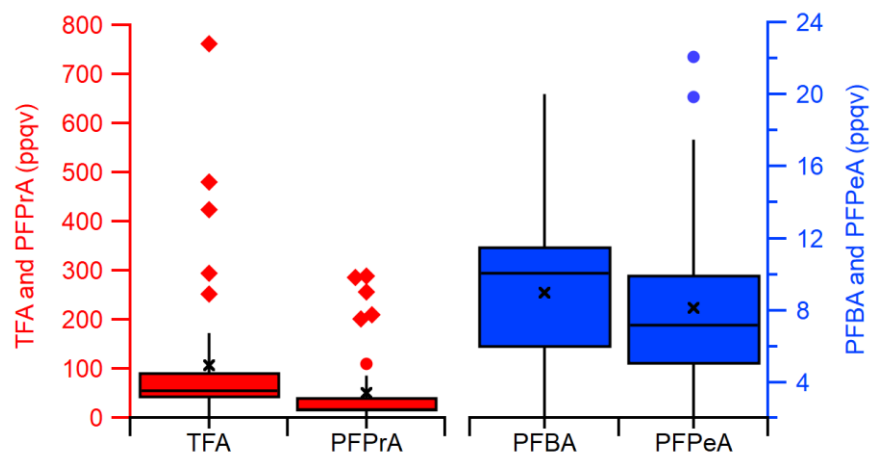


Figure 4.4 Box plot showing distribution of C2–C5 PFCA abundances measured by nylon PAS ($n = 40$) from June to October 2024 at 14 sites along the St. Lawrence River and Estuary in Quebec, Canada. The boxes represent the interquartile range (IQR), with the bottom and top boundaries of each box showing the 25th and 75th percentiles of data distribution, horizontal black lines representing the median, and black crosses representing the mean. Whiskers show the inner lower ($Q1 - 1.5 \times IQR$) and upper fences ($Q3 + 1.5 \times IQR$). Data outside the inner fences but inside the outer fences ($Q1 - 3 \times IQR$ and $Q3 + 3 \times IQR$) are outliers, denoted with circles; data outside the outer fences are far outliers, denoted with diamonds.

For reference, the PFCA concentration ranges obtained from a normal Gaussian distribution at one, two, and three standard deviations away from the means are presented in Appendix C, Table S4.5. Three TFA measurements (two from S16 and one from S40) and four PFPrA measurements (two from each S40 and S16) lie outside the respective means plus two standard deviations boundaries. TFA and PFPrA measurements from one S16 extract from lie outside the respective means plus three standard deviations boundaries.

All five far outliers identified for TFA and PFPrA, correspond to measurements from S40 ($n = 3$) and S16 ($n = 2$). The pronounced deviation of these sites from regional background levels suggests that their concentrations are most likely attributed to localized point source emissions of gas-phase TFA and PFPrA, or their very short-lived precursors. The median concentrations of TFA (55 ppqv), PFPrA (17 ppqv), PFBA (10 ppqv), and PFPeA (7.2 ppqv) measured in Quebec follow the expected trend, with PFCA abundance inversely proportional to chain length. PFBA concentrations were consistent across all 40 measurements with no outliers detected. PFPeA exhibited two outliers,

both originating from S22; however, these fell only marginally beyond the upper boundary of the data distribution.

Additional patterns in the PFCA spatial distribution were revealed upon omission of the two outliers, S40 and S16. The next highest TFA levels were measured at both Montreal sampling sites, S1 and S2, consistent with Montreal being the largest and most populated city among the surveyed locations. More unexpectedly, the second-highest TFA mixing ratios were observed at S5 in Sorel-Tracy, a relatively small town of ~35,000 residents located roughly 90 km away from Montreal. The relatively high abundance of PFCAs at this site are most likely attributable to the atmospheric transport of precursor compounds originating from the Montreal area. At present, the available data is insufficient to distinguish local sources compared with atmospheric transport, and additional research is needed. For example, high time resolution measurements of PFCAs alongside established markers of atmospheric formations, such as ozone and formic acid, would aid in source attribution (Young et al., 2024). During the day, irradiance and temperature are higher, so daytime concentration maxima combined with positive correlations to ozone and formic acid, would be indicative of atmospheric formation as the dominant source.

4.3.3 Correlation to population size

As a preliminary step towards PFCA source attribution, we determined the relationship between average C2–C5 PFCA abundances and population size at each of the 14 sites (including the two outliers) (Figure 4.5). Correlations between population size and atmospheric concentrations were negligible for Σ PFCAs ($r = -0.04$), TFA ($r = -0.03$) and PFPrA ($r = -0.07$) (Pearson Correlation, Equation S4.2, Table S4.6). PFPeA displayed a weak negative correlation with population ($r = -0.29$), though this relationship was not statistically significant ($p > 0.05$). Among the PFCAs measured, PFBA was the only compound for which atmospheric abundance showed a statistically significant correlation with population size ($r = 0.55$, $p < 0.05$). The moderate positive correlation to population suggests that the atmospheric abundance of PFBA is significantly influenced by population- or industry-dependent sources, whether through direct release of gas-phase PFBA or through emissions of short-lived PFBA-specific precursor compounds.

Upon omission of the two outliers where extremely elevated TFA and PFPrA concentrations were measured (S40 and S16), we see strong positive and statistically significant correlations between population size with both Σ PFCAAs ($r = 0.72$, $p < 0.01$) and TFA ($r = 0.74$, $p < 0.01$) (Table S4.6). The moderate positive correlation between PFBA and population size is maintained, but it is no longer statistically significant at the 95% confidence level ($p = 0.052$). A positive correlation to population was observed in previous XAD-PAS measurements by Oh et al. (2024) in their comprehensive campaign at 71 sites along the St. Lawrence River and Estuary, where elevated concentrations of Aroclor PCBs were measured in the most populated urban areas, particularly Montreal (S1) and Quebec City (S37 and surrounding sites S38–S40).

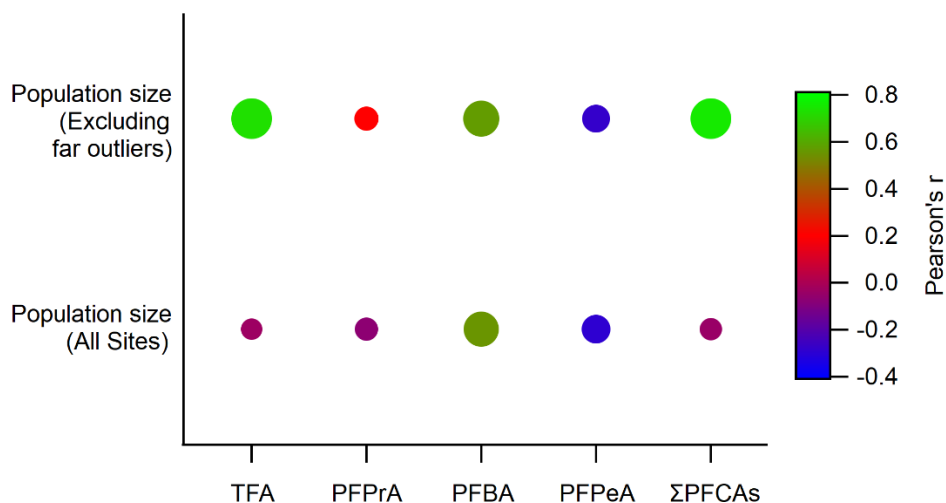


Figure 4.5 Correlation maps for PFCA atmospheric mixing ratios with population size. All correlations are based on average nylon PAS measurements determined from duplicate or triplicate samplers at each sampling site ($n = 14$). Sites exhibiting outlier TFA and PFPrA abundances, S40 and S16, were omitted in top line for comparison. Colour refers to Pearson's r for the linear relationship, point size refers to Pearson's r absolute linear relationship. When excluding outliers, the correlations between population size with TFA and Σ PFCAAs concentrations are significant, as is the correlation between population size and PFBA concentration when all sites are considered.

Upon exclusion of the two outliers, the correlation between population size and PFPeA concentrations remains unchanged, while the correlation with PFPrA shifts to weakly positive, though it remains non-significant ($p > 0.05$). The results suggest that PFPrA and PFPeA are not linked to population size, meaning their atmospheric abundances are not governed by population-dependent sources like industrial emissions and use of commercial PFAS products. Their atmospheric concentrations are likely influenced by other factors such as gas-particle partitioning

and the atmospheric degradation of long-lived precursors, which have lifetimes long enough to undergo long-range atmospheric transport and form PFCAs far from where they were emitted (Pickard et al., 2020; Thackray et al., 2020).

Although Aroclor PCBs were positively correlated to population size, Oh et al. (2024) detected non-Aroclor PCBs near the habitats of the St. Lawrence beluga whales, indicating a possible source of exposure that is not population dependent. Two of these locations overlapped with our nylon PAS sampling sites, S16 and S45, however, elevated PFCA concentrations were only observed at S16. Notably, S16 displayed the highest concentrations of Σ PFCAs of all 14 sites, while S45 had the lowest. The sources of gas-phase PFCAs in the atmosphere are complex and more research is needed to identify them and to understand the importance of both direct gas-phase emissions and atmospheric formation.

The presented results correlating PFCA abundance to population size at the 14 Quebec sites represent a starting point to this type of statistical analysis and are subject to several limitations. First, the population size of each deployment location was estimated as the number of persons living in the census subdivision, as reported by Statistics Canada Census of Population (2021). The total land area contained within each subdivision may differ greatly between locations, ranging from 53 km² for Tadoussac to 4670 km² for Montreal. In addition, the census subdivisions do not include the surrounding metropolitan areas, the inclusion of which would increase the population estimates (e.g. by a factor of 2.4 for Montreal). Second, the average PFCA abundance measured by triplicate nylon PAS at each site (duplicates at S6 and S16) was used for these calculations, and the relative standard deviation between replicates, averaging 20%, was not considered. These limitations introduce uncertainty into the population-PFCA relationship and should be considered when interpreting the observed correlations.

Many PFAS precursor compounds, such as FTOHs and FASAs have lifetimes sufficiently long to undergo long-range atmospheric transport and degrade in the atmosphere to form C2–C5 PFCAs (Pickard et al., 2018, 2020; Thackray et al., 2020; Young & Mabury, 2010). Nevertheless, the current data suggests that a substantial amount of TFA and PFBA atmospheric abundances originate from localized sources that scale with population. The shift away from long-chain PFAS toward short-chain alternatives in industrial and consumer applications has been largely driven by urban industries and manufacturers (Wang et al., 2014), potentially concentrating TFA and PFBA

precursor emissions in populated areas. The strong positive correlation to population size when excluding outliers displaying extreme emissions suggests that local emission sources of TFA can play a significant part in its atmospheric abundance, to a larger extent than for the longer chained homologues. One likely source of TFA-specific precursors are HFCs, HCFCs, and HFOs which are widely used as refrigerants, including the well-known HFC-134a and HFO-1234yf used in mobile air conditioning systems, as well as numerous others with various commercial applications. Modelled emissions of HFO-1234yf and atmospheric measurements of HFC-134a are higher in the summer when A/C units are in use and more likely to be serviced (Hu et al., 2015; Luecken et al., 2010; Plant et al., 2026). However, degradation of HFCs, HCFCs, and HFOs may not be the sole population-dependent source of gas-phase TFA. In addition to HFC-134a and HFO-1234yf, there are numerous other HFCs, HCFCs, HFOs, HFEs and fluorotelomer compounds which yield gas-phase TFA (Sulbaek Andersen et al., 2026; Young & Mabury, 2010).

Identifying patterns in PFCA abundance is challenging given the existence of localized emission events. This underscores the value of large-scale PAS networks, which are uniquely suited to characterizing both the spatial distribution of compounds across large regions and the detection of emissions which deviate from the regional baseline.

4.4 Conclusion

The current work demonstrates the suitability of the nylon passive air samplers (PAS) in advancing knowledge of PFCAs atmospheric abundance and distribution. Nylon passive air samplers proved to be well-suited for large-scale regional PFCA sampling, simultaneously measuring C2–C6 PFCA atmospheric concentration at 14 sites, and providing insight into the spatial distribution of gas-phase PFCAs over a large spatial area in the habitat of endangered St. Lawrence beluga whales. These measurements provide valuable insight into atmospheric abundance of PFCAs and represent the first step taken towards mapping the PFCA deposition along the St. Lawrence River watershed. Overall, the atmospheric gas-phase concentrations of C2–C6 PFCAs were inversely proportional to chain length. Elevated TFA and PFPrA concentrations were measured at 2 of 14 sites, one urban and one rural. Although direct gas-phase emissions of TFA and PFPrA or their very short-lived precursors from a point source are the most likely explanation, long-range transport of precursors is also possible. The findings suggest that the atmospheric abundance of TFA and PFBA in this

region can be significantly influenced by population-dependent sources such as consumer use of PFAS products. However, this relationship may not be evident for TFA due to large, localized emissions, recorded in both urban and rural areas. The source(s) of unexpectedly high TFA and PFPrA levels in a sparsely populated area of Quebec are still unknown, calling for further research to determine the extent of PFCA and PFAS contamination to rural and remote areas. The current work provides valuable information on the atmospheric abundance of gas-phase PFCAs, an essential step in the determination of PFCA deposition on both terrestrial and aquatic environments in the St. Lawrence River region of Quebec.

References

- Bjornsdotter, M. K., Yeung, L. W. Y., Karrman, A., & Jogsten, I. E. (2020). Challenges in the analytical determination of ultra-short-chain perfluoroalkyl acids and implications for environmental and human health. *Anal. Bioanal. Chem.*, 412(20), 4785–4796.
- Census Profile, 2021 Census of Population. (n.d.). Retrieved February 10, 2026, from <https://www12.statcan.gc.ca/census-recensement/2021/dp-pd/prof/index.cfm?Lang=E>
- Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., & Wallington, T. J. (2004). Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science and Technology*, 38(12), 3316–3321. <https://doi.org/10.1021/es049860w>
- Gewurtz, S. B., Auyeung, A. S., De Silva, A. O., Teslic, S., & Smyth, S. A. (2024). Per- and polyfluoroalkyl substances (PFAS) in Canadian municipal wastewater and biosolids: Recent patterns and time trends 2009 to 2021. *Science of the Total Environment*, 912. <https://doi.org/10.1016/j.scitotenv.2023.168638>
- Hu, L., Montzka, S. A., Miller, J. B., Andrews, A. E., Lehman, S. J., Miller, B. R., Thoning, K., Sweeney, C., Chen, H., Godwin, D. S., Masarie, K., Bruhwiler, L., Fischer, M. L., Biraud, S. C., Torn, M. S., Mountain, M., Nehrkorn, T., Eluszkiewicz, J., Miller, S., ... Tans, P. P. (2015). U.S. emissions of HFC-134a derived for 2008–2012 from an extensive flask-air sampling network. *Journal of Geophysical Research: Atmospheres*, 120(2), 801–825. <https://doi.org/10.1002/2014JD022617>
- Jarque, C. M., & Bera, A. K. (1987). A Test for Normality of Observations and Regression Residuals. *International Statistical Review / Revue Internationale de Statistique*, 55(2), 163. <https://doi.org/10.2307/1403192>
- Joudan, S., De Silva, A. O., & Young, C. J. (2021). Insufficient evidence for the existence of natural trifluoroacetic acid. *Environ. Sci.: Processes Impacts*, 23, 1641–1649.
- Luecken, D. J., Waterland, R. L., Papasavva, S., Taddonio, K. N., Hutzell, W. T., Rugh, J. P., & Andersen, S. O. (2010). Ozone and TFA Impacts in North America from Degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), A Potential Greenhouse Gas Replacement. *Environmental Science & Technology*, 44(1), 343–348. <https://doi.org/10.1021/es902481f>
- Oh, J., Shunthirasingham, C., Zhan, F., Li, Y., Lei, Y. D., Ben Chaaben, A., Lu, Z., Lee, K., Gobas, F. A. P. C., Hung, H., & Wania, F. (2024). Passive Air Sampling Networks Combined with Multivariate Statistics Reveal Widespread Non-Aroclor Polychlorinated Biphenyl Sources to the Canadian Atmosphere. *ACS ES&T Air*, 1(6), 481–491. <https://doi.org/10.1021/acsestair.3c00081>
- Persaud, D., Joudan, S., VandenBoer, T. C., & Young, C. J. (2026). Atmospheric Removal of Trifluoroacetic Acid by Dry and Wet Deposition: A Multiyear Analysis in Toronto. *Environmental Science & Technology Letters*, 13(2), 261–267. <https://doi.org/10.1021/acs.estlett.5c01100>

- Pickard, H. M., Criscitiello, A. S., Persaud, D., Spencer, C., Muir, D. C. G., Lehnher, I., Sharp, M. J., De Silva, A. O., & Young, C. J. (2020). Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations. *Geophysical Research Letters*, 47(10). <https://doi.org/10.1029/2020GL087535>
- Pickard, H. M., Criscitiello, A. S., Spencer, C., Sharp, M. J., Muir, D. C. G., De Silva, A. O., & Young, C. J. (2018). Continuous non-marine inputs of per- and polyfluoroalkyl substances to the High Arctic: A multi-decadal temporal record. *Atmospheric Chemistry and Physics*, 18(7), 5045–5058. <https://doi.org/10.5194/acp-18-5045-2018>
- Plant, G., Kort, E. A., Vimont, I., & Sweeney, C. (2026). Airborne Measurements Suggest That Halocarbon Emissions from the New York City Urban Region Have Comparable Climate Impacts to Its Methane Emissions. *Environmental Science & Technology*. <https://doi.org/10.1021/acs.est.5c12757>
- Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). Sources, fate and transport of perfluorocarboxylates. *Environmental Science and Technology*, 40(1), 32–44. <https://doi.org/10.1021/es0512475>
- Saini, A., Chinnadurai, S., Schuster, J. K., Eng, A., & Harner, T. (2023). Per- and polyfluoroalkyl substances and volatile methyl siloxanes in global air: Spatial and temporal trends. *Environmental Pollution*, 323. <https://doi.org/10.1016/j.envpol.2023.121291>
- Scott, B. F., Spencer, C., Mabury, S. A., & Muir, D. C. G. (2006). Poly and perfluorinated carboxylates in north American precipitation. *Environmental Science and Technology*, 40(23), 7167–7174. <https://doi.org/10.1021/es061403n>
- Shapiro, S. S., & Wilk, M. B. (1965). An Analysis of Variance Test for Normality (Complete Samples). *Biometrika*, 52(3/4), 591. <https://doi.org/10.2307/2333709>
- Shoeib, M., Schuster, J., Rauert, C., Su, K., Smyth, S. A., & Harner, T. (2016). Emission of poly and perfluoroalkyl substances, UV-filters and siloxanes to air from wastewater treatment plants. *Environmental Pollution*, 218, 595–604. <https://doi.org/10.1016/j.envpol.2016.07.043>
- Siegl, W. O., Wallington, T. J., Guenther, M. T., Henney, T., Pawlak, D., & Duffy, M. (2002). R-134a Emissions from Vehicles. *Environmental Science & Technology*, 36(4), 561–566. <https://doi.org/10.1021/es011108x>
- Sulbaek Andersen, M. P., Wallington, T. J., Burkholder, J. B., Madronich, S., Hanson, M. L., Van Hoomissen, D., & Solomon, K. R. (2026). Yields of perfluorocarboxylic acids from the atmospheric oxidation of Montreal Protocol related gases. *Environmental Science: Atmospheres*. <https://doi.org/10.1039/d5ea00179j>
- Tansel, B., Katsenovich, Y., Quinete, N. S., Ocheje, J., Nasir, Z., & Manzano, M. M. (2024). PFAS in biosolids: Accumulation characteristics and fate profiles after land application. *Journal of Environmental Management*, 370, 122395. <https://doi.org/10.1016/j.jenvman.2024.122395>
- Thackray, C. P., & Selin, N. E. (2017). Uncertainty and variability in atmospheric formation of PFCAs from fluorotelomer precursors. *Atmospheric Chemistry and Physics*, 17(7), 4585–4597. <https://doi.org/10.5194/acp-17-4585-2017>

- Thackray, C. P., Selin, N. E., & Young, C. J. (2020). A global atmospheric chemistry model for the fate and transport of PFCAs and their precursors. *Environmental Science: Processes and Impacts*, 22(2), 285–293. <https://doi.org/10.1039/c9em00326f>
- Vanhauwaert, E., Carmichael, L., Nistorescu, I., Crilley, L., Shunthirasingham, C., Hung, H., Young, C., & Vandenboer, T. C. (2025). Selective ultra-trace atmospheric passive sampling of gaseous perfluoroalkyl carboxylic acids. *Environmental Science: Processes & Impacts*. <https://doi.org/10.1039/d5em00297d>
- Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C., & Hungerbühler, K. (2014). Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: Production and emissions from quantifiable sources. *Environment International*, 70, 62–75. <https://doi.org/10.1016/j.envint.2014.04.013>
- Wang, Z., Cousins, I. T., Scheringer, M., & Hungerbühler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSA) and their potential precursors. *Environment International*, 60, 242–248. <https://doi.org/10.1016/j.envint.2013.08.021>
- Wang, Z., Wang, Y., Li, J., Henne, S., Zhang, B., Hu, J., & Zhang, J. (2018). Impacts of the Degradation of 2,3,3,3-Tetrafluoropropene into Trifluoroacetic Acid from Its Application in Automobile Air Conditioners in China, the United States, and Europe. *Environmental Science & Technology*, 52(5), 2819–2826. <https://doi.org/10.1021/acs.est.7b05960>
- Wania, F., & Shunthirasingham, C. (2020). Passive air sampling for semi-volatile organic chemicals. *Environmental Science: Processes and Impacts*, 22(10), 1925–2002. <https://doi.org/10.1039/d0em00194e>
- Wong, F., Shoeib, M., Katsoyiannis, A., Eckhardt, S., Stohl, A., Bohlin-Nizzetto, P., Li, H., Fellin, P., Su, Y., & Hung, H. (2018). Assessing temporal trends and source regions of per- and polyfluoroalkyl substances (PFASs) in air under the Arctic Monitoring and Assessment Programme (AMAP). *Atmospheric Environment*, 172, 65–73. <https://doi.org/10.1016/j.atmosenv.2017.10.028>
- World Meteorological Organization. (2022). Scientific Assessment of Ozone Depletion (No. 278; Ozone Research and Monitoring, pp. 448–483).
- Yazici, B., & Yolacan, S. (2007). A comparison of various tests of normality. *Journal of Statistical Computation and Simulation*, 77(2), 175–183. <https://doi.org/10.1080/10629360600678310>
- Young, C. J., Joudan, S., Tao, Y., Wentzell, J. J. B., & Liggio, J. (2024). High Time Resolution Ambient Observations of Gas-Phase Perfluoroalkyl Carboxylic Acids: Implications for Atmospheric Sources. *Environmental Science and Technology Letters*, 11(12), 1348–1354. <https://doi.org/10.1021/acs.estlett.4c00897>
- Young, C. J., & Mabury, S. A. (2010). Atmospheric perfluorinated acid precursors: Chemistry, occurrence, and impacts. *Reviews of Environmental Contamination and Toxicology*, 208, 1–109. https://doi.org/10.1007/978-1-4419-6880-7_1
- Young, C. J., & VandenBoer, T. C. (2023, October). PFAS: Unraveling the analytical challenges: Separations and selectivity for measurements of atmospheric PFAS. *Separation Science*, (2), 12–15.

Chapter 5. Conclusions and future directions

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IN wrote and TCV edited this work.

5.1 Conclusions

In Chapter 2, the robustness of our nylon passive air sampler (PAS) method was enhanced through the optimization of several analytical and field-associated quality assurance and quality control (QA/QC) parameters. The effectiveness of the trifluoroacetic acid (TFA) internal standard (IS), $^{13}\text{C}_1\text{-TFA}$, and perfluorobutanoic acid (PFBA) IS, $^{13}\text{C}_4\text{-PFBA}$, in quantifying perfluoropropionic acid (PFPrA) was assessed. $^{13}\text{C}_1\text{-TFA}$ was demonstrated to be the preferable choice and a viable substitute for the PFPrA IS, an important and novel finding. The accuracy of TFA quantitation was improved by replacing the $^{13}\text{C}_1\text{-TFA}$ IS with the $^{13}\text{C}_2\text{-TFA}$ IS. Our nylon PAS were successfully calibrated for the uptake of $\text{PFBA}_{(\text{g})}$, a first for this compound. The measured linear uptake rate of $203 \pm 7 \frac{\text{PFBA}_{(\text{g})} (\text{ng}\cdot\text{m}^{-3})\cdot\text{t}(\text{h})}{\text{PFBA}_{(\text{filter})}(\text{ng})}$ closely aligned with the predicted rate for PFBA (161 ± 17), within a factor of 1.3. The simultaneous determination of the linear uptake rate for TFA from its residual presence in the permeation oven was in good agreement with our group's prior robust determination using the same atmospheric chamber. The relative errors between the measured and predicted PFBA uptake rates (26%), as well as between the two measured TFA uptake rates (25%) were nearly identical to the overall average relative standard deviation observed among replicate PAS in field measurements (26%). This close agreement indicates that the observed differences fall within the overall precision of the PAS method. Through these measurements, we demonstrated that Fuller's Law is a useful predictor of PFCA uptake rates, thereby increasing our confidence in the accuracy of the predicted uptake rates in determining air concentrations without additional time-consuming chamber calibrations.

Overall, our QA/QC testing on field-deployed nylon PAS determined that C2–C6 PFCAs are largely unaffected by sampling biases during deployment. A novel intercomparison of nylon PAS and sorbent-impregnated polyurethane-foam (SIP) PAS at a wastewater treatment plant (WWTP) provided an initial external validation of our nylon PAS method. Good agreement between sampler types confirmed the WWTP as a point source of ultrashort- and short-chain PFCAs, with TFA and PFPrA dominating emissions in both samplers, highlighting the value of including ultrashort-chain PFCAs in atmospheric measurements. Robust calibration, strong selectivity for gas-phase acids, and low replicate variability make the nylon PAS well suited for reliable quantitation of gas-phase PFCAs. While SIP PAS provide a more comprehensive representation of whole air composition, they exhibit greater variability and higher uncertainty for ionizable compounds. Overall, these

evaluations and improvements to the nylon PAS method greatly increased our confidence in our reported gas-phase PFCA atmospheric concentrations, which we estimate to be accurate within a factor of 2.

Chapter 3 illustrated the suitability of nylon PAS for multi-location atmospheric sampling in an urban city, obtaining comparable mixing ratios of TFA, PFPrA, and PFBA at three sites spanning 40 km across the Greater Toronto Area, with abundances decreasing with increasing chain length. Nylon PAS were effective in capturing variation in PFCA distribution profiles over separate deployments at Toronto Pearson International Airport as well as differences in PFCA levels compared with sites in the surrounding area. During the spring, highly elevated PFPrA mixing ratios at the airport in comparison to neighbourhood sites indicated the presence of a point source of gas-phase PFPrA, a novel finding. The applicability of nylon PAS was further extended by sampling C2–C6 PFCAs across four distinct indoor environments, including academic and home office settings where individuals typically spend a substantial portion of their time. Nylon PAS proved to be well-suited for indoor air quality monitoring, offering a particularly valuable tool for laboratories conducting ultra-trace PFCA analyses. Although the majority of indoor environments can be weak PFCA point sources to the outdoor environment, indoor-to-outdoor transport is likely negligible. This represents the most comprehensive PAS investigation of indoor TFA and PFPrA air concentrations to date, providing valuable insights on indoor sources and exposure risks.

In Chapter 4, the largest nylon PAS sampling network to date was set up along the St. Lawrence River and Estuary, the habitat of the endangered St. Lawrence beluga whales. This large-scale regional sampling provided insight into the spatial distribution of PFCAs across both urban and rural locations, as well as the region as a whole. The broad spatial coverage afforded by the nylon PAS provided signs of distinct source types and enabled preliminary source attribution at some sites. These included PFCA formation via long-range atmospheric transport of precursor compounds from Montreal to Sorel-Tracy, direct gas-phase emissions at one of three Quebec City locations, and short-lived TFA and PFBA precursor emissions which scale with population size. Overall, the work in Chapters 3 and 4 demonstrates the suitability of nylon PAS deployment at multiple locations simultaneously, including urban and rural areas, point sources such as airports, as well as indoor environments, advancing our knowledge of gas-phase PFCA sources and atmospheric spatial distribution.

5.2 Future directions

To further improve the analytical method, the concentrator column separation should be optimized to resolve both the $^{13}\text{C}_2$ -TFA IS interference and the co-elution of sulfate with PFPrA, while maintaining a good separation of C2–C6 PFCAs from one another and from major atmospheric anions, thereby enabling accurate quantitation in a single analytical run. This longer gradient method would further aid in the identification and resolution of potential isobaric interferences with C3–C6 PFCAs, as was illustrated for TFA. The incorporation of a mass-labelled PFPrA IS into the method is an important step towards the accurate identification and quantitation of PFPrA. In analyses where the inclusion of the PFPrA IS is not feasible, utilizing the fragment ion at m/z 119 (formed after the loss of carbon dioxide, CO_2) as a qualitative confirmation ion would greatly aid in PFPrA identification, and the use of the remaining fragment ions for peak identification should be investigated: TFA (m/z 113 $\rightarrow$ 69), PFBA (213 $\rightarrow$ 169), and PFPeA (263 $\rightarrow$ 219). Due to unexpectedly elevated PFPrA concentrations measured in multiple locations, the existence of potential isobaric interference should be investigated. This could be accomplished by re-analyzing the extracts using highly selective chromatography techniques such as LC-MS/MS, to monitor a qualifier fragment ion and verify that the ratio of qualifier to quantifier ions in the sample is within the acceptable percentage from that in an analytical standard. The effectiveness of the nylon PAS component washing procedure for removing PFCAs and other contaminants should be evaluated by analyzing the aqueous rinse following each cleaning stage. In addition, obtaining spike and recovery values at a PFBA spike mass comparable to that collected on the nylon filters during chamber calibration would be highly beneficial. This approach would provide a straightforward and efficient means of improving the accuracy of the PFBA uptake rate and consequently, the reported air concentrations. To improve inter-method comparability, the SIP PAS method should utilize mass-labelled IS and experimentally derived TFA and PFPrA partition coefficients.

To better resolve emission sources at airports, future studies should select secure sampling sites in close proximity to aircraft during and immediately after landing, as the inclusion of such sites represents a critical gap in the current understanding of aircraft contributions to PFCA levels. Given that background contamination remains an ongoing challenge in analytical laboratories, the deployment of nylon PAS as a routine tool for tracking and managing indoor PFCA contamination should be further explored. In addition, studying the presence of PFCAs on surfaces would aid in the improvement of indoor air quality. We aim to use our nylon PAS PFCA measurements, as well

as deposition and water samples collected during the same time period at locations along the St. Lawrence River and Estuary to model the PFCA deposition at the scale of the watershed and compare with levels measured in the water. Expanding measurements to other suspected emission sources beyond WWTP and airports, for example industrial regions and landfills, is essential to increase our understanding of major PFCA sources, and the first step towards lowering emissions. Looking ahead, it would be beneficial to expand our nylon PAS sampling approach to other acidic species with similar properties as TFA, such as haloacetic acids (HAAs) like monochloroacetic acid (MCA), or the smallest perfluoroalkyl sulfonic acid (PFSA), trifluoromethane sulfonic acid (TFMS) with subsequent analysis by liquid chromatography (LC). This would address the lack of measurements for these compounds and expand the utility of nylon PAS past ultrashort- and short-chain PFCAs. Finally, one important long-term goal is the development of a large permanent network of nylon PAS to monitor the abundance of PFCAs, in particular TFA and PFPrA, on a regional, national, or even international scale. In doing so, we would address a critical gap in our knowledge of ultrashort-chain PFCA sources, behaviour, and fate in the atmosphere.

Appendix A: Supporting information for Chapter 2

Method development and validation of nylon passive air samplers for measurement of gas-phase PFCAs

S2.1 Supporting figures and tables for the methods section

Table S2.1 List of PFCA and PFSA analytes and their acronyms and molecular weights (MW). Precursor and product ions for UPLC-MS/MS detection, allocation of the surrogate standards (SS) and internal standards (IS), and instrument limits of detection (iLOD) and quantitation (iLOQ).

Class	# of C	Analyte	Acronym	MW	Precursor ion m/z	Quantifier product ion m/z	Qualifier product ion m/z	Cone Voltage	Collision Voltage	Allocation of SS or IS	iLOD (pg/m ³)	iLOQ (pg/m ³)
PFCA	2	trifluoroacetic acid	TFA	114	112.9	68.9	-	6	10	¹³ C ₂ -TFA	5.77	19.2
	3	perfluoropropanoic acid	PFPrA	164	162.9	118.9	119.1	25	10	¹³ C ₃ -PFPrA	3.84	12.8
	4	perfluorobutanoic acid	PFBA	214	213	169	-	6	10	¹³ C ₄ -PFBA	0.055	0.182
	5	perfluoropentanoic acid	PFPeA	264	263	219	-	6	10	¹³ C ₄ -PFBA	0.046	0.152
	6	perfluorohexanoic acid	PFHxA	314	313	269.1	119	26	10, 15	¹³ C ₂ -PFHxA	0.084	0.279
	7	perfluoroheptanoic acid	PFHpA	364	363	319	169	18	10, 18	¹³ C ₄ -PFOA	0.005	0.016
	8	perfluorooctanoic acid	PFOA	414	413	369	169	22	10, 18	¹³ C ₄ -PFOA	0.031	0.104
	9	perfluorononanoic acid	PFNA	464	463	419	169, 219	28	10, 20, 20	¹³ C ₅ -PFNA	0.038	0.125
	10	perfluorodecanoic acid	PFDA	514	513	469.1	169, 219	28	10, 22, 22	¹³ C ₂ -PFDA	0.063	0.211
	11	perfluoroundecanoic acid	PFUnDA	564	563	519	169, 269	28	11, 25, 25	¹³ C ₂ -PFUnDA	0.052	0.175
	12	perfluorododecanoic acid	PFDoDA	614	613	569.1	169	20	12	¹³ C ₂ -PFDoDA	0.053	0.176

Class	# of C	Analyte	Acronym	MW	Precursor ion m/z	Quantifier product ion m/z	Qualifier product ion m/z	Cone Voltage	Collision Voltage	Allocation of SS or IS	iLOD (pg/m ³)	iLOQ (pg/m ³)
	13	perfluorotridecanoic acid	PFTTrDA	664	663	619	169	10	14, 25	¹³ C ₂ -PFD ₀ DA	0.001	0.002
	14	perfluorotetradecanoic acid	PFTeDA	714	713	669	169	10	14, 28	¹³ C ₂ -PFD ₀ DA	0.092	0.308
	16	perfluorohexadecanoic acid	PFHxDA	814	813	769	169	24	14, 30	¹³ C ₂ -PFD ₀ DA	0.091	0.304
	18	perfluorooctadecanoic acid	PFODA	914	913	869	169	28	16, 34	¹³ C ₂ -PFD ₀ DA	0.048	0.160
PFSA	1	trifluoromethane sulfonic acid	TFMS	150	149	79.8	99	6	20	¹³ C ₄ -PFBS	0.07	0.23
	2	perfluoroethane sulfonic acid	PFEtS	200	199	79.8	99	6	30	¹³ C ₄ -PFBS	0.09	0.29
	3	perfluoropropane sulfonic acid	PFP _r S	250	248.9	79.8	99	6	28, 24	¹³ C ₄ -PFBS	0.05	0.18
	4	perfluorobutane sulfonic acid	PFBS	300	299	79.8	98.8	6	28, 26	¹³ C ₄ -PFBS	0.140	0.467
	5	perfluoropentane sulfonic acid	PFPeS	350	348.9	79.8	99	6	32	¹³ C ₄ -PFBS	0.009	0.028
	6	perfluorohexane sulfonic acid	PFH _x S	400	400.2	79.8	99	6	40, 36	¹⁸ O ₂ -PFH _x S	0.115	0.383
	7	perfluoroheptane sulfonic acid	PFHpS	450	448.9	79.8	99	6	36	¹⁸ O ₂ -PFH _x S	0.092	0.307
	8	perfluorooctane sulfonic acid	PFOS	500	499	79.8	98.8	6	39	¹³ C ₄ -PFOS	0.002	0.007
	9	perfluorononane sulfonic acid	PFNS	550	548.9	79.8	99	6	40	¹³ C ₄ -PFOS	0.004	0.014
	10	perfluorodecane sulfonic acid	PFDS	600	599	79.8	98.8	6	44	¹³ C ₄ -PFOS	0.028	0.092
	11	perfluoroundecane sulfonic acid	PFUnDS	650	649	79.8	99	6	50	¹³ C ₄ -PFOS	0.001	0.002
	12	perfluorodecane sulfonic acid	PFD ₀ DS	700	698.9	79.8	99	6	50	¹³ C ₄ -PFOS	0.059	0.198
	13	perfluorotridecane sulfonic acid	PFTTrDS	750	749	79.8	99	6	55	¹³ C ₄ -PFOS	0.188	0.628

Class	# of C	Analyte	Acronym	MW	Precursor ion m/z	Quantifier product ion m/z	Qualifier product ion m/z	Cone Voltage	Collision Voltage	Allocation of SS or IS	iLOD (pg/m ³)	iLOQ (pg/m ³)
Surrogate standards (SS)												
PFCA	2	¹³ C ₂ -TFA		116	115	70	-	6	10	¹³ C ₈ -PFOA	-	-
	3	¹³ C ₃ -PFPrA		167	166	121	-	20	10	¹³ C ₈ -PFOA	-	-
	4	¹³ C ₄ -PFBA		218	217	172	-	6	10	¹³ C ₈ -PFOA	-	-
	6	¹³ C ₂ -PFHxA		316	315	270	-	26	10	¹³ C ₈ -PFOA	-	-
	8	¹³ C ₄ -PFOA		418	417	372	376	22, 10	10	¹³ C ₈ -PFOA	-	-
	9	¹³ C ₅ -PFNA		469	468	423	-	28	10	¹³ C ₈ -PFOA	-	-
	10	¹³ C ₂ -PFDA		516	515	470	-	28	10	¹³ C ₈ -PFOA	-	-
	11	¹³ C ₂ -PFUnDA		566	565	520	-	28	11	¹³ C ₈ -PFOA	-	-
	12	¹³ C ₂ -PFDoDA		616	615	570	-	20	12	¹³ C ₈ -PFOA	-	-
PFSA	4	¹³ C ₄ -PFBS		304	303	80	99	6	30	¹³ C ₈ -PFOS	-	-
	6	¹⁸ O ₂ -PFHxS		404	402.9	84	-	6	40	¹³ C ₈ -PFOS	-	-
	8	¹³ C ₄ -PFOS		504	503	79.8	98.8	6	39	¹³ C ₈ -PFOS	-	-
Internal Standards (IS)												
PFCA	8	¹³ C ₈ -PFOA		422	421	375.9	-	10	10	-	-	-
PFSA	8	¹³ C ₈ -PFOS		508	506.8	79.8	-	6	39	-	-	-



Figure S2.1 From left to right: steps for the deployment of PAS. From right to left: steps for the collection of PAS (Carmichael, 2022).

Table S2.2 PAS deployment dates and sampling times: at Pearson International Airport, three Toronto sites as part of SWAPIT, and indoors in a chemistry laboratory.

Sample name	Date and time deployed	Date and time retrieved	Sampling time (d)	Sampling time (h)
Pearson International Airport				
November – January	2023-11-03 11:00	2024-01-19 11:00	77.0	1848.0
November – March	2023-11-03 11:00	2024-03-08 11:00	126.0	3024.0
January – March	2024-01-19 11:00	2024-03-08 11:00	49.0	1176.0
March – May	2024-03-19 11:00	2024-05-17 9:00	58.9	1414.0
SWAPIT				
Toronto – High Park	2024-01-29 17:00	2024-03-08 14:00	38.9	933.0
Toronto – Evergreen Brickworks	2024-01-29 13:40	2024-03-11 10:30	41.9	1004.8
Toronto – U of T Scarborough	2024-02-12 15:00	2024-03-11 12:44	27.9	669.7
Quebec				
Quebec City (S39)	2024-06-20 10:38	2024-10-16 20:00	118.4	2841.4
Indoor: Chemistry Laboratory				
Lab 1	2025-01-27 18:59	2025-04-28 12:04	90.7	2177.1

Table S2.3 UPLC-MS/MS operating parameters for analysis of C4–C18 PFCAs and PFASs.

Equipment	Operating Parameters		
LC	Waters Acquity UPLC Xevo TQ-S		
Sampler	Waters Acquity UPLC Sample Manager 1 μL sample injection		
Mobile Phase	A: 10 mM ammonium acetate in water B: 10 mM ammonium acetate in MeOH		
Gradient control for C4–C18 PFAS	Flow set to 0.5 mL/min.		
	Time (min)	%A	%B
	Initial	98	2
	3.00	5	95
	3.10	0	100
	4.00	0	100
	4.10	98	2
6.70	98	2	
Isolator column	Waters Isolator column 2.1×50mm PN: 186004476		
Analytical column	Waters Cortecs UPLC C18 1.6 μm 2.1×50mm PN: 186007093		
MS	Waters Xevo TQ-S Z-spray, ESI, pump at 0.5 mL/min, SIM		

Table S2.4 UPLC-MS/MS operating parameters for analysis of ultrashort-chain (C1–C3) PFCAs and PFASs

Equipment	Operating Parameters		
LC	Waters Acquity UPLC Xevo TQ-S		
Sampler	Waters Acquity UPLC Sample Manager 3 μL sample injection		
Mobile Phase	A: 0.025% acetic acid in water B: 20 mM ammonium acetate in MeOH		
Gradient control for C1–C3 PFAS	Flow set to 0.3 mL/min.		
	Time (min)	%A	%B
	Initial	80	20
	3.00	20	80
	4.00	20	80
	4.10	0	100
	5.00	0	100
	5.10	80	20
	8.00	80	20
Isolator column	Waters Atlantis Premier BEH C18 AX 2.5 μm VanGuard FIT 2.1×50mm PN: 186009375		
Analytical column	Waters Atlantis Premier BEH C18 AX 1.7 μm VanGuard FIT 2.1×100mm PN: 186009360		
MS	Waters Xevo TQ-S Z-spray, ESI, pump at 0.3 mL/min, SIM		

Table S2.5 Calculated equivalent air volumes (V_{air}) for PFCAs and PFSA on SIP disks. Calculated values were used to estimate the equivalent air volumes for nine PFSAs (TFMS, PFETs, PFPrS, PFPeS, PFHpS, PFNS, PFUnDS, PFDods, PFTrDS) and three PFCAs (TFA, PFPrA, PFHpA).

Compound	V_{air} (m ³)	V_{air} value also used for:
PFBS	171.5971	TFMS, PFETs, PFPrS
PFHxS	158.7499	PFPeS, PFHpS
PFOS	201.6739	PFNS
PFDS	146.653	PFUnDS, PFDods, PFTrDS
PFBA	211.5625	
PFPeA	177.578	TFA, PFPrA
PFHxA	223.8836	PFHpA
PFOA	174.626	
PFNA	212.453	
PFDA	212.453	
PFUnDA	196.0252	
PFDoda	218.9806	
PFTrDA	236.0437	
PFTeDA	231.261	
PFPeDA	233.5824	
PFHxDA	227.5474	

Table S2.6 Recoveries (%) of surrogate standards spiked prior to extraction in method blanks (MB), field blanks (FB), and samples at WWTP sites, where PC is primary clarifier, AT is between aeration tanks, and R is upwind reference site. Spiking mass was 10 times lower than usual (50 pg instead of 500 pg). For all surrogate standards with an average recovery below 50%, an external recovery using the average recovery value was applied to the native PFAS in all samples.

Site	PFBA - ¹³ C ₄	PFHxA - ¹³ C ₂	PFHxS - ¹⁸ O ₂	PFOA - ¹³ C ₄	PFNA - ¹³ C ₅	PFOS - ¹³ C ₄	PFDA - ¹³ C ₂	PFUnDA - ¹³ C ₂	PFDoda - ¹³ C ₂
MB	27.0	10.2	1.32	31.4	15.1	25.7	6.75	17.1	1.31
FB - R	57.6	16.4	16.6	90.5	70.8	112.7	101.2	32.2	69.5
FB - PC	53.1	49.5	18.1	33.2	38.1	89.0	25.0	40.3	22.6
FB - AT	35.3	14.3	1.23	31.1	39.8	21.5	43.2	35.5	56.4
PC - 1	20.6	29.4	64.4	26.6	45.8	109.1	6.53	52.3	4.15
PC - 2	14.4	29.8	26.1	7.60	2.43	96.6	0.06	0.05	34.1
AT - 1	62.5	30.9	94.8	63.1	38.0	80.9	117.8	10.2	58.4
AT - 2	28.4	0.08	63.9	44.4	24.5	57.4	0.94	19.8	7.44
R - 1	105	183	96.0	102	1.39	98.2	34.3	31.1	6.70
R - 2	102	75.9	11.9	16.7	58.6	103.8	40.3	60.6	69.4
Average (%)	50.6	44.0	39.4	44.6	33.5	79.5	37.6	29.9	33.0

S2.2 Standard Operating Procedure for Pimoroni Enviro+ Sensor

1. Before plugging in power, plug in the USB extender (to the USB port closer to the center), the keyboard and mouse, and the HDMI cable (connected to a monitor). Ensure the power switch on the USB extender is in the ON position.
2. Plug in the power to the outside USB port and wait for the desktop to load.
3. Change the date and time with the following command: `Sudo date -s 'yyyy-mm-dd hh:mm:ss'`, for example: `'2025-01-20 10:55:30'`.
4. Set the file name:
 - a. Open the file browser (from the app dock on the top left).
 - b. Open 'Pimoroni' folder.
 - c. Decide what sensor data you want to save: 'weather', 'particulates', 'gas' or 'enviropius all' and locate the python file that corresponds to that analysis (note the file name):
 - i. `Weather_save.py`
 - ii. `Particulates_save.py`
 - iii. `Gas_save.py`
 - iv. `Enviropius_all_save.py`
 - d. Right click the corresponding .py file, e.g. the 'weather_save.py' file, and select 'text editor'.
 - e. Find the line (where <FILE_NAME> is a specific file name):
`dat = open ('<FILE_NAME >', 'A')`
 - f. Replace the <FILE_NAME> with your desired file name, e.g. 'weather Jan 9 2025'. Ensure you do not remove the single quotation marks. If you specify a file that does not exist, one will automatically be created for you.
 - g. Save the file.
5. Run the data collection:
 - a. Open the terminal app (black rectangle icon). Type the following command to move to the Pimoroni folder: `cd Pimoroni`, then hit enter. Use the following command to run the python file you edited in step 4: `python weather_save.py`
 - b. Readings will show up in the terminal window and are being written to the file you specified in step 4f.
 - c. Stop the readings at any time using the following keyboard shortcut: `Ctrl+C`.
 - d. The USB extender with the keyboard and mouse, as well as the HDMI cable, can now be disconnected and the Pi Enviro+ relocated to the measurement area. The Pi Enviro+ will continue measuring and recording data.
 - e. Note that the power must remain plugged in! Loss of power will reset the Pi Enviro+ and the readings will need to be initiated again starting with step 5a.
 - f. Plugging the USB extender back in will also reset the Pi Enviro+, terminating data collection.
6. To stop collection and retrieve the file, unplug the power from the Pi Enviro+, then reconnect the HDMI and USB extender with mouse and keyboard, then reconnect power. Data collection will be stopped already. Plug in a USB stick and use file explorer to copy the file you chose in step 4f from the 'Pimoroni' folder to the USB drive. Append a .txt extension to the file(s) on the USB stick to make it easier to open them on another PC.

S2.3 Supporting equations, figures and tables for the results and discussion section

S2.3.1 Supporting information for Section 2.3.2

Improving the quantitation of PFPrA

F-tests (two sample for variance) were performed on the quantified PFPrA concentrations (ng/mL) using the $^{13}\text{C}_1$ -PFPrA IS compared with the $^{13}\text{C}_1$ -TFA IS and $^{13}\text{C}_4$ -PFBA IS showed that the sample variances were equal (F value < F critical) (Table S2.7).

Table S2.7 Results of F-tests and two sample t-tests assuming equal variance performed on PAS extracts from samples deployed at High Park and Evergreen Brickworks during SWAPIT. PFPrA concentrations determined using the $^{13}\text{C}_1$ -PFPrA IS compared to the $^{13}\text{C}_1$ -TFA IS and $^{13}\text{C}_4$ -PFBA IS. An F value lower than the F critical value means the variances are equal. For the t-test a value of 4 was used for the degrees of freedom, and the T critical value was 2.78. A P value below 0.05 (shown in **bold**) indicates a statistically significant difference between values.

Sampling Location	Test statistic	$^{13}\text{C}_1$ -PFPrA vs. $^{13}\text{C}_1$ -TFA	$^{13}\text{C}_1$ -PFPrA vs. $^{13}\text{C}_4$ -PFBA
High Park	F	6.08	15.25
	F critical	9.55	19.00
	T stat	0.91	3.09
	P value	0.42	0.04
Evergreen Brickworks	F	1.34	2.69
	F critical	19.00	19.00
	T stat	2.12	8.87
	P value	0.10	0.001

Table S2.8 Peak areas of $^{13}\text{C}_1$ -TFA, $^{13}\text{C}_1$ -PFPrA, and $^{13}\text{C}_4$ -PFBA internal standards in aqueous C2–C6 PFCA standards and extracts of PAS (n = 3) deployed at Evergreen Brickworks.

	Peak areas in standards	Peak areas in PAS
$^{13}\text{C}_1$ -TFA	930 – 1970	680 – 1300
$^{13}\text{C}_1$ -PFPrA	950 – 1950	800 – 1000
$^{13}\text{C}_4$ -PFBA	940 – 1870	1560 – 2700

Table S2.9 TFA and PFPrA average concentrations (pg/m³) measured in PAS deployed at Pearson International Airport, analyzed using two separate techniques: the concentrator column and short gradient compared with the loop and long gradient. ¹³C₂-TFA displayed a co-eluting isobaric interference when analyzed with the short gradient.

PAS	PFCA	Short gradient (pg/m ³)	Long gradient (pg/m ³)	Ratio (short/long gradient)
Nov–Jan	TFA	13	20	0.7
	PFPrA	51	8	6.5
Nov–Mar	TFA	90	141	0.6
	PFPrA	75	15	5.1
Jan–Mar	TFA	173	258	0.7
	PFPrA	229	56	4.1
Mar–May	TFA	417	609	0.7
	PFPrA	4127	2130	1.9

Table S2.10 Peak areas of ¹³C₂-TFA and ¹³C₁-PFPrA IS in a 500 ppt C2–C6 PFCA standard, PAS extracts deployed in Quebec City (QC S39-1) and at Pearson International Airport (YYZ-5 and YYZ-13). Two separate aliquots of each sample and standard were analyzed, each spiked with either ¹³C₂-TFA or ¹³C₁-PFPrA prior to IC-MS analysis utilizing the loop and long gradient method.

	QC S39-1	YYZ-5	YYZ-13	500 ppt standard
¹³ C ₂ -TFA	1955	1272	1185	2105 (QC) 1282 (YYZ)
Ratio ¹³ C ₂ -TFA (standard : sample)	1.1	1.0	1.1	-
¹³ C ₁ -PFPrA	426	208	281	683
Ratio ¹³ C ₁ -PFPrA (standard : sample)	1.6	3.3	2.4	-

In contrast to the nearly identical retention time observed for PFPrA and its internal standard under the short gradient separation conditions (Figure S2.2a), the longer gradient caused a retention time shift of approximately 0.8 min for PFPrA and ¹³C₁-PFPrA in a sample extract, compared with a standard (Figure S2.2b). This shift in retention time makes identification of PFPrA difficult in the absence of the PFPrA IS, particularly in samples with complex matrices. Additionally, some samples display a second peak in the PFPrA channel, eluting ≤ 2 min after PFPrA. Since only one peak was observed for the same sample under the short gradient conditions, it is possible for the interfering peak to co-elute with PFPrA, similarly to what was observed for TFA (Section 2.3.1), which suggests that the short gradient separation may overestimate PFPrA levels in some samples.

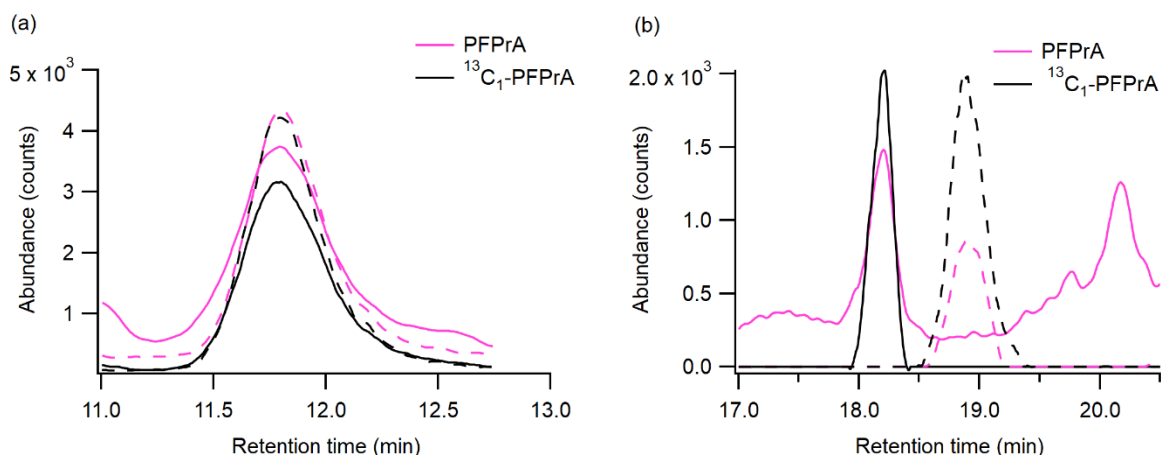


Figure S2.2 Chromatograms depicting the abundance of PFPrA (pink, m/z 163) and $^{13}\text{C}_1$ -PFPrA (black, m/z 164) signals (solid lines) in a PAS sample (QC39-1) deployed in Quebec City (Jun. 20 – Oct. 16, 2024). Overlaid dashed lines represent PFPrA (pink) and $^{13}\text{C}_1$ -PFPrA (black) in a 500 ppt standard. (a) shows separation using the concentrator column (750 μL injection) and a short gradient, (b) shows separation using the loop (250 μL) and a long gradient.

S2.3.2 Supporting information for Section 2.3.3

Extraction efficiency of C2–C6 PFCAs from nylon filters

In Sections 2.3.3, 2.3.5, 2.3.6, and 2.3.7, a Welch t-test (Equation S2.1) was used to calculate a t statistic for two average values, when provided with the original sample sizes and standard deviations. When provided, the t critical values were obtained from Microsoft Excel. A t statistic greater than the t critical value indicates a significant difference. An easier way to visualize this statistical difference is through calculation of a p value, which was done in Excel. At a 95% confidence interval, a p value below 0.05 indicates a significant difference exists, while a p value above 0.05 indicates that a significant difference does not exist.

Equation S2.1 T statistic for two sample (Welch) t-test using two average values ($\bar{x}$) and their respective sample sizes (n) and standard deviations (s).

$$t = \frac{(\bar{x}_1 + \bar{x}_2)}{\sqrt{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)}}$$

Table S2.11 % Recoveries of 4 ng TFA, 1 ng PFPrA, 0.5 ng C4–C6 PFCAs spiked in method blanks extracted with solvents of varying NaOH concentrations (n = 3). The notation RT describes the extraction solvent and samples which were stored at room temperature. All recoveries were blank subtracted.

	0 mM	1 mM	2 mM	3 mM	3 mM (RT)	4 mM
TFA	9.7 ± 2.3	82 ± 19	77 ± 6	71 ± 14	72 ± 9	74 ± 3
PFPrA	35 ± 43	-83 ± 119	38 ± 69	50 ± 29	20 ± 53	78 ± 57
PFBA	-	106 ± 23	131 ± 13	136 ± 26	114 ± 19	115 ± 19
PFPeA	-	89 ± 8	107 ± 4	129 ± 57	102 ± 2	104 ± 7
PFHxA	-	104 ± 10	130 ± 33	106 ± 5	99 ± 2	104 ± 3

Table S2.12 Method limits of detection (mLOD) and quantitation (mLOQ), and instrument limits of detection (iLOD) and quantitation (iLOQ) obtained during the low concentration extraction efficiency experiment. iLODs and iLOQs obtained during the high concentration extraction efficiency experiment are provided for reference. The 3 mM NaOH extraction solvent was used for all trials.

	High concentration spike		Low concentration spike			
	iLOD (ng)	iLOQ (ng)	mLOD (ng)	mLOQ (ng)	iLOD (ng)	iLOQ (ng)
TFA	-	-	0.34	1.12	0.16	0.53
PFPrA	0.30	1.01	1.32	4.39	0.83	2.78
PFBA	0.02	0.07	0.24	0.81	0.19	0.65
PFPeA	0.10	0.32	0.16	0.53	0.15	0.50
PFHxA	0.02	0.07	0.05	0.17	0.03	0.09

Table S2.13 Statistical comparison of C2–C6 PFCA recoveries from spiked method blanks (n = 3) extracted using 3 mM NaOH at 4 °C and room temperature. The high concentration spike consisted of 20 ng C3–C6 PFCAs and the low concentration spike was 4 ng TFA, 1 ng PFPrA, 0.5 ng C4–C6 PFCAs. A value of 4 was used for degrees of freedom in calculations. The t critical value at 95% confidence is 2.78.

	High concentration spike		Low concentration spike	
	t value	p value	t value	p value
TFA	-	-	0.23	0.83
PFPrA	0.94	0.40	0.74	0.50
PFBA	7.81	0.001	1.18	0.30
PFPeA	0.00	1.00	0.82	0.46
PFHxA	0.91	0.41	2.25	0.09

S2.3.3 Supporting information for Section 2.3.5

Calibration of PFBA and revisiting TFA using atmospheric chamber

Table S2.14 Statistical comparison of measured and predicted PFBA_(g) linear uptake rates PFBA_(g) (ng m⁻³) t(h) / [PFBA_(filter) (ng)] onto nylon PAS. A Welch t-test at a 95% confidence interval was performed between the measured PFBA uptake rate determined from our chamber calibration (without^a and with^b correction for plausible 82% recovery), and the predicted PFBA uptake rate which was calculated using the measured TFA_(g) uptake rate of 113 ± 12 TFA_(g) (ng m⁻³) t(h) / [TFA_(filter) (ng)] to and Fuller's Law.

Predicted uptake rate	Measured uptake rate	t _{calculated}	t _{critical}	p value
161 ± 17	203 ± 7 ^a	7.32	2.12	0.000002
	167 ± 5 ^b	1.16	2.12	0.26

Table S2.15 Statistical comparison of the measured TFA_(g) linear uptake rate onto nylon PAS determined from our chamber calibration, 146 ± 12 TFA_(g) (ng m⁻³) t(h) / [TFA_(filter) (ng)] to previously measured and predicted uptake rates. A Welch t-test at a 95% confidence interval was performed between our measured TFA_(g) uptake rate, our group's prior TFA_(g) measured uptake rate and the predicted rate which was based on previous HNO_{3(g)} calibrations. Both measured uptake rates were corrected for the 83% extraction efficiency of TFA. In the calculation of the predicted uptake rate, the extraction efficiency of NO₃⁻ was not determined or corrected for.

Study	TFA uptake rate	DF	t _{calculated}	t _{critical}	p value
Vanhouwaert et al. (2025) – measured rate	113 ± 12	16	4.85	2.12	0.0002
Carmichael (2022) – predicted rate	182 ± 68	10	1.45	2.23	0.18

S2.3.4 Supporting information for Section 2.3.6

Duration of PAS deployment and potential sampling bias

Table S2.16 Statistical comparison of C2–C5 PFCAs measured at Pearson International Airport using PAS during a 6-month deployment (n = 3) compared with the weighted average of two shorter deployments (n = 5). A value of 6 was used for degrees of freedom in calculations. The t critical value at 95% confidence is 2.45. PFHxA was not measured in any samples.

PFCA	t value	p value
TFA	1.32	0.24
PFPrA	3.37	0.02
PFBA	0.61	0.57
PFPeA	5.57	0.001

S2.3.5 Supporting information for Section 2.3.7

Passive air sampling at a wastewater treatment plant: comparison between nylon PAS and SIP PAS and observed temporal trends

Table S2.17 Statistical representation of C2–C6 PFCA on-site enrichment at the primary clarifier and aeration tank for nylon PAS and SIP PAS measurements. For nylon PAS calculations, a value of 4 was used for the DF, and for SIP PAS calculations a value of 2 was used for the DF.

	Primary clarifier		Aeration tank	
	Nylon PAS	SIP PAS	Nylon PAS	SIP PAS
TFA	0.002	0.45	0.86	0.79
PFPrA	0.49	0.42	0.49	0.46
PFBA	0.001	0.37	0.28	0.55
PFPeA	0.003	0.34	0.001	0.98
PFHxA	-	0.27	-	0.51

Table S2.18 Ratio of average C2–C6 PFCA concentrations measured using nylon PAS to SIP PAS at three sites within the WWTP. Error shown is the propagated error associated with the ratio calculations, determined using the standard deviation between triplicate nylon PAS measurement and the relative error between duplicate SIP disk measurements. *PFPrA levels cannot be directly compared as the two methods used different internal standards to quantify PFPrA: PFPrA in SIPs was quantified using $^{13}\text{C}_3$ -PFPrA for the LC-MS/MS, while for nylon PAS $^{13}\text{C}_1$ -TFA was used for the IC-MS.

	Reference Site		Primary Clarifier		Between Aeration Tanks	
	PAS/SIP	Error	PAS/SIP	Error	PAS/SIP	Error
TFA	1.9	1.5	1.8	1.0	1.6	0.6
PFPrA*	0.2	0.1	0.1	0.1	0.1	0.1
PFBA	2.8	0.9	0.6	0.6	1.3	1.3
PFPeA	7.0	1.1	0.9	1.0	1.9	2.0
PFHxA	-	-	-	-	1.6	0.1
ΣPFCAs	0.6	0.1	0.6	0.1	0.8	0.1
ΣC2, C4-C6 PFCAs	2.0	1.1	1.4	0.4	1.5	0.3

Table S2.19 Statistical comparison of C2–C6 PFCA atmospheric concentrations measured at a WWTP using nylon PAS (n = 3) and SIP disks (n = 2). A value of 3 was used for the DF and the t critical value at the 95% confidence interval was 3.18.

	Reference site		Primary clarifier		Aeration tank	
	t value	p value	t value	p value	t value	p value
TFA	1.59	0.21	1.87	0.16	2.07	0.13
PFPrA	3.89	0.03	2.19	0.12	2.65	0.08
PFBA	6.85	0.006	0.57	0.61	0.42	0.70
PFPeA	51.5	0.00002	0.09	0.94	1.11	0.35
PFHxA	-	-	-	-	7.79	0.004

Table S2.20 Recoveries (%) of 20 ng each of native compounds TFA, PFPrA, TFMS, PFEtS, PFPeS, and 25 ng each of surrogate standards ¹³C₂-TFA, ¹³C₃-PFPrA, and ¹³C₄-PFBS in blank SIP disks prior to extraction.

	TFA	TFMS	PFPrA	PFEtS	PFPeS	¹³ C ₂ -TFA	¹³ C ₃ -PFPrA	¹³ C ₄ -PFBS
Spike 1	178	117	84	103	98	98	102	108
Spike 2	180	129	80	111	88	81	84	76
Spike 3	175	103	77	100	99	91	96	92
Spike 4	143	104	70	101	100	106	111	88
Average	169	113	78	104	96	94	98	91
Standard Deviation	18	12	6	5	5	11	11	13

Table S2.21 Statistical comparison of C4–C10 PFCA and PFOS atmospheric concentrations measured at a WWTP using SIP PAS in 2009 (n = 2) and 2023 (n = 2). A value of 2 was used for the DF and the t critical value at the 95% confidence interval was 4.30.

	Reference site		Primary clarifier		Aeration tank	
	t value	p value	t value	p value	t value	p value
PFBA	0.92	0.46	1.03	0.41	0.27	0.81
PFPeA	36.5	0.001	137	0.0001	0.67	0.57
PFHxA	0.04	0.97	0.03	0.98	4.05	0.06
PFHpA	0.52	0.65	0.44	0.70	0.87	0.48
PFOA	0.84	0.49	0.51	0.66	1.55	0.26
PFNA	0.69	0.56	0.29	0.80	0.13	0.91
PFDA	0.74	0.53	1.29	0.33	15.4	0.004
PFOS	0.20	0.86	0.45	0.69	3.03	0.09

Appendix B: Supporting information for Chapter 3

Nylon passive air sampler measurement of gas-phase C2–C6 PFCAs in the Greater Toronto Area

S3.1 Supporting equations and tables for the results and discussion section

Table S3.1 Mean atmospheric mixing ratios (ppqv) and concentrations measured using replicate (n) nylon PAS. Mass loadings (pg/m³) are also provided for SWAPIT measurements. Relative standard deviations (%) for replicate measurements are shown in brackets.

Study of Winter Air Pollution in Toronto (SWAPIT)							
Location	n	Units	TFA	PFPrA	PFBA	PFPeA	PFHxA
Toronto, ON – High Park	3	ppqv	87.9 (34)	59.9 (23)	10.6 (39)	<2.7	<1.2
		pg/m ³	444	436	101	<32	<17
Toronto, ON – Evergreen Brickworks	3	ppqv	77.6 (9)	70.0 (13)	8.0 (8)	<2.5	<1.1
		pg/m ³	393	509	75.7	<30	<15
Scarborough, ON – University of Toronto, Scarborough Campus	3	ppqv	72.3 (16)	60.3 (18)	7.9 (6)	<3.8	<1.7
		pg/m ³	367	288	60.6	<45	<23
Pearson International Airport							
Location	n	Units	TFA	PFPrA	PFBA	PFPeA	PFHxA
November to January	2	ppqv	4.0 (121)	7.1 (53)	22.6 (7)	1.6 (27)	<0.4
January to March	3	ppqv	50.9 (18)	31.3 (4)	18.5 (21)	2.2 (24)	<0.6
March to May	5	ppqv	124 (57)	582 (37)	23.2 (35)	1.4 (53)	<0.6
Toronto, ON Site 1 (York University)	3	ppqv	80.5 (13)	5.9 (39)	14.2 (23)	0.5 (54)	<0.2
Brampton, ON Site 2	3	ppqv	39.9 (24)	3.0 (15)	10.2 (21)	0.1 (19)	<0.2
Toronto, ON, Reference Site	3	ppqv	41.2 (19)	4.8 (27)	11.4 (4)	0.5 (16)	<0.2
Indoor							
Location	n	Units	TFA	PFPrA	PFBA	PFPeA	PFHxA
Lab 1	3	ppqv	2433 (11)	4099 (2)	37.6 (22)	17.8 (13)	2.7 (20)
Lab 2	3	ppqv	50.3 (12)	22.3 (82)	17.1 (61)	0.1 (173)	0.6 (15)
Office 1	3	ppqv	35.8 (59)	36.5 (45)	14.9 (30)	<0.5	<0.7
Office 2	3	ppqv	8.7 (74)	15.7 (44)	8.3 (26)	<0.5	1.6

Table S3.2 Outcome (p values) of Welch t-test showcasing differences between C2–C5 PFCA concentrations measured at Pearson International Airport and surrounding three sites from November 2023 to March 2024.

	TFA	PFPrA	PFBA	PFPeA
Site 1	0.17	0.008	0.04	0.006
Site 2	0.33	0.008	0.004	0.001
Reference	0.33	0.008	0.003	0.003

Table S3.3 Outcome (p values) of Welch t-test showcasing differences between C2–C5 PFCA concentrations measured at York University (Site 1) and two nearby sites from November 2023 to March 2024. Significant differences at the 95% confidence interval are **bolded**.

	TFA	PFPrA	PFBA	PFPeA
Site 2	0.007	0.47	0.19	0.82
Reference	0.009	0.11	0.16	0.09

Table S3.4 Outcome (p values) of Welch t-test showcasing differences between C2–C6 PFCA concentrations measured in Lab 1 compared with Lab 2, Office 1 and Office 2. With the exception of the bolded entry, all presented differences are significant at the 95% confidence interval.

	TFA	PFPrA	PFBA	PFPeA	PFHxA
Lab 2	0.0001	2.7E-07	0.05	0.0002	0.003
Office 1	0.0001	2.7E-07	0.01	-	-
Office 2	9.9E-05	2.6E-07	0.004	-	0.02

Table S3.5 Outcome (p values) of Welch t-test showcasing differences C2–C6 PFCA concentrations measured in three indoor locations Lab 2 compared with Office 1 and Office 2. A value of 4 was used for degrees of freedom. Significant differences at the 95% confidence interval are **bolded**.

	TFA	PFPrA	PFBA	PFPeA	PFHxA
Lab 2 vs Office 1	0.32	0.38	0.76	-	-
Lab 2 vs Office 2	0.001	0.59	0.22	-	8.54E-05
Office 1 vs Office 2	0.10	0.12	0.08	-	-

Table S3.6 Method limits of detection (mLOD) in mixing ratios (ppqv) for nylon PAS during selected deployments. SWAPIT: average deployment duration of 36 days (~1 month), Pearson International Airport: deployment duration 59 days (~2 months) at the airport (March to May) and one average deployment of 179 days (~6 months) in surrounding area, and indoor: average of 91 days (~3 months).

	SWAPIT	Airport	Airport	Indoor
	1 month	2 months	6 months	3 months
TFA	3.1	4.5	1.5	11.5
PFPPrA	2.6	5.5	1.8	9.2
PFBA	0.8	1.9	0.6	2.8
PFPeA	3.0	0.7	0.2	0.5
PFHxA	1.3	0.6	0.2	0.7

Equation S3.1 Estimated annual TFA emissions (E) from Lab 1. An air exchange rate (AER) of 0.72 h^{-1} and a room volume of 200 m^3 were assumed. The average TFA mass loading measured in Lab 1 was used for calculations (11.3 ng/m^3), and a value of $1.77 \times 10^{20} \text{ mol}$ was used as an estimation of the moles of air in the atmosphere (Seinfeld & Pandis, 2006; Trenberth et al., 1987).

$$E = AER \times V \times C \left(\frac{\text{ng}}{\text{m}^3} \right)$$

$$E = 0.72 \text{ h}^{-1} \times 200 \text{ m}^3 \times 11.3 \text{ ng m}^{-3} = 1627.2 \text{ ng h}^{-1} = 14.3 \text{ mg yr}^{-1}$$

$$\begin{aligned} \text{TFA mixing ratio} &= \frac{0.0143 \text{ g yr}^{-1}}{114.023 \frac{\text{g}}{\text{mol}} \text{ TFA} \times (1.77 \times 10^{20} \text{ mol air})} = 7.06 \times 10^{-25} \text{ mol mol}^{-1} \\ &= 7.06 \times 10^{-10} \text{ ppqv} \end{aligned}$$

Appendix C: Supporting information for Chapter 4

Nylon passive air sampling network for atmospheric measurements of C2–C6 PFCAs along the St. Lawrence River and Estuary, Quebec

S4.1 Supporting equations and tables for the results and discussion section

Table S4.1 Method limits of detection (mLODs) in ppqv for a 117 day (four month) average PAS deployment.

TFA	PFPrA	PFBA	PFPeA	PFHxA
8.25	0.732	2.31	0.654	0.182

Table S4.2 Mean atmospheric mixing ratios (ppqv) and measured using replicate (n) nylon passive air samplers at locations along the St. Lawrence River, Quebec. Relative errors (%) are displayed for duplicate measurements (n = 2) and relative standard deviations (%) are displayed for triplicate measurements (n = 3).

Site #	n	TFA		PFPrA		PFBA		PFPeA		PFHxA
		ppqv	Error (%)	ppqv	Error (%)	ppqv	Error (%)	ppqv	Error (%)	ppqv
S1	3	95.2	11	43.0	21	11.2	9	3.66	25	<0.184
S2	3	103	13	17.8	22	11.2	9	6.46	15	<0.184
S5	3	91.9	6	11.0	29	8.6	10	8.32	26	<0.183
S6	2	75.6	19	14.7	5	11.0	11	7.49	21	<0.181
S7	3	33.1	18	18.4	55	10.7	4	5.59	15	<0.183
S37	3	67.6	17	17.2	46	13.1	11	9.71	6	<0.181
S39	3	49.7	12	23.3	72	11.1	5	4.45	13	<0.181
S40	3	324	27	233	20	13.5	3	12.8	9	<0.180
S45	3	28.7	15	4.77	7.6	4.30	0.1	2.51	0.4	<0.183
S16	2	621	45	273	12	8.00	5	14.8	3	<0.181
S57	3	33.1	35	47.0	117	4.52	17	6.07	18	<0.180
S58	3	50.9	5	22.8	61	4.91	10	7.49	3	<0.181
S19	3	45.2	22	35.1	47	6.04	5	8.05	7	<0.181
S22	3	42.2	8	24.6	76	8.27	23	18.9	20	<0.182

Equation S4.1 T statistic for two sample (Welch) t-test using two average values ($\bar{x}$) and their respective sample sizes (n) and standard deviations (s).

$$t = \frac{(\bar{x}_1 + \bar{x}_2)}{\sqrt{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)}}$$

Table S4.3 Ratio of PFPeA concentrations to PFBA at 14 sites along St. Lawrence River, Quebec and their statistical significance (Welch t-test). Instances where PFPeA was higher than PFBA are **bolded**.

	PFPeA/PFBA	p value
S1	0.33	0.001
S2	0.58	0.004
S5	0.97	0.86
S6	0.68	0.04
S7	0.52	0.001
S37	0.74	0.02
S39	0.40	0.000
S40	0.95	0.38
S45	0.58	0.002
S16	1.85	0.0006
S57	1.34	0.11
S58	1.53	0.001
S19	1.33	0.006
S22	2.28	0.01

Histograms (Figure S4.1) depict distribution of individual C2–C5 PFCA concentrations measured in 40 extracts from PAS deployed along the St. Lawrence River, Quebec. An assessment of the normality of data distribution was conducted on individual C2–C5 PFCA concentrations via two statistical tests, the Shapiro-Wilk and Jarque-Bera tests. The results illustrate that the concentration distributions for PFCAs, except PFBA, are not normally distributed at the 99% confidence level (Shapiro-Wilk) and the 95% confidence level (Jarque-Bera). Due to this outcome, the Tukey IQR method is appropriate for determining outliers as it makes no assumptions on the data distribution. The upper limits (i.e. inner and outer fences) of the data distribution are presented in Table S4.5. Data outside the inner fences but inside the outer fences are classified as outliers. Data outside the outer fences are classified as far outliers. The outer fences for TFA and PFPrA are approximately equivalent to their respective means plus one standard deviation (σ), which in a normal Gaussian distribution encompasses 68.3% of the data. The outer fences for PFBA and PFPeA are greater than their respective means plus 3σ , which in a normal distribution encompasses 99.7% of the data. The inner fence for PFBA is approximately equal to the mean plus 3σ (i.e. 99.7% of data), while the inner fence for PFPeA is approximately equal to the mean plus 2σ (i.e. 95.5% of data).

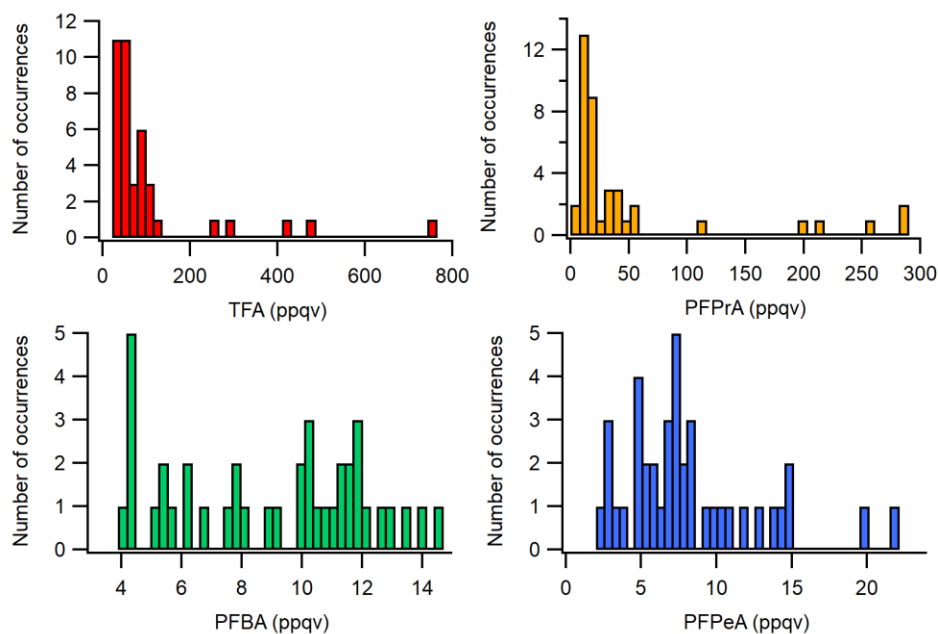


Figure S4.1 Histograms depicting distribution of C2–C5 abundances in PAS extracts (n = 40).

Table S4.4 Statistical outcome for Shapiro-Wilk and Jarque-Bera tests on C2–C5 PFCA concentrations measured in PAS extracts (n = 40). A Shapiro-Wilk test statistic, W, closer to 1 indicates normality, while smaller values of W indicate deviation from normality. P values below 0.05 show that at the 95% confidence level, the PFCA concentration distributions do not follow a normal Gaussian distribution. A Jarque-Bera test statistic, JB, higher than the critical value, 4.097, indicates departure from normality.

Statistical Test	Test Statistic	TFA	PFPrA	PFBA	PFPeA
Shapiro-Wilk	W	0.54	0.58	0.93	0.90
	p value	5.50E-10	1.62E-09	0.02	0.002
Jarque-Bera	JB	191	43.2	3.1	11.5

Table S4.5 Upper inner ($Q3 + 1.5 \times IQR$) and outer fences ($Q3 + 3 \times IQR$) for C2–C5 PFCAs distribution in PAS extracts ($n = 40$), where IQR is the interquartile range, from the 25th to 75th percentiles of data distribution. The inner and outer fences are compared to the mean plus one, two, and three standard deviations (σ), representing 68.3%, 95.5, and 99.7% of a normal Gaussian data distribution, respectively, with closest values shown in **bold** font.

	TFA	PFPrA	PFBA	PFPeA
Inner fence	173	86	20	17
Outer fence	253	130	28	25
Mean + σ	253	131	12	13
Mean + 2σ	399	210	15	17
Mean + 3σ	545	289	19	22

Equation S4.2 Formula for calculating t statistic for Pearson Correlation, where r is the Pearson correlation coefficient, and n is the sample size.

$$t_{\text{statistic}} = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}}$$

Table S4.6 Statistical outcome of Pearson Correlation between population size and gas-phase PFCA concentrations measured along the St. Lawrence River, QC. A Pearson coefficient (r) value between -0.1 and 0.1 indicates a negligible correlation. Significant relationships at the 95% confidence level, are shown in **bold** font.

	All sites		Excluding S40 and S16	
	r	p value	r	p value
TFA	-0.03	0.91	0.72	0.009
PFPrA	-0.07	0.81	0.21	0.51
PFBA	0.55	0.041	0.57	0.052
PFPeA	-0.29	0.32	-0.27	0.39
ΣC2–C5 PFCAs	-0.04	0.88	0.74	0.006