Analytical Methods

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Anal. Methods*, 2026, **18**, 3600

Direct-injection suppressed ion chromatography-mass spectrometry with online preconcentration for short- and ultra short-chain perfluoroalkyl carboxylic acids in fresh water

Jessica Clouthier, Trevor C. VandenBoer and Cora J. Young *

This work developed a novel analytical method to detect short- and ultra-short chain perfluoroalkyl carboxylic acids (PFCAs) in freshwater samples by direct injection using ion chromatography mass spectrometry (IC-MS). Ultra-short chain PFCAs, including trifluoroacetic acid (TFA), are often present in aqueous environments at higher concentrations than longer chain PFCAs, however there are currently a limited number of methods that can analyze them. Detection limits ranged between 1.3 and 2.8 ng L^{-1} (ppt) of the PFCAs (C2–C6) analyzed and were comparable to those of other LC-MS and GC-MS methods. The precision of this method ranged from 0.4–7.6% for all the PFCAs (C2–C6). An advantage of this method is that small samples sizes under 1 mL can be used. This method was applied to real freshwater samples including tap water, precipitation, lake water, and river water. TFA was detectable in most of the samples with online pre-concentration and no other additional pretreatment sample preparation; however, method performance decreased in samples with high conductivity. A new unidentified isobaric interferent for TFA was present in most of the freshwater samples.

Received 19th December 2025
Accepted 2nd March 2026

DOI: 10.1039/d5ay02105g

rsc.li/methods

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a widely used man-made class of organofluorinated compounds containing over 4700 chemicals.[1] Perfluoroalkyl acids (PFAA) are a subset of PFAS that are widely used in many consumer and industrial products including stain repellents, non-stick food paper or pans, and firefighting foams.[2,3] Perfluoroalkyl carboxylic acids (PFCA, $C_nF_{2n+1}COOH$), a major class of PFAAs, are highly polar, stable in the environment, resistant to photolysis, and are miscible and highly soluble in water. They have large acid dissociation constants, low Henry's law constants, and low octanol–water partitioning coefficients.[4] Long chain (≥8 carbons) PFCAs are toxic in the environment, bioaccumulate, and magnify in food chains.[5,6] While short chain (≤7 carbons) PFCAs do not bioaccumulate in the conventional sense they are present in humans[7] and also accumulate in plants and are phytotoxic.[8,9] The high persistence of all PFCAs leads to their accumulation in the environment.[8,10–12] Ultra-short-chain (2–4 carbons) PFCAs are often present in much higher concentrations in the environment, especially aqueous environments, in comparison to other PFCAs.[13,14] In particular, trifluoroacetic acid (TFA), the shortest PFCA with a pK_a of 0.23–0.47,[15,16] is frequently found at much higher abundance than other PFAS.[13,17] Ultra-short-chain PFCAs are highly water soluble and mobile in water, resulting in their rapid entry into the water cycle, while their very persistent nature prevents many removal processes from reducing their burden in freshwater.[13,18]

One major source of ultra-short-chain PFCAs to the aquatic environment is atmospheric formation from several precursor gases. The Montreal Protocol is a global agreement to regulate and phase out chlorofluorocarbons (CFCs), commonly used as refrigerants, due to their role as stratospheric ozone-depleting substances. Montreal Protocol-mandated CFC replacements have degradation pathways known to produce ultra-short-chain PFCAs.[19–22] The most recent Kigali Amendment was added to further limit the production of CFCs and their prior replacements.[22] One major class of new replacements to satisfy the Kigali Amendment are hydrofluoroolefins (HFOs), which were selected due to their shorter atmospheric lifetimes as well as their lower global warming potentials in comparison to CFC and previous replacement compounds. However, some HFOs have a 100% degradation yield of TFA under atmospheric conditions.[8] The increased usage of HFOs under the Kigali Amendment to the Montreal Protocol is therefore expected to cause an increase in ultra-short-chain PFCA production and, as a result, concentrations in the environment.[23] Environmental increases of TFA and other ultra-short-chain PFCAs have already been attributed to the introduction of CFC replacements.[9,24] Another source of TFA to natural waters is photooxidation of molecules containing an aryl-CF_3 group, including

Department of Chemistry, York University, Toronto, ON, Canada. E-mail: youngcj@yorku.ca

This journal is © The Royal Society of Chemistry 2026

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

pharmaceuticals and pesticides.[25–27] Additionally, the biodegradation of PFAS,[28] as well as emissions from landfills, industry, and wastewater,[25,29] are possible contributors to the environmental burden of ultra-short-chain PFCAs. The relative contributions of these sources to ultra-short-chain PFCA contamination in fresh waters are not yet well understood.

Quantitative measurements of ultra-short-chain PFCAs in fresh waters are increasingly important given the prevalence of these molecules and their expected accumulation in fresh and marine waters. The main instruments currently used to separate and quantify environmental PFCAs are liquid and gas chromatographs fitted with mass spectrometers. Liquid chromatography (LC) has been the method of choice for separation of PFCAs without requiring derivatization, with a growing variety of stationary phases being reported fit for use including reverse phase (RP),[17] hydrophilic liquid interaction (HILIC),[30] ion exchange (IE),[25,31] and mixed-mode ion exchange within an RP column (MM).[24,30,32] A notable difference typically exists between instruments, where ion chromatography (IC) system components are made entirely of inert polymeric materials like polyether ether ketone (PEEK) instead of stainless steel in LC systems, to prevent analyte–surface interactions for ionic species. Here, we use LC as an umbrella term encompassing RP, HILIC, IE, and MM, unless further delineation is required, and IC to denote the different instrumentation. With applications for longer chain PFCAs, LC tandem mass spectrometry (LC-MS/MS) has been used because PFCAs are surfactant molecules, water-soluble, and thus readily amenable to electrospray ionization (ESI). LC systems often contain fluoropolymer components, like polytetrafluorethylene (PTFE) and these materials leach ultrashort-chain PFAS creating a contamination source of PFCAs, including TFA.[33] To overcome PFCA contamination in LC systems, trap columns have been used to delay their elution and reduce backgrounds in the method to improve detection limits.[34] It is also difficult to impossible to retain short-chain PFCAs on traditional RP columns because they are too polar to partition into the stationary phase under most standard mobile phase solvent conditions. This has only recently been mitigated through the use of MM columns, where reasonable retention factors (k') have been obtained.[24,25] Gas chromatographs with mass spectrometers (GC-MS) have also been used because they are widely available, relatively inexpensive, contain no fluoropolymer parts, and produce excellent separation and resolution. The disadvantage of GC-MS is that PFCAs are non-volatile and therefore any environmental sample containing them must be derivatized. There are many different derivatization methods used when analyzing PFCAs, including 2,4-difluoroaniline,[35–38] benzyl bromide,[39] pentafluorophenyl diazoethane,[40,41] dimethyl sulfate,[42–44] Fischer esterification,[45] and diphenyl diazomethane.[46] Derivatization methods are time consuming, often requiring extensive sample preparation, in addition to the use of hazardous reagents. Few derivatization methods have been effectively applied to short-chain PFCAs[46] because they often produce extremely volatile products that are difficult to retain on a GC column.[42,47,48]

Previous analytical methods, whether LC- or GC-based, for ultra-short-chain PFCAs required cleanup steps to reduce matrix effects and/or to concentrate the PFCA concentrations from the initial samples, including "clean" samples like ice cores.[49] Commonly used cleanup strategies included liquid–liquid extraction (LLE)[44,50] and solid phase extraction (SPE).[51,52] With ultra-short-chain PFCA pervasiveness in the environment, including within analytical laboratories, any sample handling could result in contamination.[46] Relatively high levels in environmental water samples, on the order of 20 ng L^{-1} to 3 μg L^{-1},[53,54] are above typical LC-MS/MS instrumental detection limits, which suggests that direct injection should be possible. However, ionisation suppression, caused by other matrix components of environmental samples (*e.g.*, Cl^- and NO_3^- in groundwater samples) often necessitates cleanup steps. Methods that allow for the direct injection quantitation of PFCAs in aqueous environmental samples on LC and IC systems are emerging and becoming available on the market to fill this gap.[49,55–57] For TFA, LC-MS/MS direct-injection methods have been developed for water[25] and more complex matrices, such as wine[58] and urine.[59]

The objective of this work was to develop a direct injection method that exploits the fully ionized state of ultra-short-chain PFCAs as they are found in freshwater environmental samples using IC coupled to mass spectrometry (IC-MS), a subset of LC that separates ionic compounds based on their hydrated ionic radius. Herein, we show that ultra-short-chain PFCAs can be separated readily from environmental anions because of adsorption and ionic interactions with the column functional groups, reducing the likelihood of matrix effects from the on-column separation, while also determining detection limits, optimized separation parameters, and environmental concentrations.

Experimental section

Reagents and materials

Nomenclature of the PFCAs can be found in the SI (Table S1). Salts of PFCAs include sodium trifluoroacetate (TFA; C2; Aldrich Chemicals, 98%), sodium pentafluoropropionate (PFPrA; C3; Aldrich Chemicals, 99%), sodium perfluorobutanoate (PFBA; C4; Synquest Laboratories, 98%), sodium perfluoropentanoate (PFPeA; C5; Synquest Laboratories, 97–103%), and sodium perfluorohexanoate (PFHxA; C6; Synquest Laboratories, 98%). Mass-labeled $^{13}C_2$-TFA (>97%) was purchased from Toronto Research Chemicals (Toronto, ON, Canada). Inorganic anion stock solutions were prepared from a primary mixed anion standard concentrate (Dionex Seven Anion Standard II in deionized water, Thermo Scientific) which contained F^-, Cl^-, NO_2^-, Br^-, and NO_3^- as sodium salts, PO_4^{3-} as the monobasic potassium salt, and SO_4^{2-} as the dibasic sodium salt. Calibration standards and eluents were prepared with Milli-Q water (18.2 MΩ cm at 25 °C) obtained from an in-house system (Direct 8; EMD Millipore). The mobile phase also contained methanol (UHPLC Grade; Fisher Chemical, MA, US) and 100 mM sodium hydroxide (NaOH; prepared from 49–51% in water for IC eluent; Sigma-Aldrich).

Ion chromatograph-mass spectrometer

A Thermo Scientific (Waltham, Massachusetts, USA) ICS-6000 coupled to a single quadrupole ISQ-EC-MS was used to

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

separate and analyze select PFCAs and inorganic and organic anions. A Thermo Scientific AS-AP autosampler delivers 750 μL of aqueous sample onto an anion exchange column (TAC-ULP1 5 × 23 mm) where its anionic contents are preconcentrated. Sample anions of C2–C6 PFCAs and seven inorganic anions are then separated with a gradient program for sodium hydroxide (NaOH) using an AG24 IonPac guard (2 × 50 mm) and AS24 IonPac microbore analytical anion-exchange column (2 × 250 mm, 11 μm particle size, 55% divinylbenzene (DVB) cross-linking, alkanol quaternary ammonium ion functional group). The separation method was optimized with a gradient elution program at a mobile phase flow rate of 0.35 mL min^{-1} over 25 minutes. The starting condition of 10 mM NaOH was held for 7 minutes, then linearly ramped up to 40 mM NaOH over 2 minutes and ramped up again to 52 mM NaOH for an additional 11 minutes. The 52 mM NaOH condition was maintained for 23 minutes, after which the mobile phase was returned stepwise to the initial 10 mM NaOH and held for 2 minutes to re-equilibrate. These conditions were maintained while the next injection was prepared using the AS-AP (Fig. S1).

The column effluent was passed through a suppressor (ADRS 600, 2 mm) in external water mode with an auxiliary (AXP) pump providing a flow through the regenerant ports at 1 mL min^{-1} and with an applied current of 87 mA. The eluent then passes through a conductivity cell, with measurements recorded at 5 Hz before a secondary AXP pump introduces 0.2 mL min^{-1} of methanol. The eluent is ionized under negative electrospray ionization conditions followed by detection by the MS operating in selective ion monitoring (SIM) mode for each analyte of interest listed in Table 1 as well as for $^{13}C_2$ TFA (m/z 115). The vaporizer temperature was set to 450 °C, the ion transfer temperature to 250 °C, and the source voltage to −3000 V. A nitrogen gas generator supplied the sheath gas at 45 psig and the auxiliary gas at 5 psig. The chromatographic peaks and mass spectrum were analyzed using the Chromeleon™ 7 software package.

Calibration and QA–QC

A mixed PFCA standard containing the internal standard $^{13}C_2$-TFA (250 ppt) was prepared and used to generate a 7-point calibration curve to quantify the samples (5–500 ppt). $^{13}C_2$-TFA, an ultra-short PFCA, was the only internal standard used to normalize all the PFAS. Future work could incorporate additional isotopically labelled standards for short chain PFCAs (C4–C6) to have higher certainty in their quantification. TFA and PFPrA were present as contaminants in the Milli-Q water, with concentrations ranging from <LOD to 86 ppt (TFA averaged 11 ppt; PFPrA averaged 44 ppt; n = 13). Milli-Q water was therefore not suitable to be used as a sample blank; however, it was used to prepare all the standards. To account for TFA contamination in the standards, a reagent blank composed of Milli-Q water spiked with $^{13}C_2$-TFA was analyzed in triplicate for each calibration. The average of the TFA signal in this reagent blank was subtracted from the 6 remaining standards and used as a correction for the contamination. IC-MS systems use non-fluorinated components, which leach lower concentrations of PFAS, reducing contamination.[33] The standard deviation of the eluent background, which did not contain a TFA peak, was used as a method blank to determine range limits. This was done by running the instrument method in triplicate without injecting anything. Background levels of TFA from the IC-MS system components were negligible, especially in comparison to the fluctuating levels of lab contamination in standards prepared using Milli-Q water. The standard deviation of the method blank was determined similarly for all PFCAs within their retention time ranges and was divided by the peak heights (signals) of each calibration standard to determine the signal to noise ratio. The signal to noise ratio was plotted against the concentration of the standards to determine the slope, then to calculate the limit of detection (LOD) 3 was divided by the slope, and 10 was divided by the slope to determine the limit of quantification (LOQ). The precision was calculated by determining the relative standard deviation from the 125 ppt mixed standard (n = 6) using the internal standard $^{13}C_2$-TFA to normalize the peak area for all PFCAs.

Environmental and drinking water samples

All drinking and surface water samples were collected into pre-cleaned (pre-rinsed 3× with Milli-Q water and final 1× rinse with methanol) 125 mL polypropylene bottles and stored at room temperature for 9 days. Eleven tap water samples were collected in March 2023 from homes across the Greater Toronto Area, ON, Canada and our laboratory (Fig. S2). Lake and river samples were collected from shorelines in March 2023. Lake

Table 1 Separation parameters for PFCAs (C2–C6) were evaluated to assess the quality control of the IC-MS method using external calibration with the internal standard $^{13}C_2$-TFA. Parameters included the retention time, retention factor, resolution, precision, and the LOD. The calibration linearity r^2 ranged from 0.9909–0.9975 for standards spanning 5 ppt to 500 ppt[a]

Anions	Quantitation ion (m/z)	Retention time (t_r, min)	Retention factor (k')	Closest-eluting ion	Resolution (R)[b]	Precision[c] (%)	Instrumental LOD (ppt)	Instrumental LOD (pg)
TFA	113	9.8	2.17	NO_2^-	0.50	1.4	2.10	1.57
PFPrA	163	11.1	2.60	Br^-	0.74	7.6	1.33	1.00
PFBA	213	12.7	3.11	PO_4^{3-}	0.44	3.5	2.84	2.13
PFPeA	263	16.2	4.24	NO_3^-	1.38	1.0	1.89	1.41
PFHxA	313	22.1	6.17	PFPeA	2.76	0.4	2.30	1.73

[a] Calibration linearity starts to drop around 5 ppt when using a 1000 ppt standard as the upper limit standard. [b] Calculated from the closest-eluting ion. [c] Calculated with a 125 ppt mixed standard with $^{13}C_2$-TFA (n = 6).

 This journal is © The Royal Society of Chemistry 2026

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

samples were collected from within 1 m of the shorelines of Lake Huron (43.232 N, 81.911 W), Lake Simcoe (44.547 N, 79.216 W), and Lake Ontario (43.635 N, 79.347 W). River samples were collected from the Ausable River Cut (43.222 N, 81.865 W) and the West Don River (43.730 N, 79.375 W), and a single pond sample was collected from the Moccasin Trail Pond (43.7338 N, 79.332 W). For all of these samples, the collections began with at least three rinses of the sampling containers with the water of interest. The conductivity, chloride, and dissolved organic carbon (DOC) content of these water bodies, where available, are provided for context in Table S2. Precipitation was collected between June 16th and July 15th, 2021, and August 17th to September 16th, 2021, from the rooftop of the Petrie Science and Engineering Building at York University in Toronto, ON, Canada (43.774 N, 79.507 W). Precipitation was collected with our automated wet deposition collector[60] into 10 L polypropylene jerry cans, with a subsample transferred into pre-cleaned 1 L polypropylene bottles which were stored at room temperature. Our cleaning procedure has demonstrated that the method performs effectively for these samples.[61] Sampling blanks were not possible to include because of the TFA contamination in the Milli-Q water. Therefore, for direct sample injection, the instrument detection limits coupled with the use of an isotopically labeled internal standard define the method detection limits, alongside rigorous lab and sampling practices.

Results and discussion

Method performance

PFCAs are present in environmental fresh waters at trace levels and are orders of magnitude lower than other anions. For example, short- and ultra-short chain PFCAs are present at sub-ppt to low-ppb levels, while anions such as chloride and nitrate are typically present at ppb to ppm levels.[62,63] The shorter the PFCA chain length, the more similar the properties of the PFCA to these matrix ions. For these PFCAs, selectivity of analysis can be improved by first separating them from other major environmental anions. Retention of ultra-short-chain PFCAs, particularly TFA, is difficult with traditional LC stationary phases, such as C18. Using modern LC MM stationary phases, retention of ultra-short chain PFCAs is possible, but matrix effects remain problematic.[64] Here, we applied IE to explicitly separate C2 to C6 ionic PFCAs from major environmental ions using an aqueous hydroxide gradient and an alkanol quaternary ammonium ion based anion exchange column (Fig. 1). The optimized method retained the PFCAs, with retention factors (k') ranging from 2.17 for TFA to 6.17 for the C6 PFCA (Table 1). The PFCAs were separated from their closest neighboring ion with resolution (R) ranging from 0.50 for TFA to 2.76 for the C6 PFCA (Fig. 1 and Table 1). The traditional conductivity detector used for ion exchange chromatography cannot detect PFCAs at environmental levels. Thus, we coupled a MS in SIM mode for the detection of these trace analytes as well as providing additional selectivity. Full peak resolution ($R \geq 1.5$) is not required when the anions can be further distinguished by their mass to charge ratios within the MS. The precision was under 10% for all PFCAs, with the majority under 5% (Table 1). The method accuracy was previously determined and reported for precipitation samples ($n = 201$), with percent relative errors ranging from 0.34 to 23%.[61] Particular attention was paid to ensuring the functionality of the suppressor to protect the instrument, without which the aqueous hydroxide eluent could precipitate within the ESI source and/or damage the MS. Shutdown sequences were written in Chromeleon to ensure that the MS would be shut down in the event of suppressor failure (see SI; Section S1). Use of this suppressed IC-MS method led to instrumental limits of detection (LODs) at the single digit ppt level (Table 1). Our TFA LOD is comparable to other reported detection limits, though lower than most (Table 2). Our LODs are somewhat higher than those achieved for C4 and longer PFCAs by LC-MS/MS, which are in the sub-ppt range.[13,24,51] Considering that a single quadrupole is used here, these performance outcomes due to ion-selective retention represent a promising new avenue for aqueous sample PFAS analysis, particularly for ultra-short-chain homologues. We expect that using MS with higher resolving power or tandem MS could further improve method performance. The LOQs for this method were all under 10 ppt (TFA: 7.0 ppt; PFPrA: 4.4 ppt; PFBA: 9.4 ppt; PFPeA: 6.3 ppt; PFHxA: 7.7 ppt).

Previous methods for the quantitative determination of TFA and other short chain PFCAs have often relied on sample preparation to minimize matrix effects (Table 2). The most common approach involves solid phase extraction (SPE) using a weak anion exchange resin. While the resins themselves have not, to our knowledge, demonstrated separation of TFA from matrix ions, it is possible to remove weak matrix acids (*e.g.*, organic acids) by adjusting the solution pH.[46] Concentrating TFA in samples with SPE can result in poor recoveries and difficulties for any subsequent analytical technique as it increases ion competition at the anion exchange sites due to high concentrations of other anions, like chloride in ocean water samples.[46] Sample handling, including extractions, is always cautioned to be undertaken with extreme care because avoiding contamination with ultra-short chain PFCAs is a challenge.[33,46] Methods that minimize sample handling are highly desirable; as a result, direct injection of aqueous samples is the most appealing. Tentative results of TFA were previously obtained by injecting and analyzing filtered water samples with supercritical fluid chromatography (SFC) tandem MS.[29] This was done by diluting the water samples with mass labeled PFBA and correcting with blank water injections because there was poor recovery (<5%) of TFA with SPE-WAX, so some sample preparation was still preformed for this direct injection method.[29] Methods for direct injection of TFA in water samples were previously developed using a hybrid of HILIC and non-suppressed IE columns with electrospray ionization coupled to tandem MS (LC-MS/MS).[25,32] Direct injection of environmental samples for quantitative determination of TFA and other ultra-short-chain PFCAs with our IC-MS method is expected to work, as the instrument and its components were developed for the analysis of major ions in aqueous environmental samples. With the low instrumental LODs and clear separation from matrix ions, quantitative determination should

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

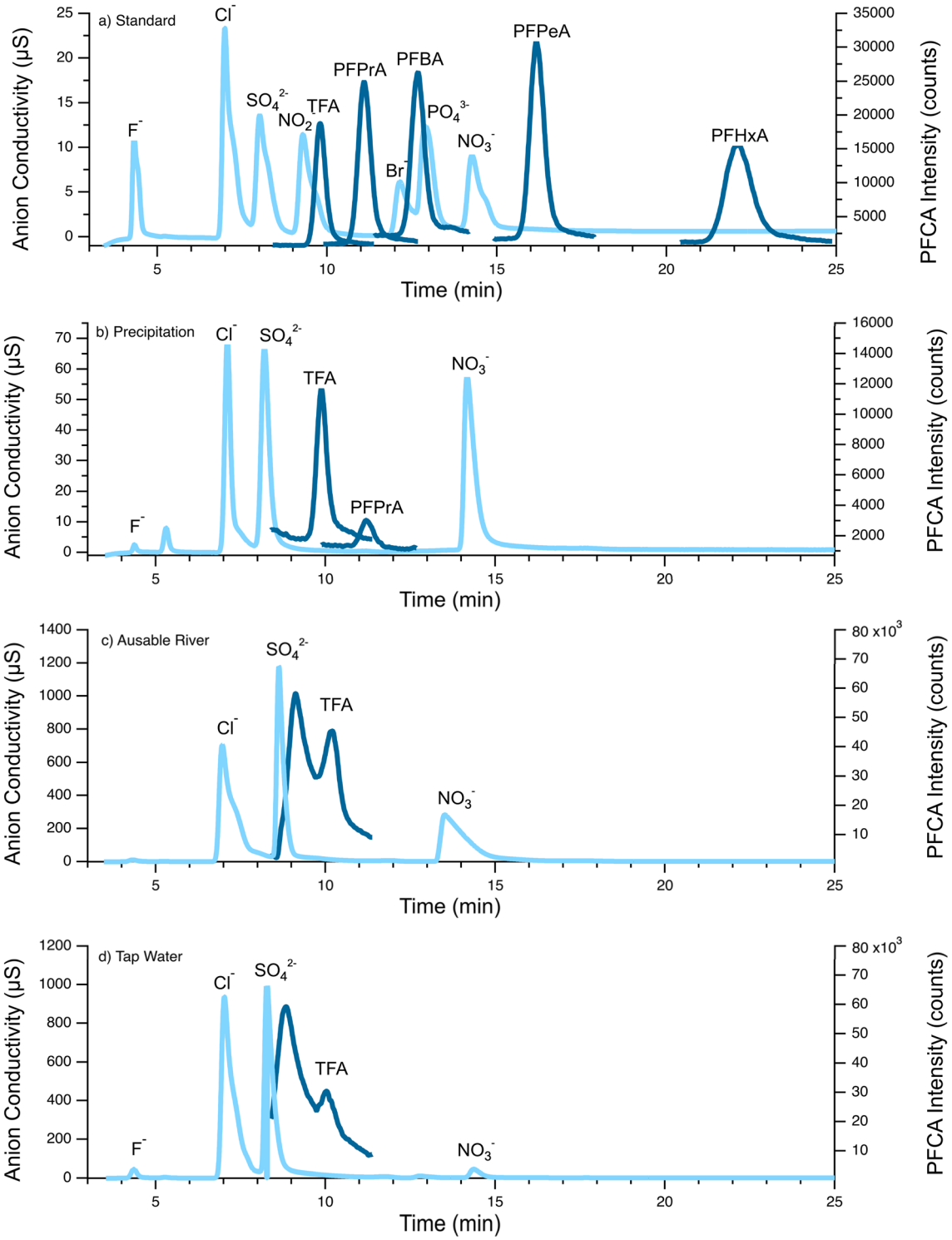

Fig. 1 IC-MS separation of (a) the major inorganic anions (light blue, conductivity, left axis) from C2–C6 PFCAs (dark blue, raw MS signal intensity, right axis) in an analytical standard containing trifluoroacetic acid (TFA, 500 ppt, *m/z* 113), perfluoropropionic acid (PFPrA, 500 ppt, *m/z* 163), perfluorobutanoic acid (PFBA, 500 ppt, *m/z* 213), perfluoropentanoic acid (PFPeA, 500 ppt, *m/z* 263), and perfluorohexanoic acid (PFHxA, 500 ppt, *m/z* 313), along with fluoride (F^-, 20 ppb), chloride (Cl^-, 100 ppb), nitrite (NO_2^-, 100 ppb), sulfate (SO_4^{2-}, 100 ppb), bromide (Br^-, 100 ppb), phosphate (PO_4^{3-}, 200 ppb), and nitrate (NO_3^-, 100 ppb). The same separation performed on real environmental samples is shown for precipitation (b), the Ausable River (c), and tap water (d). The separation of TFA and PFPrA from the prevalent anions (F^-, Cl^-, SO_4^{2-}, NO_3^-) is illustrated using selected ion counts from the mass spectrometer. Note that an unlabeled peak corresponding to the known elution region of a mixture of organic acids is present in the conductivity trace of panel (b).

This journal is © The Royal Society of Chemistry 2026

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Table 2 Selected comparison to published analytical methods reporting performance criteria for trifluoroacetic acid (TFA) in environmental freshwater samples[a]

Study	Sample volume	Sample preparation	Separation	Method limit of detection (concentration)	Instrument limit of detection	Pre-injection concentration factor
This work	750 µL	Online concentration	Suppressed IE	2.10 ppt	2.10 ppt	None
Zheng[31]	300 mL	SPE	Non-suppressed IE	27 ppt	NR	1500
Ye[46]	500 mL	SPE and derivatization	GC-phenyl methyl-polysiloxane	14.60 ppt	55 fg	500
Pickard[24]	100 mL	SPE	MM	0.151 ppt	NR	200
Liang[32]	10 µL	None	MM	3.5–5 ppt	NR	None
Scheurer[25]	100 µL	Centrifugation	Non-suppressed IE	16.7 ppt[b]	NR	None
Björnsdotter[29]	500 mL	Sonication, filtration, and dilution	SFC	34 ppt	NR	1000
Wang[30]	2 mL	Vortexed, filtered, and online SPE	MM	3.285 ppt	NR	None

[a] NR: not reported. IE: ion exchange. MM: mixed mode. SFC: supercritical fluid chromatography. [b] Converted from LOQ 50 pg mL^{-1} (divided by 3).

be possible across a wide variety of samples. A downside of direct injection using liquid chromatography is the inability to analyze other major anions alongside the PFAS in samples. The additional anion concentration information gives insight into sample sources, transportation and fate in the environment. The co-elution of these major anions present in environmental samples needs to be considered to prevent matrix suppression, regardless of whether LC or IC separation is used prior to detection and quantitation.[25]

Mass spectrometry optimization

Organic modifiers can improve electrospray ionization by lowering surface tension, allowing for a more stable and reproducible Taylor cone, and producing smaller droplets, all of which improve ion formation and increase instrument sensitivity. Unfortunately, organic solvents are not compatible with suppressed IC, as they result in an accelerated degradation of the suppressor. Thus, our aqueous hydroxide separation method was designed to perform methanol addition after the conductivity detector and before the MS to allow the benefits of the addition of organic solvent without damaging the suppressor. Currently, methanol was the only organic modifier tested with this method. Methanol at 0.2 mL min^{-1} was combined with the suppressed outflow from the IC (0.35 mL min^{-1}), resulting in a total flow of 0.55 mL min^{-1}. Although the addition of methanol resulted in a 37% dilution of the analyte peaks, we found that its introduction increased the signal intensity of TFA by a factor of 2.5 (Fig. 2).

Real sample analysis

Here we characterize the presence and variability of ultra-short-chain PFCAs—primarily TFA and PFPrA—in laboratory standards, tap water, precipitation, and regional freshwater systems across the Greater Toronto Area and Ontario. Results are interpreted in the context of known sources (*e.g.*, laboratory contamination, atmospheric deposition, and agricultural runoff) and compared with previously reported concentrations to assess environmental relevance. Consistent levels of TFA and PFPrA were detected in the Milli-Q water used to prepare standards, necessitating their subtraction during each analytical batch. As a result, Milli-Q water was not useful toward obtaining field blanks. TFA was the only PFCA that was detectable with direct injection in tap water samples. Nine of the eleven tap water samples from across the Greater Toronto Area (GTA) were above the LOD for TFA. The TFA concentrations in tap water ranged widely from <2.10 to 673 ppt, with a median of 165 ppt (Fig. 3). These concentrations are comparable to previously measured TFA levels in Toronto area drinking water in 2022 (271 ppt)[46] and Indiana, USA in 2020 (79 ppt).[31] While most tap

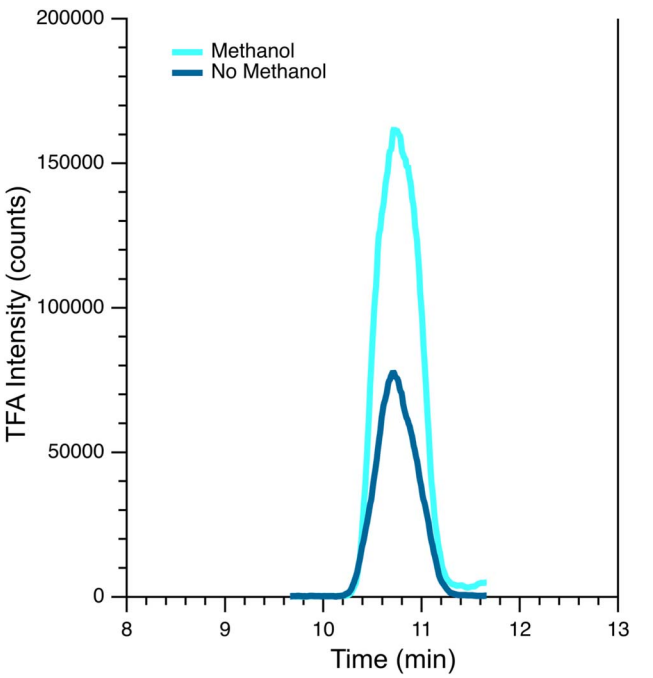

Fig. 2 Chromatogram depicting the TFA signal in the presence (light blue) and absence (dark blue) of methanol for injections of a 1 ppm TFA standard.

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

water in the GTA is from Lake Ontario, the samples here came from different water treatment facilities, which could impact TFA levels. Building or personal filtration systems,[32] which were not tracked in this study, could also play a role in the removal of TFA in water systems, which could explain the wide range of concentrations.

Two summertime precipitation samples that were analyzed had detectable levels of TFA (645 and 508 ppt) and PFPrA (104 and 144 ppt) (Fig. 4). Concentrations in this study are higher than those reported from wintertime precipitation samples collected at the same location, with TFA and PFPrA levels of 150 and 62.3 ppt, respectively.[46] TFA was within the upper range of summertime precipitation concentrations collected in Ohio, USA in 2019 where the summed PFAS ranged from 50–850 ppt, with TFA accounting for around 90% of the measured PFAS (which did not include PFPrA).[65]

TFA was the only detectable PFCA by direct injection in all three lake samples (177–867 ppt) where Lake Ontario had the lowest concentration and Lake Simcoe had the highest concentration (Fig. 4). Analyzed lake water contained similar levels of TFA to surface water measured in USA[54] and Sweden.[66] The concentrations of TFA present in the Great Lakes are much higher compared to previous measurements of long chain PFCAs made in 2006–2017. Lake Ontario TFA levels are approximately 10-fold higher than the sum of C4–C12 PFCAs (19.4 ppt)[67] and the Lake Huron TFA concentrations were 67 times the sum of C4–C12 PFCAs (7.2 ppt).[67] The highest amount of TFA (1636 ppt) across all freshwater samples was measured in the Ausable River, which drains agricultural land and empties into Lake Huron. Agricultural runoff has previously been associated with elevated TFA in freshwater and has been attributed to transformations of pesticides containing an aryl CF_3 group.[25,66,68,69] NO_3^- levels in the Ausable River sample were 15.5 times higher than in Lake Ontario, consistent with the endpoint of fertilizer ammonium nitrification and subsequent loss of the highly mobile NO_3^- anion to the aquatic environment.[70,71]

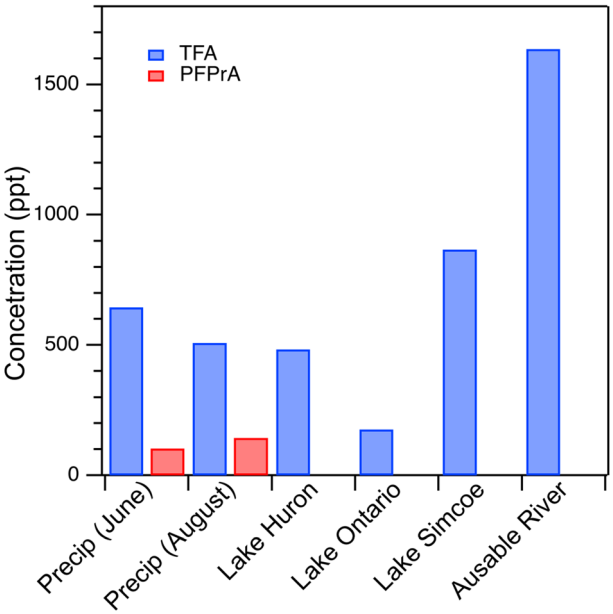

Fig. 4 Measured TFA (blue) and PFPrA (red) concentrations (ppt) in freshwater samples collected around Ontario.

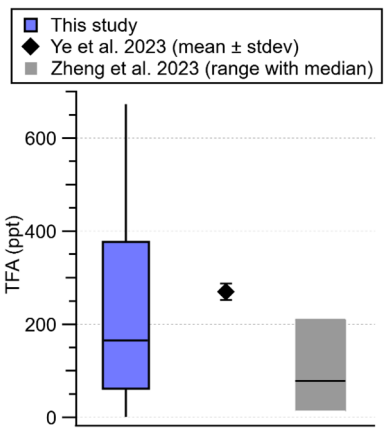

Fig. 3 Boxplot of TFA in Greater Toronto Area tap water samples (n = 11) collected in March 2023, reported in ppt. Horizontal lines represent 25th, 50th (median), and 75th percentiles, while the vertical lines represent the full range of the measurements. Shown with TFA tap water measurements from North America from Ye *et al.*[46] (Toronto, n = 1, mean ± standard deviation of 3 replicate extractions) and Zheng *et al.*[31] (Indiana, range shown with median, n = 81). Measurements below LOD were included as $\frac{1}{2}$LOD.

Matrix impacts

This direct injection method was found to work with freshwater environmental samples only. The chloride content in ocean water was determined to have too much of a matrix effect in the conductivity to analyze without additional cleanup steps. The composition of the sample is always important to take into consideration for a quantitative method, as some of our freshwater samples were challenging to analyze by direct injection due to very high concentrations and conductivity of ionic constituents. For example, the Moccasin Trail Pond and Don Valley West River samples had extremely high matrix signals arising around a 6-minute retention time and leading to an overloaded asymmetric peak, alongside others (Fig. S3) indicating that the matrix was composed of high quantities of organic acids and/or chloride. The absolute water conductivity was not measured for these specific samples, though separate measurements of the Don River during the same time period reported >2000 μS cm^{-1} conductivity, which was 5–37 times higher than those of the Ausable River and Lakes Ontario and Huron (Table S2). Substantial chloride content was also found in the Don River, consistent with the widespread use of salt to de-ice roads in this region during winter. Though we do not have measurements for Moccasin Trail Pond, its proximity to major roadways suggests it would also be highly contaminated with road salt. We were unable to quantify these samples without further cleanup steps due to the loss of the entire $^{13}C_2$-TFA internal standard counts in the mass spectrometer, indicative of strong matrix suppression of TFA. This questions the validity of some previously published TFA direct injection

 This journal is © The Royal Society of Chemistry 2026

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

methods using LC-MS/MS[32] which also reported that $^{13}C_2$-TFA did not generate a parallel signal in spiked samples.

Analytical interferences in this method can also arise from compounds that have similar retention times to the target analyte and yield negative ions at the same mass to charge ratio used for selected ion monitoring. This is a known analytical challenge in PFAS analysis using reverse phase and other separations. Multiple papers have retroactively determined that some PFAS measurements were false positives or artificially inflated.[72–74] *Cis*-acetylacrylic acid was previously identified as an isobaric interferent for TFA, however it has only been reported in biological samples and is unlikely to be present in freshwater samples.[75] A similar issue was observed here, with an unknown isobaric interference detected at 113 *m*/*z* with a similar retention time to that of TFA. This was found in tap water, lake water, and river water samples, but was not present in the precipitation samples. Given the anion exchange separation method used, the unknown isobaric interference is likely an acid. Under the gradient eluent conditions of this method, it elutes about one minute before the TFA peak and exhibits a much larger peak area. This further confirms that *cis*-acetylacrylic acid is unlikely to be the interferent in our samples, as mono-organic acids elute earlier in the separation than TFA with retention times around 5–6 minutes. Organic acids present in our samples are represented by an unlabeled peak in Fig. 1 and S3. Comparisons with the internal standard can help verify that the correct peak is being analyzed, as ion chromatography is well known to experience shifts in retention time that depend not only on the concentration of the target analyte but also on other competing ions in the sample matrix that can undergo exchange on the analytical column. The internal standard is therefore especially useful in samples where the TFA peak area is below detection limits, allowing a retention time to be assigned correctly, and preventing the isobaric interference from potentially causing an artificially inflated PFAS measurement. In cases where there is a significant TFA signal, reducing the concentrations of both the matrix and the analyte by removing the on-line concentration step in the sample preparation results improved separation. By injecting with a 250 μL loop instead of 750 μL into the concentrator column, the resolution between TFA and the isobaric interference in the Ausable River sample improved from 1.03 to 1.87 (Fig. 5) and allowed TFA detection in the Moccasin Trail Pond sample (Fig. S6). We attempted to determine the identity of the isobaric interference. Using an expanded mass window, we determined that the *m*/*z* 113 signal corresponded to the *M* + 2 isotope of a larger signal at *m*/*z* 111. The relative signal abundances were consistent with isotopes of sulfur (Table S3). We initially suspected that the signal corresponded to methyl sulfate. We compared the retention times of an authentic methyl sulfate standard to that of the unknown, including through standard addition. The retention times did not fully match across *m*/*z* 111–113 (Fig. S4a–c). Moreover, standard addition of methyl sulfate to the sample resulted in the splitting of the unknown peak, indicating that methyl sulfate is not an exact match for the unknown present in the sample.

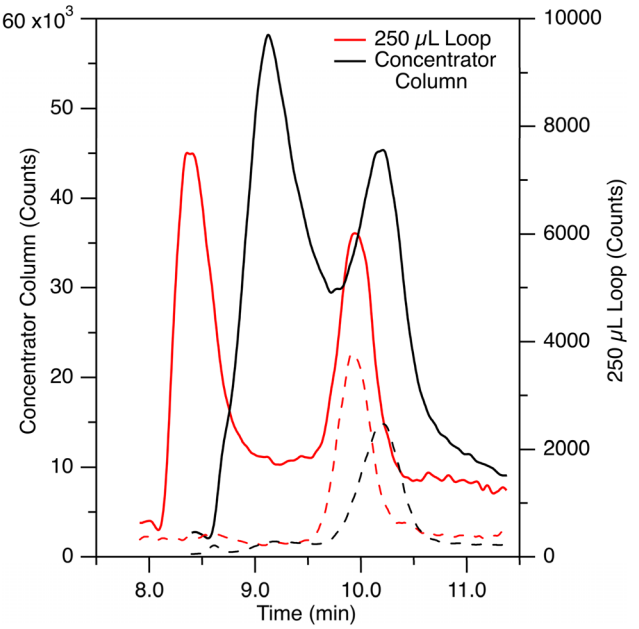

Fig. 5 Chromatogram of TFA in the Ausable River sample at 113 *m*/*z* (solid lines), injected using a 250 μL loop (red) and 750 μL to a concentrator column (black), overlaid with dashed lines representing $^{13}C_2$ TFA at 115 *m*/*z* for each injection.

Conclusions and implications

Here, we demonstrated a suppressed ion chromatography method to physically separate PFCAs from major environmental anions to reduce the background matrix and improve the LODs. A single quadrupole MS is used to filter other acids in the sample to improve separation.

The sample type and method used are important in determining the amount of TFA in the environment. Matrix effects in different sample types can lead to inaccurate analysis of the TFA concentration if they are not taken into consideration. High conductivity signals indicating large amounts of chloride and a loss of the internal standard $^{13}C_2$-TFA signal show a suppression of TFA in some sample types, which limited the application of our method. When internal standard suppression is paired with isobaric acids that contain similar properties to TFA, precautions need to be taken when analyzing different sample types by both direct and SPE methods to selectively only analyze TFA and not report inflated concentrations.

Conflicts of interest

There are no conflicts of interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5ay02105g.

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Acknowledgements

Funding was provided by a Natural Science and Engineering Research Council Discovery Grant and a Canada Foundation for Innovation John Evans Leadership Fund Grant. Thanks to Shira Joudan and Mayré Rodríguez for instrument assistance and to Daniel Persaud for precipitation sample collection.

References

1 OECD, *Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFASs)*, 2018.
2 R. C. Buck, J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voogt, A. A. Jensen, K. Kannan, S. A. Mabury and S. P. J. van Leeuwen, Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins, *Integr. Environ. Assess. Manage.*, 2011, **7**(4), 513–541.
3 A. Ritscher, Z. Wang, M. Scheringer, J. M. Boucher, L. Ahrens, U. Berger, S. Bintein, S. K. Bopp, D. Borg, A. M. Buser, *et al.*, Zürich Statement on Future Actions on Per- and Polyfluoroalkyl Substances (PFASs), *Environ. Health Perspect.*, 2018, **126**(8), 084502.
4 R. Sander, Compilation of Henry's Law Constants (Version 5.0.0) for Water as Solvent, *Atmos. Chem. Phys.*, 2023, **23**(19), 10901–12440.
5 J. W. Martin, M. M. Smithwick, B. M. Braune, P. F. Hoekstra, D. C. G. Muir and S. A. Mabury, Identification of Long-Chain Perfluorinated Acids in Biota from the Canadian Arctic, *Environ. Sci. Technol.*, 2004, **38**(2), 373–380.
6 P. Li and H. Cao, Comprehensive Assessment on the Ecological Stress of Rapid Land Urbanization per Proportion, Intensity, and Location, *Ecosyst. Health Sustainability*, 2019, **5**(1), 242–255.
7 F. Pérez, M. Nadal, A. Navarro-Ortega, F. Fàbrega, J. L. Domingo, D. Barceló and M. Farré, Accumulation of Perfluoroalkyl Substances in Human Tissues, *Environ. Int.*, 2013, **59**, 354–362.
8 K. R. Solomon, G. J. M. Velders, S. R. Wilson, S. Madronich, J. Longstreth, P. J. Aucamp and J. F. Bornman, Sources, Fates, Toxicity, and Risks of Trifluoroacetic Acid and Its Salts: Relevance to Substances Regulated under the Montreal and Kyoto Protocols, *J. Toxicol. Environ. Health, Part B*, 2016, **19**(7), 289–304.
9 F. Freeling, M. Scheurer, J. Koschorreck, G. Hoffmann, T. A. Ternes and K. Nödler, Levels and Temporal Trends of Trifluoroacetate (TFA) in Archived Plants: Evidence for Increasing Emissions of Gaseous TFA Precursors over the Last Decades, *Environ. Sci. Technol. Lett.*, 2022, **9**(5), 400–405.
10 A. G. Berends, J. C. Boutonnet, C. G. De Rooij and R. S. Thompson, Toxicity of Trifluoroacetate to Aquatic Organisms, *Environ. Toxicol. Chem.*, 1999, **18**(5), 1053–1059.
11 K. Huang, Y. Li, D. Bu, J. Fu, M. Wang, W. Zhou, L. Gu, Y. Fu, Z. Cong, B. Hu, *et al.*, Trophic Magnification of Short-Chain Per- and Polyfluoroalkyl Substances in a Terrestrial Food Chain from the Tibetan Plateau, *Environ. Sci. Technol. Lett.*, 2022, **9**(2), 147–152.
12 J. W. Martin, J. Franklin, M. L. Hanson, K. R. Solomon, S. A. Mabury, D. A. Ellis, B. F. Scott and D. C. G. Muir, Detection of Chlorodifluoroacetic Acid in Precipitation: A Possible Product of Fluorocarbon Degradation, *Environ. Sci. Technol.*, 2000, **34**(2), 274–281.
13 I. J. Neuwald, D. Hübner, H. L. Wiegand, V. Valkov, U. Borchers, K. Nödler, M. Scheurer, S. E. Hale, H. P. H. Arp and D. Zahn, Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated, *Environ. Sci. Technol.*, 2022, **56**(10), 6380–6390.
14 Y. Duan, H. Sun, Y. Yao, Y. Meng and Y. Li, Distribution of Novel and Legacy Per-/Polyfluoroalkyl Substances in Serum and Its Associations with Two Glycemic Biomarkers among Chinese Adult Men and Women with Normal Blood Glucose Levels, *Environ. Int.*, 2020, **134**, 105295.
15 J. C. Boutonnet, P. Bingham, D. Calamari, C. d. Rooij, J. Franklin, T. Kawano, J.-M. Libre, A. McCul-loch, G. Malinverno, J. M. Odom, *et al.*, Environmental Risk Assessment of Trifluoroacetic Acid, *Hum. Ecol. Risk Assess.: Int. J.*, 1999, **5**(1), 59–124.
16 D. Bowden, S. Clegg and P. Brimblecombe, The Henry's Law Constant of Trifluoroacetic Acid and Its Partitioning into Liquid Water in the Atmosphere, *Chemosphere*, 1996, **32**(2), 405–420.
17 J. Janda, K. Nödler, H. J. Brauch, C. Zwiener and F. T. Lange, 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, *Environ. Sci. Pollut. Res. Int.*, 2019, **26**(8), 7326–7336.
18 I. J. Neuwald, D. Hübner, H. L. Wiegand, V. Valkov, U. Borchers, K. Nödler, M. Scheurer, S. E. Hale, H. P. H. Arp and D. Zahn, Occurrence, Distribution, and Environmental Behavior of Persistent, Mobile, and Toxic (PMT) and Very Persistent and Very Mobile (VPvM) Substances in the Sources of German Drinking Water, *Environ. Sci. Technol.*, 2022, **56**(15), 10857–10867.
19 C. J. Young and S. A. Mabury, Atmospheric Perfluorinated Acid Precursors: Chemistry, Occurrence, and Impacts, *Rev. Environ. Contam. Toxicol.*, 2010, **208**, 1–109.
20 UNEP, Handbook for the Montreal Protocol on Substances That Deplete the Ozone Layer, in *Ozone Secretariat*, United Nations Environment Programme, 2018.
21 UNEP, The Montreal Protocol on Substances That Deplete the Ozone Layer, as Either Adjusted and/or Amended in London 1990, Copenhagen 1992, Cienna 1995, Montreal 1997, Beijing 1999, in *Ozone Secretariat*, United Nations Environment Programme, 2000.
22 UNEP, *Report of the Twenty-Eighth Meeting of the Parties to the Montreal Protocol on Sustances That Deplete the Ozone Layer, Kigali*, United Nations Environment Programme, 2016, vol. **2**, pp. , pp. 49–52.
23 Z. Wang, Y. Wang, J. Li, S. Henne, B. Zhang, J. Hu and J. Zhang, Impacts of the Degradation of 2,3,3,3-Tetrafluoropropene into Trifluoroacetic Acid from Its Application in Automobile Air Conditioners in China, the

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

United States, and Europe, *Environ. Sci. Technol.*, 2018, **52**(5), 2819–2826.

24 H. M. Pickard, A. S. Criscitiello, C. Spencer, M. J. Sharp, D. C. G. Muir, A. O. De Silva and C. J. Young, Continuous Non-Marine Inputs of per- and Polyfluoroalkyl Substances to the High Arctic: A Multi-Decadal Temporal Record, *Atmos. Chem. Phys.*, 2018, **18**(7), 5045–5058.

25 M. Scheurer, K. Nödler, F. Freeling, J. Janda, O. Happel, M. Riegel, U. Müller, F. R. Storck, M. Fleig, F. T. Lange, *et al.*, Small, Mobile, Persistent: Trifluoroacetate in the Water Cycle – Overlooked Sources, Pathways, and Consequences for Drinking Water Supply, *Water Res.*, 2017, **126**, 460–471.

26 A. P. Bhat, T. F. Mundhenke, Q. T. Whiting, A. A. Peterson, W. C. K. Pomerantz and W. A. Arnold, Tracking Fluorine during Aqueous Photolysis and Advanced UV Treatment of Fluorinated Phenols and Pharmaceuticals Using a Combined 19F-NMR, Chromatography, and Mass Spectrometry Approach, *ACS Environ. Au*, 2022, **2**(3), 242–252.

27 Z. Guo, G. W. Tremblay, J. Chen and S. Joudan, Spontaneous Aqueous Defluorination of Trifluoromethylphenols: Substituent Effects and Revisiting the Mechanism, *Environ. Sci.:Processes Impacts*, 2024, **27**(7), 1852–1863.

28 M. Sun, J. Cui, J. Guo, Z. Zhai, P. Zuo and J. Zhang, Fluorochemicals Biodegradation as a Potential Source of Trifluoroacetic Acid (TFA) to the Environment, *Chemosphere*, 2020, **254**, 126894.

29 M. K. Björnsdotter, L. W. Y. Yeung, A. Kärrman and I. E. Jogsten, Ultra-Short-Chain Perfluoroalkyl Acids Including Trifluoromethane Sulfonic Acid in Water Connected to Known and Suspected Point Sources in Sweden, *Environ. Sci. Technol.*, 2019, **53**(19), 11093–11101.

30 Y. Wang, M. Liu, S. Vo Duy, G. Munoz, S. Sauvé and J. Liu, Fast Analysis of Short-Chain and Ultra-Short-Chain Fluorinated Organics in Water by on-Line Extraction Coupled to HPLC-HRMS, *Sci. Total Environ.*, 2024, **943**, 173682.

31 G. Zheng, S. M. Eick and A. Salamova, Elevated Levels of Ultrashort- and Short-Chain Perfluoroalkyl Acids in US Homes and People, *Environ. Sci. Technol.*, 2023, **57**(42), 15782–15793.

32 S. H. Liang, J. A. Steimling and M. Chang, Analysis of Ultrashort-Chain and Short-Chain (C1 to C4) per- and Polyfluorinated Substances in Potable and Non-Potable Waters, *J. Chromatogr. Open*, 2023, **4**, 100098.

33 S. Joudan, J. Gauthier, S. A. Mabury and C. J. Young, Aqueous Leaching of Ultrashort-Chain PFAS from (Fluoro)Polymers: Targeted and Nontargeted Analysis, *Environ. Sci. Technol. Lett.*, 2024, **11**(3), 237–242.

34 R. Sayed, A. A. Omran, R. S. Farag, H. A. Mahmoud and M. Soliman, Overcoming Challenges in the Analysis of the Ubiquitous Emerging Contaminant Trifluoroacetic Acid Employing Trap Column Liquid Chromatography Tandem Mass Spectrometry, *J. Hazard. Mater.*, 2025, **491**, 137976.

35 A. De Silva and S. A. Mabury, Isolating Isomers of Perfluorocarboxylates in Polar Bears (Ursus Maritimus) from Two Geographical Locations, *Environ. Sci. Technol.*, 2004, **38**(24), 6538–6545.

36 J. W. Martin, S. A. Mabury, C. S. Wong, F. Noventa, K. R. Solomon, M. Alaee and D. C. G. Muir, Airborne Haloacetic Acids, *Environ. Sci. Technol.*, 2003, **37**(13), 2889–2897.

37 J. Wu, J. W. Martin, Z. Zhai, K. Lu, L. Li, X. Fang, H. Jin, J. Hu and J. Zhang, Airborne Trifluoroacetic Acid and Its Fraction from the Degradation of HFC-134a in Beijing, China, *Environ. Sci. Technol.*, 2014, **48**(7), 3675–3681.

38 B. F. Scott and M. Alaee, Determination of Haloacetic Acids from Aqueous Samples Collected from the Canadian Environment Using an in Situ Derivatization Technique, *Water Qual. Res. J. Can.*, 1998, **33**(2), 279–293.

39 Y. Fujii, K. H. Harada and A. Koizumi, Analysis of Perfluoroalkyl Carboxylic Acids in Composite Dietary Samples by Gas Chromatography/Mass Spectrometry with Electron Capture Negative Ionization, *Environ. Sci. Technol.*, 2012, **46**(20), 11235–11242.

40 H. Frank, D. Renschen, A. Klein and H. Scholl, Trace Analysis of Airborne Haloacetates, *J. High Resolut. Chromatogr.*, 1995, **18**(2), 83–88.

41 H. Frank, E. H. Christoph, O. Holm-Hansen and J. L. Bullister, Trifluoroacetate in Ocean Waters, *Environ. Sci. Technol.*, 2001, **36**(1), 12–15.

42 D. Zehavi and J. N. Seiber, An Analytical Method for Trifluoroacetic Acid in Water and Air Samples Using Headspace Gas Chromatographic Determination of the Methyl Ester, *Anal. Chem.*, 1996, **68**(19), 3450–3459.

43 C. E. Wujcik, T. M. Cahill and J. N. Seiber, Extraction and Analysis of Trifluoroacetic Acid in Environmental Waters, *Anal. Chem.*, 1998, **70**(19), 4074–4080.

44 T. M. Cahill, J. A. Benesch, M. S. Gustin, E. J. Zimmerman and J. N. Seiber, Simplified Method for Trace Analysis of Trifluoroacetic Acid in Plant, Soil, and Water Samples Using Headspace Gas Chromatography, *Anal. Chem.*, 1999, **71**(20), 4465–4471.

45 I. Langlois, U. Berger, Z. Zencak and M. Oehme, Mass Spectral Studies of Perfluorooctane Sulfonate Derivatives Separated by High-Resolution Gas Chromatography, *Rapid Commun. Mass Spectrom.*, 2007, **21**(22), 3547–3553.

46 R. X. Ye, R. A. Di Lorenzo, J. T. Clouthier, C. J. Young and T. C. VandenBoer, A Rapid Derivatization for Quantitation of Perfluorinated Carboxylic Acids from Aqueous Matrices by Gas Chromatography-Mass Spectrometry, *Anal. Chem.*, 2023, **95**(19), 7648–7655.

47 J. E. Naile, A. W. Garrison, J. K. Avants and J. W. Washington, Isomers/Enantiomers of Perfluorocarboxylic Acids: Method Development and Detection in Environmental Samples, *Chemosphere*, 2016, **144**, 1722–1728.

48 G. Lv, L. Wang, S. Liu and S. Li, Determination of Perfluorinated Compounds in Packaging Materials and Textiles Using Pressurized Liquid Extraction with Gas Chromatography-Mass Spectrometry, *Anal. Sci.*, 2009, **25**(3), 425–429.

49 H. M. Pickard, A. S. Criscitiello, D. Persaud, C. Spencer, D. C. G. Muir, I. Lehnherr, M. J. Sharp, A. O. De Silva and

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

C. J. Young, Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations, *Geophys. Res. Lett.*, 2020, **47**(10), e2020GL087535.

50 C. E. Wujcik, D. Zehavi and J. N. Seiber, Trifluoroacetic Acid Levels in 1994-1996 Fog, Rain, Snow and Surface Waters from California and Nevada, *Chemosphere*, 1998, **36**(6), 1233–1245.

51 S. Taniyasu, K. Kannan, L. W. Y. Yeung, K. Y. Kwok, P. K. S. Lam and N. Yamashita, 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), *Anal. Chim. Acta*, 2008, **619**(2), 221–230.

52 L. W. Y. Yeung, C. Stadey and S. A. Mabury, Simultaneous Analysis of Perfluoroalkyl and Polyfluoroalkyl Substances Including Ultrashort-Chain C2 and C3 Compounds in Rain and River Water Samples by Ultra Performance Convergence Chromatography, *J. Chromatogr. A*, 2017, **1522**, 78–85.

53 F. Freeling, D. Behringer, F. Heydel, M. Scheurer, T. A. Ternes and K. Nödler, Trifluoroacetate in Precipitation: Deriving a Benchmark Data Set, *Environ. Sci. Technol.*, 2020, **54**(18), 11210–11219.

54 T. M. Cahill, Increases in Trifluoroacetate Concentrations in Surface Waters over Two Decades, *Environ. Sci. Technol.*, 2022, **56**(13), 9428–9434.

55 A. Ganci, V. Thibert, D. D'Addona, N. De Clercq and J.-F. Garnier, *Direct Injection of Drinking Water for the Analysis of 54 PFAS Compounds by LC-MS/MS Aligned with Current and Evolving Global Regulations*, 2024.

56 K. L. Organtini, G. E. Cleland and K. J. Rosnack, *Large Volume Direct Injection Method for the Analysis of Perfluorinated Alkyl Substances (PFAS) in Environmental Water Samples in Accordance with ASTM 7979-17*, 2019.

57 H. Lee, S. Roberts, C. M. Butt, S. Lodge, R. Ye, C. Young and T. Vandenboer, Simultaneous Quantitation of Ultrashort-, Short- and Long-Chain PFAS in Water by a Single Direct Injection LC-MS/MS Method, SCIEX Technical Note MKT-34163-A, 2025.

58 F. Freeling and R. Mira de Orduña Heidinger, Tracking Trifluoroacetate (TFA) through Time: A 78-Year Record from Archived Wines, *Environ. Sci. Technol.*, 2025, **59**(49), 26762–26769.

59 D. C. G. Muir, F. Freeling, S. Nilsson, B. Bugsel, K. Bowles, P. Hobson, L. Toms and J. F. Mueller, Trifluoroacetic Acid in Australian Human Urine Samples, *Environ. Sci. Technol. Lett.*, 2025, **12**(10), 1411–1417.

60 A. A. Colussi, D. Persaud, M. Lao, B. K. Place, R. F. Hems, S. E. Ziegler, K. A. Edwards, C. J. Young and T. C. VandenBoer, Cost Effective Off-Grid Automatic Precipitation Samplers for Pollutant and Biogeochemical Atmospheric Deposition, *Atmos. Meas. Tech.*, 2024, **17**(12), 3697–3718.

61 D. Persaud, S. Joudan, T. C. Vandenboer and C. J. Young, Atmospheric Removal of Trifluoroacetic Acid by Dry and Wet Deposition: A Multiyear Analysis in Toronto, *Environ. Sci. Technol. Lett.*, 2026, **13**(2), 261–267.

62 J. A. Morales, L. S. De Graterol and J. Mesa, Determination of Chloride, Sulfate and Nitrate in Groundwater Samples by Ion Chromatography, *J. Chromatogr. A*, 2000, **884**(1–2), 185–190.

63 K. R. Burow, B. T. Nolan, M. G. Rupert and N. M. Dubrovsky, Nitrate in Groundwater of the United States, 1991-2003, *Environ. Sci. Technol.*, 2010, **44**(13), 4988–4997.

64 M. K. Björnsdotter, L. W. Y. Yeung, A. Kärrman and I. Ericson Jogsten, Challenges in the Analytical Determination of Ultra-Short-Chain Perfluoroalkyl Acids and Implications for Environmental and Human Health, *Anal. Bioanal. Chem.*, 2020, **412**(20), 4785–4796.

65 K. A. Pike, P. L. Edmiston, J. J. Morrison and J. A. Faust, Correlation Analysis of Perfluoroalkyl Substances in Regional U.S. Precipitation Events, *Water Res.*, 2021, **190**, 116685.

66 M. K. Björnsdotter, L. W. Y. Yeung, A. Kärrman and I. E. Jogsten, Mass Balance of Perfluoroalkyl Acids, Including Trifluoroacetic Acid, in a Freshwater Lake, *Environ. Sci. Technol.*, 2022, **56**(1), 251–259.

67 S. B. Gewurtz, L. E. Bradley, S. Backus, A. Dove, D. McGoldrick, H. Hung and H. Dryfhout-Clark, Perfluoroalkyl Acids in Great Lakes Precipitation and Surface Water (2006-2018) Indicate Response to Phase-Outs, Regulatory Action, and Variability in Fate and Transport Processes, *Environ. Sci. Technol.*, 2019, **53**(15), 8543–8552.

68 H. Joerss, F. Freeling, S. van Leeuwen, J. Hollender, X. Liu, K. Nödler, Z. Wang, B. Yu, D. Zahn and G. Sigmund, Pesticides Can Be a Substantial Source of Trifluoroacetate (TFA) to Water Resources, *Environ. Int.*, 2024, **193**, 109061.

69 A. P. Bhat, W. C. K. Pomerantz and W. A. Arnold, Finding Fluorine: Photoproduct Formation during the Photolysis of Fluorinated Pesticides, *Environ. Sci. Technol.*, 2022, **56**(17), 12336–12346.

70 F. S. Liu, B. R. Lockett, R. J. Sorichetti, S. A. Watmough and M. C. Eimers, Agricultural Intensification Leads to Higher Nitrate Levels in Lake Ontario Tributaries, *Sci. Total Environ.*, 2022, **830**, 154534.

71 B. Singh and E. Craswell, Fertilizers and Nitrate Pollution of Surface and Ground Water: An Increasingly Pervasive Global Problem, *SN Appl. Sci.*, 2021, **3**(4), 1–24.

72 J. Bangma, B. M. Kitrina, C. M. Fisher, S. Genualdi, T. C. Guillette, C. A. Huset, J. Mccord, B. Ng, B. J. Place, J. L. Reiner, A. Robuck and A. E. Rodowa, PFAS Ghosts: How to Identify, Evaluate, and Exorcise New and Existing Analytical Interference, *Anal. Bioanal. Chem.*, 2024, **2024**, 1777–1785.

73 J. P. Benskin, M. Bataineh and J. W. Martin, Simultaneous Characterization of Perfluoroalkyl Carboxylate, Sulfonate, and Sulfonamide Isomers by Liquid Chromatography-Tandem Mass Spectrometry, *Anal. Chem.*, 2007, **79**(17), 6455–6464.

74 K. Abraham, A. H. El-Khatib, T. Schwerdtle and B. H. Monien, Perfluorobutanoic Acid (PFBA): No High-

 This journal is © The Royal Society of Chemistry 2026

Open Access Article. Published on 02 March 2026. Downloaded on 6/6/2026 3:06:20 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Level Accumulation in Human Lung and Kidney Tissue, *Int. J. Hyg. Environ. Health*, 2021, **237**, 113830.

75 Z. Pan, S. Li, Q. Zhao, J. Li, Y. Dong, A. G. L. Borthwick, W. Sun and N. Xu, Anthropogenic PFAS or Natural Products? Natural Products Cause Overestimation of C2-C5 Perfluoroalkyl Carboxylic Acid Levels, *Environ. Sci. Technol.*, 2025, **59**(22), 11194–11204.