Supplementary Information for:

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

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Table S1. Acronyms, number of carbons, and full nomenclature of PFCAs analyzed in this study.

Acronym	Number of Carbons	Full Nomenclature
TFA	C2	Trifluoroacetic acid
PFPrA	C3	Pentafluororpropionic acid
PFBA	C4	Perfluorobutanoic acid
PFPeA	C5	Perfluoropentanoic acid
PFHxA	C6	Perfluorohexanoic acid

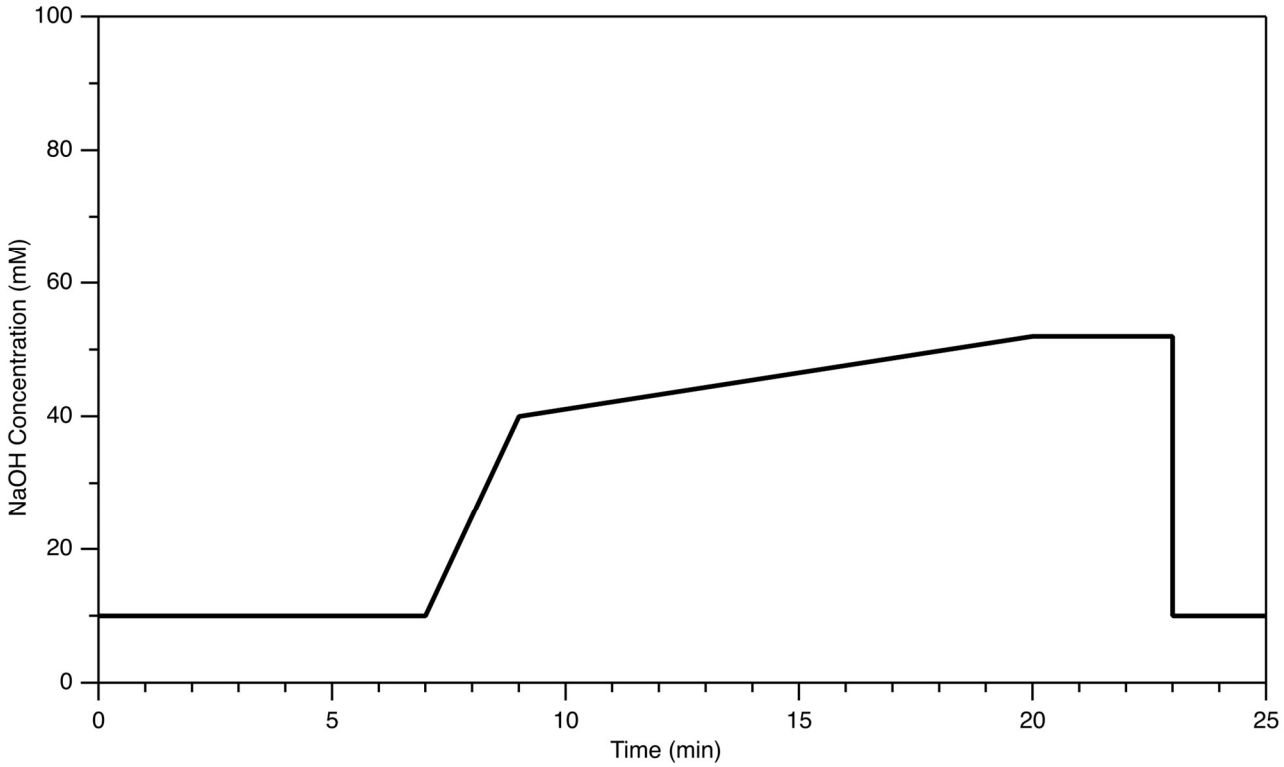

Figure S1. Sample eluent gradient of sodium hydroxide (NaOH) method used.

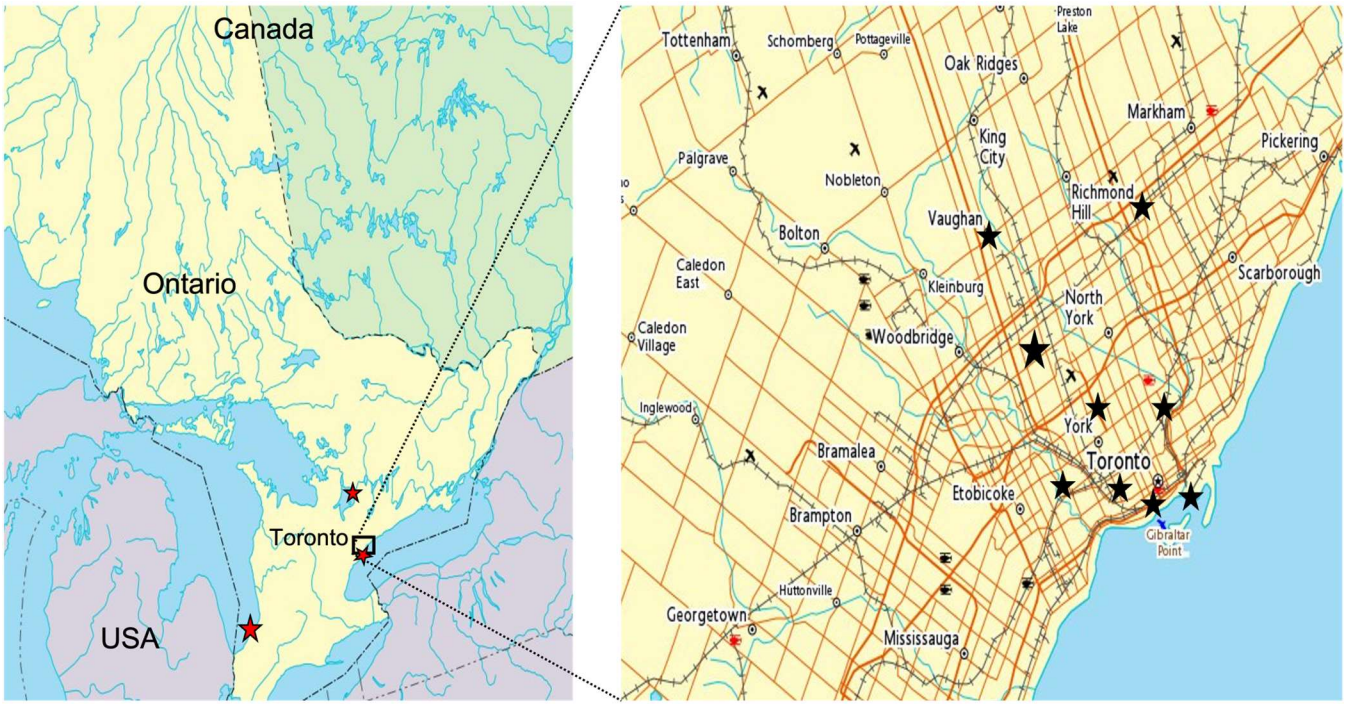

Figure S2. Map of sampling locations showing the surface water collection sites (red stars) and approximate tap water collection sites (black stars).

Table S2. Selected water chemistry parameters reported from freshwater bodies sampled in this study.

Sampling location	Sampling coordinates	Date collected	Conductivity (µS/cm)	Chloride (mg/L)	Dissolved organic carbon (mg/L)	Source
Don River	43.688333, -79.362222	February 28, 2023	8040	2580	N/A	1
Don River	43.688333, -79.362222	March 30, 2023	2350	541	2.3	1
The Cut (Ausable River)	43.193333, -81.813889	March 21, 2023	469	19.3	4.47	1
Toronto Inner Harbour (Lake Ontario)	43.63158, -79.36994	May 23, 2023	487	68.9	2.44	2
Ausable River Mouth (Lake Huron)	43.29403, -81.83008	June 8, 2022	215	8.31	1.98	2

1 Province of Ontario, Provincial (Stream) Water Quality Monitoring Network, https://data.ontario.ca/dataset/provincial-stream-water-quality-monitoring-network

2 Province of Ontario, Water Chemistry (Great Lakes Nearshore Areas), https://data.ontario.ca/dataset/water-chemistry-great-lakes-nearshore-areas

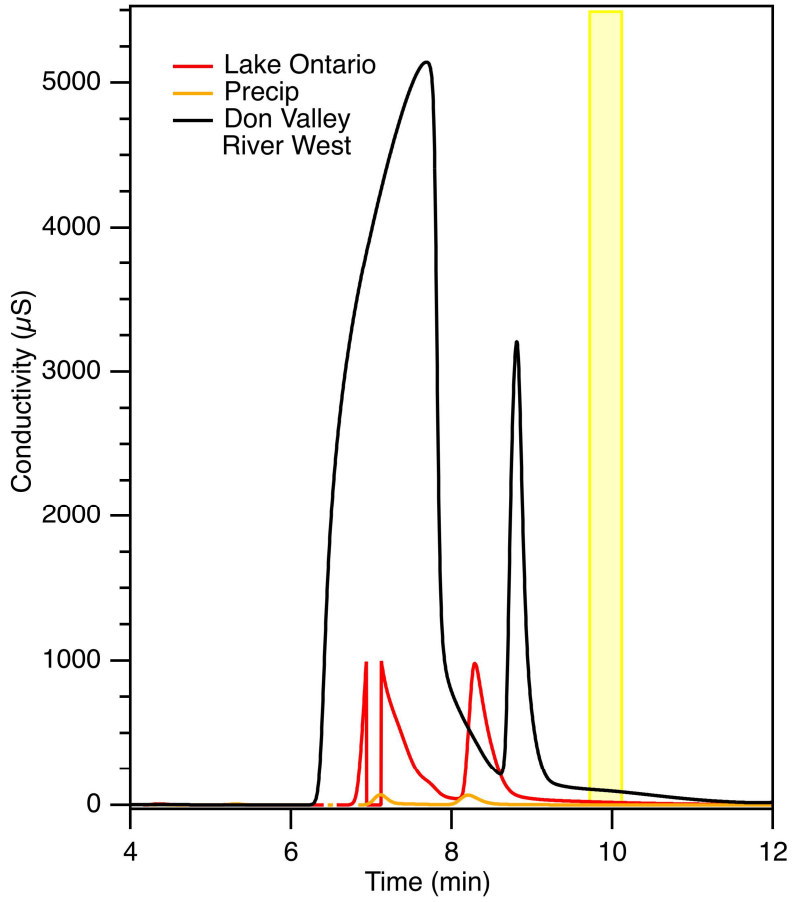

Figure S3. Conductivity detector chromatograms of freshwater samples with different levels of matrix: Don West River (black), Lake Ontario (red), and precipitation (orange). Note that the large conductivity peak from 6-8 minutes in the Don West River sample (black) includes organic acids and TFA elutes at around 9.8 min shown with the yellow bar.

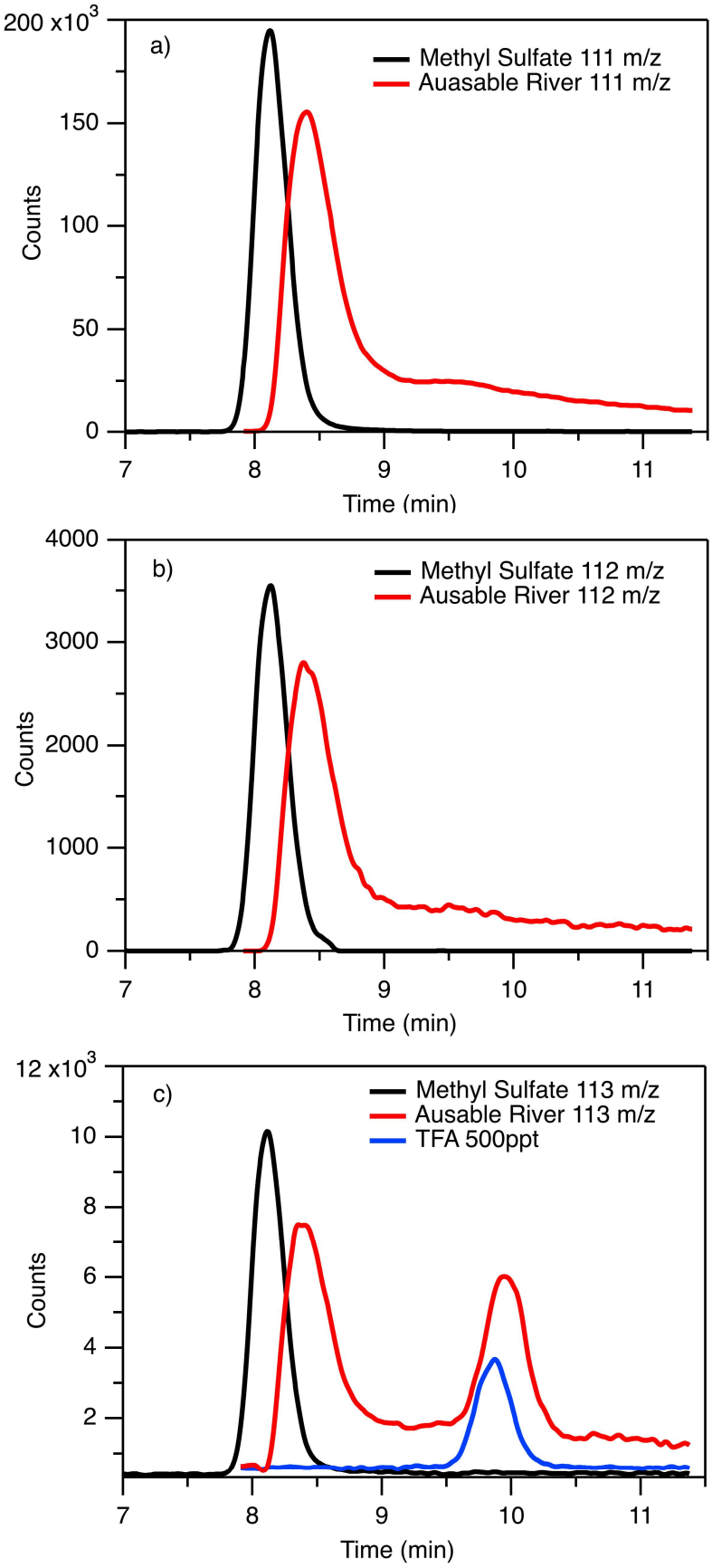

Figure S4. Chromatograms of Methyl Sulfate (black), and the Ausable River (red), and TFA (blue) at the m/z of 111 (a), 112 (b), and 113 (c) showing the different retention times.

Table S3. Ausable River and Methyl Sulfate comparison of the peak areas and the different m/z ratios of the total sample.

	m/z	Area (counts)	Ratio
Ausable River	111	57073	0.937
	112	1012	0.166
	113	2828	0.046
Methyl Sulfate	111	59523	0.943
	112	1048	0.166
	113	2564	0.041

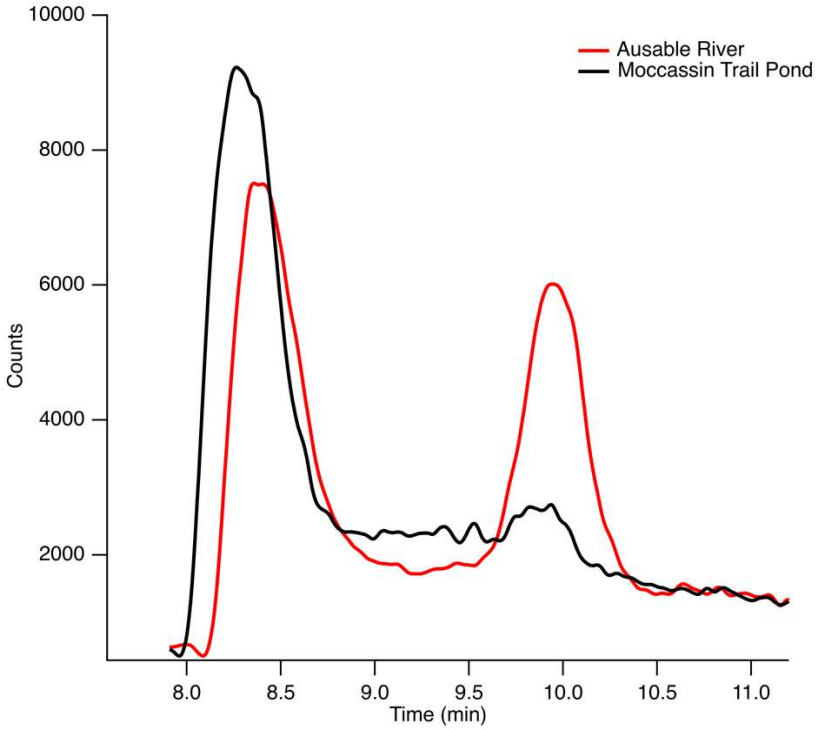

Figure S5. Chromatogram of the samples Ausable River (red) and Moccasin Trail Pond (black) at 113 m/z with a 250 mL injection loop. The first peak around 8.5 min is the unknown acid and the second peak around 9.8 min is TFA.

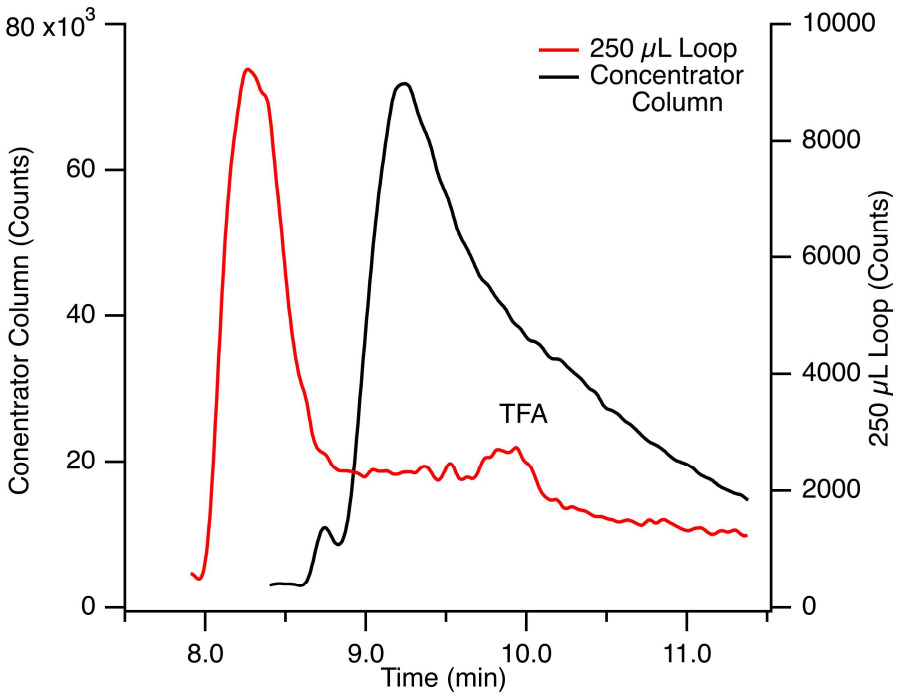

Figure S6. Chromatogram of the Moccasin Trail Pond sample injected with a 250 mL loop (Red) and a concentrator column (Black).

S1. Emergency Shutdown Procedure:

A major concern in running a mass spectrometer (MS) coupled with ion chromatography is the possibility of introducing salt into the system. While the suppressor functions in the system to convert the hydroxide eluent into water, we have encountered many instances in which the suppressor can fail. This results in significant downtime to clean the MS and, in the worst case scenario, MS damage. The main reoccurring issue involves the auxiliary pump (AXP) used to recycle water into the suppressor shutting off. An AXP is mandatory when running an IC-MS system, because the MS vaporizes the eluent, which prevents using the system in the traditional recycle mode. Thus, the suppressor for the IC-MS requires the use of two pumps: the analytical pump and the AXP. The instrument software, Chromeleon 7, only allows the suppressor to be linked to one pump (by default the analytical pump), allowing an immediate shutoff if the pump disconnects or goes outside of the set pressure range. Therefore, an issue with the AXP does not automatically turn off the suppressor or prevent flow into the MS, which can cause salt to flow into the mass spectrometer and create clogging throughout the system (needle, ion transfer tube, and front

optics). Therefore, when running an IC-MS system emergency shutdowns must be in place to prevent damage to the mass spectrometer.

There are two different ways we have incorporated emergency shutdown methods while operating the system. The first is under the queue tab in the Chromeleon 7 software at the bottom of the page is a section labelled Emergency Instrument Method where when an "Abort" occurs you can run an instrument method. Different error levels can be set under the Chromeleon Instrument Configuration Manager (Blue Chromeleon). By opening each module attached to the system and clicking on the error tab, a drop down menu appears that enables selection from a variety of possible errors (ranges from pressure limits to motor stalls) and the ability to set each error to a message error level. The possible error levels are Ignore, Warning, Error, and Abort. Any error that is set to Abort, while samples are running in the queue, triggers the emergency shutdown method.

A specific emergency shutdown method can be created for any system configuration; however, data collection cannot occur, and all possible information logging must be deselected. This includes the conductivity detectors, MS detector, and the pump pressure diagnostic logger. The method we use is 1 minute long with the application flow rates and eluent concentrations used and the shutdown occurs in the script editor. Specific naming conventions will vary across instrumentation configurations; however, the general instructions follow; the valve that switches between waste and the mass spectrometer is set to go to waste at time 0 min, the remaining steps occur at the 1 min mark where all pumps motors are set to off (analytical pump, AXP suppressor), the system queue is aborted, the suppressor mode is set to off. We leave MS on with only the MeOH running using the AXP pump for the MS until we manually shut the vaporizer temperatures off to allow the system to cool down below the boiling point.

The second emergency shutdown method we use is built into our script editors of for our analytical methods. Under the conditional dropdown menu you can insert a trigger. We use multiple triggers for either conductivity increases or pressure failures. The gradual increase is set to trigger if the conductivity signal is above 5 mS for longer than 5 min (300 s), with a 0.1 delay, limit set to INFINITE, hysteresis set

to 0, and allowing immediate execution. The commands we have set the system to execute if this occurs are: 1) switch the MS valve to waste; 2) set the gradient of the pump back to 10 mM of NaOH; and 3) abort the queue but keep the remaining system running until we manually check to determine why the high background is occurring. The catastrophic increase is set to trigger if the conductivity signal is above 55 mS for longer than 3 min (180 s), with a 0.1 delay, limit set to INFINITE, hysteresis set to 0, and allowing immediate execution. The commands we have set the system to execute if this occurs are: 1) switch the MS valve to waste; 2) abort the queue; 3) shut off all pumps (analytical pump, AXP mass spectrometer, and AXP suppressor); 4) shut off the suppressor; and 5) set the MS vaporizer temperature to 0 °C, ion transfer tube temperature to 150 °C, and the gas pressures (sweep, sheath, and aux) to 2. A third trigger can be used for the pressure of the AXP suppressor pump falling below a specific pressure, as well as many other conditions.