Target and Nontarget Screening of PFAS in Drinking Water for a Large-Scale Survey of Urban and Rural Communities in Québec, Canada

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Abstract

Limited monitoring data are available regarding the occurrence of emerging per- and polyfluoroalkyl substances (PFAS) in drinking water. Here, we validated an analytical procedure for 42 PFAS with individual detection limits of 0.001-0.082 ng/L. We also evaluated how different sample pH conditions, dechlorinating agents, and storage holding times might affect method performance. PFAS were analyzed in tap water samples collected at a large spatial scale in Quebec, Canada, covering 376 municipalities within 17 administrative regions. Target and nontarget screening revealed the presence of 31 and 23 compounds, respectively, representing 24 homolog classes. Overall, 99.3% of the tap water samples were positive for at least one PFAS and the ΣPFAS ranged from below detection limits to 108 ng/L (95^{th} percentile: 13 ng/L). On average, ΣPFAS was 12 times higher in tap water produced from surface water than groundwater; however, 6 of the top 10 contaminated locations were groundwater-based. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) had high detection rates (88% and 80%, respectively). PFOS (median: 0.15 ng/L; max: 13 ng/L) and PFOA (median: 0.27 ng/L; max: 8.1 ng/L) remained much lower than current Health Canada guidelines but higher than USEPA's 2022 interim health advisory values. Short-chain (C3-C6) perfluoroalkyl sulfonamides were also recurrent, especially the C4 homolog (FBSA: detection rate of 50%). The 6:2 fluorotelomer sulfonyl propanoamido dimethyl ethyl sulfonate (6:2 FTSO2PrAdDiMeEtS) was locally detected at ~15 ng/L and recurred in 8% of our samples. Multiple PFAS that are most likely to originate from aqueous film-forming foam were also reported for the first time in tap water, including X:3 and X:1:2 fluorotelomer betaines, hydroxylated X:2 fluorotelomer sulfonates, N-trimethylammoniopropyl perfluoroalkane sulfonamides (TAmPr-FHxSA and TAmPr-FOSA), and N-sulfopropyl dimethylammoniopropyl perfluoroalkane sulfonamidopropyl sulfonates (N-SPAmP-FPeSAPS and N-SPAmP-FHxSAPS).

Keywords

Drinking water; PFAS; Nontarget screening; Canada; Geographical mapping.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) represent a vast group of fluorinated chemicals with uses in cosmetics, coatings, textiles, food packaging, fluoropolymer manufacturing, enhanced oil recovery, aqueous film-forming foams (AFFFs; firefighting against oil fires), and other miscellaneous applications (Glüge et al. 2020). Their high thermal and chemical stability makes them persistent in the environment (Cousins et al. 2020); some PFAS also bioaccumulate at high levels in humans and wildlife with potential toxic effects (Fenton et al. 2021; Hoffman et al. 2011).

The environmental occurrence of two specific PFAS classes, the perfluoroalkyl carboxylic acids (PFCA, e.g., perfluorooctanoic acid (PFOA)) and perfluoroalkyl sulfonates (PFSA, e.g., perfluorooctane sulfonate (PFOS)), has been widely studied in the past two decades. One key exposure pathway for humans is through the consumption of tainted drinking water (Hoffman et al. 2011). As such, Health Canada, the United States Environmental Protection Agency (USEPA), State jurisdictions, the European Union, and others have established (or are in the process of implementing) guideline limits for PFCA and PFSA homologues in drinking water.

A screening study of 6 PFAS in >36,000 drinking water samples was conducted as part of USEPA's Unregulated Contaminant Monitoring Rule 3 (UCMR3); it was estimated that more than 6 million US residents had PFOS and/or PFOA above EPA drinking water advisory levels (of 70 ng/L at the time), mainly linked to industrial sites and military fire training areas (Hu et al. 2016). In Europe, large fluoropolymer manufacturers, AFFF use sites, and secondary emissions from wastewater were also important contributors to the contamination of rivers and public supply drinking water (Zafeiraki et al. 2015; Jeong et al. 2022). Treatment processes at wastewater and drinking water treatment plants (WWTP and DWTP, respectively) are not always efficient at removing PFAS, and some homologs can increase after treatment due to the transformation of precursor compounds (Gonzalez et al. 2021; Xiao et al. 2018).

Methods to characterize PFAS in drinking water typically involve weak-anion exchange SPE to reach a suitable concentration factor prior to targeted analysis of PFCA (C4-C14), PFSA (C4-C10), and a few negative ion mode precursors (e.g., 6:2 fluorotelomer sulfonate (6:2 FtS) and perfluorooctane sulfonamide (FOSA)) by liquid chromatography tandem mass spectrometry (LC-MS/MS). However, the characterization of extractable organofluorine (EOF) in drinking water revealed that a non-negligible fraction of the total PFAS could be missed by targeted analysis (Jiao et al. 2022). Previous PFAS-related nontarget studies have mostly addressed contaminated samples such as AFFFs, AFFF-impacted groundwater, industry-impacted environments, and WWTP effluents (Barzen-Hanson et al. 2017; D'Agostino et al. 2014; Jeong et al. 2022; Wang et al. 2018; Washington et al. 2020). Comparatively, nontarget studies on PFAS in drinking water are scarce (Wang et al. 2022).

Jiao et al. (2022) compared summed 34 target PFAS and EOF in drinking water around Taihu Lake, China. More than 68% of the EOF could not be explained by targeted LC-MS/MS analysis, and suspect screening revealed the presence of several emerging PFAS, such as hydrido-perfluorocarboxylic acids (H-PFCA) and *p*-perfluorous nonenoxybenzenesulfonate (OBS) (Jiao et al. 2022). In another study, suspect screening of PFAS in drinking water (private wells) from an AFFF-impacted community in El Paso County, Colorado, USA, revealed the presence of short-chain (C3-C6) perfluoroalkyl sulfonamides and unsaturated PFOS (McDonough et al. 2021), analytes that are not yet included in standardized EPA methods (537, 537.1, 533, 1633). Previous studies typically did not include positive ion mode PFAS in their targeted or nontargeted procedures for drinking water, representing another important knowledge gap. Some of the newly introduced AFFFs in Canada have resulted in several zwitterionic PFAS emerging in surface waters of Ontario (D'Agostino & Mabury 2017). However, their presence in finished tap water has not yet been documented. Standardized methodologies for PFAS in drinking water currently include the

negative ion mode PFAS, and it is unknown whether they are transferrable to positive ion mode PFAS.

In this study, we set out to document the presence of emerging PFAS in treated drinking water. The first part of the project was devoted to expanding current drinking water methods to novel AFFF-derived PFAS, including emerging polyfluoroalkyl betaines (D'Agostino & Mabury 2017). Factors influencing the performance of an automated solid-phase extraction (SPE) method were examined prior to validating the optimized method for limits of detection (LODs), recovery, linearity, accuracy, and precision. In the second part of the project, target and nontarget screening were applied to characterize PFAS across a set of 463 tap water samples collected at a large spatial scale in Québec, Canada. A PFAS mapping was established, and trends are discussed with respect to watersheds and the type of source used for drinking water production. Several of the newly identified precursors are detected for the first time in finished drinking water, suggesting that they persist through the treatment train and contribute to human exposure.

2. Materials and methods

2.1. Chemicals and standards

Certified standards of negative ion mode PFAS were purchased from Wellington Laboratories (Guelph, ON, Canada), DuPont (Wilmington, DE, USA), or Synquest Laboratories (Alachua, FL, USA). Standards of positive ion mode PFAS were purchased from Wellington Laboratories (Guelph, ON, Canada) or Fluobon (Beijing, China). Details on target analytes, internal standards, and other chemicals and materials are provided in the Supporting Information (**Text S1**; **Tables S1-S2**).

2.2. Sample collections

Tap water samples were collected across Québec, Canada, in the summer-fall of 2018, 2019, and 2020. A total of 463 tap water samples were obtained from the sampling efforts, corresponding to

376 municipalities within 17 administrative regions (**Table S3**). Their geographical distribution is shown in **Figure 1**. Some locations were resampled across different years to confirm the observed PFAS levels/profiles. Due to covid-19 travelling restrictions, the scope of the 2020 survey (n = 43) was relatively limited compared to that achieved in 2018 (n = 141) and 2019 (n = 279).

High-density polyethylene bottles (HDPE, 500 mL) were pre-rinsed at the analytical facilities using deionized water, 50:50 methanol (MeOH)/HPLC-water, and HPLC-water, and dried before use. Chlorine-treated drinking water samples were collected from public distribution points using the following procedure. Operators (University personnel) were asked to carefully rinse their hands (with no soap) and dry them before collecting the samples, wearing laboratory nitrile gloves. The tap water was left to flow for ~3 min, after which the HDPE bottles were rinsed three times with the site tap water and filled. Sodium thiosulfate powder was added to the samples to achieve a concentration of 100 mg/L (Husk et al. 2019; McLaughlin et al. 2011; Xiao et al. 2018). Samples were placed in an icebox with ice until the reception at the laboratory, where they were stored at 4 °C until solid-phase extraction (SPE), preferably within one month of sample collection.

2.3. Targeted analyses

The protocol is based on a previously described automated SPE method (Kaboré et al. 2018), with some modifications. Off-line automated SPE was conducted using a Thermo/Dionex Autotrace 280 system. Solvent lines were purged daily, and SPE sample lines were rinsed before the start and at the end of each batch, sequentially using a MeOH/HPLC-water mixture (50:50 v/v) and HPLC-water. Surrogate internal standards (IS_{surrog}; **Table S2**) were spiked to the drinking water samples (150 µL of a 10 ng/mL mixture prepared in MeOH), and the samples were homogenized by the operator. For improved retention of short-chain PFCAs, the sample pH was adjusted to ~6.5 with acetic acid before solid-phase extraction. SPE cartridges (Strata X-AW, 200 mg/6 mL) were conditioned with 0.2% NH_4OH (of a 28-30% solution) in MeOH (2 x 4 mL) and with HPLC-water (2 x 4 mL). Samples (500 mL) were loaded onto the cartridges at a controlled flow rate of 10

mL/min; every 5-10 min, bottles were gently swirled by the operator. Following sample loading, the inner surface of bottles was also rinsed with 5 x 4 mL of ultrapure water, and then the rinse fraction was loaded onto the cartridges. Further rinsing of the HDPE bottles with organic solvent was also tested. Cartridges were dried on the Autotrace for 30 min using a N_2 flux. An alternate drying method was enlisted in case of incomplete cartridge drying (using cartridge centrifugation and further drying on a vacuum pump connected to an SPE manifold). Analytes were eluted into Autotrace fitted glass tubes with 2 x 4 mL of 0.2% NH_4OH in MeOH, and the organic extracts were subsequently pipetted onto pre-weighed 15-mL polypropylene (PP) centrifuge tubes.

Extracts were evaporated to 1 mL under a gentle N_2 flux and mild heating (40-45 °C), after which injection/performance internal standards (IS_{inj}; **Table S2**) were spiked to the samples (150 µL of a 10 ng/mL MPFAC-C-IS solution prepared in MeOH). Following brief vortex-mixing, extracts were further concentrated (N_2, 40-45 °C) to <350 µL, and the final extract volume was gravimetrically adjusted to 400 µL in all samples. Following brief vortex-mixing and centrifugation (5 min, 5000 rpm), a 120-µL aliquot of the extract was transferred to an LC-MS injection vial (PP, 250 µL) and 30 µL of HPLC-water was added. The final extract composition was 80:20 MeOH/Water, which allowed for increasing the injection volume from 7 µL (Kaboré et al. 2018) to 15 µL. Higher water percentages were not considered to reduce the risk of time-dependent sorption artifacts during the LC-MS batch sequence (Martin et al. 2019).

PFAS analysis was conducted using ultra-high-performance liquid chromatography coupled with high-resolution mass spectrometry (UHPLC-HRMS) through an electrospray ionization source run in negative and positive ion modes (Martin et al. 2019). Chromatographic separation was performed with a Thermo Hypersil Gold C18 column (100 mm × 2.1 mm; 1.9 µm particle size) thermostated at 40 °C. Mobile phases were (A) 0.1% formic acid in HPLC-water and (B) 0.1% formic acid in acetonitrile. The Dionex Ultimate 3000 LC system was interfaced with a Q-Exactive Orbitrap mass

spectrometer with a mass scan range set at *m/z* 150-1000 (full scan acquisition mode). Details on the delay column and LC-MS acquisition method are provided in **Table S4**.

2.4. Quality assurance/quality control (QA/QC)

QA/QC was conducted for each LCMS batch sequence using in-house protocols (**Text S2**), adapted from EPA methods (e.g., method 533) and recommendations of Department of Defense / Department of Energy consolidated Quality System Manuals (DoD/DOE QSM version 5.3, Table B-15). Solvent-based calibration curves (iCAL) and SPE-extracted matrix-matched calibration curves (mCAL) all had determination coefficients (R^2) >0.9900 (in most cases, >0.9950) (**Table S5**). Initial (ICV) and continued (CCV) calibration verification standards (n = 51) had accuracies within 70-130% for 36/42 compounds (**Table S6**). Method limits of detection were derived from the EURACHEM method and were in the range of 0.001-0.082 ng/L (**Table S7**). Method blanks and field blanks (n = 42) had low levels of specific anionic PFAS (**Table S8**). Matrix spikes to commercially bottled water (n = 16) had accuracy within 70-130% in most instances (**Table S9**).

2.5. Nontarget screening

A few tap water sampling sites with higher PFAS levels or unusual PFAS profiles (based on the 2018-2019 database) were selected for nontarget screening. Larger volume samples (2-3 L) were collected during the third survey at these sites, including two samples from the Montreal and Laurentides region (surface water sourced tap water), and the hotspots from the Abitibi and Lanaudière regions (groundwater sourced tap water). For nontarget analysis, between 4 and 6 tap water bottles (500 mL each) per site were submitted to SPE (without internal standards) and then composited in one extract (for each site) to favor detections by nontarget analysis. Method blanks were run likewise to allow spectrum subtraction. Data acquisition was performed in full scan MS over an *m/z* range of 150-1000 and a resolution setting of 70,000 FWHM at *m/z* 200 (Thermo

UHPLC-HRMS Orbitrap Q-Exactive). Negative and positive ionization modes were acquired in separate injections to maximize the number of data points per chromatographic peak.

Nontarget data filtering was performed as described in our previous biosolids study (Munoz et al. 2022). In the first step, the blank background was subtracted using the XCMS Online software (pairwise subtraction, using the Xcalibur raw files of a tap water sample *vs.* the method blank), and a signal intensity threshold of 1E4 was applied to eliminate features of low intensity. The dataframe of remaining features (accurate *m/z*, retention time, and intensity) was further submitted to mass defect filtering to eliminate the features outside the scope of characteristic PFAS defect ranges (Barzen-Hanson et al. 2017). Measured *m/z* were converted to Kendrick mass scale, and extracted peaks with CF_2-normalized mass defects of 0.85-1.0 or 0-0.15 were retained, using an in-house script programmed with Anaconda (Python). Additional rules were applied as described elsewhere (Munoz et al. 2022); however, our initial script was modified to avoid the exclusion of single homologs that may be present in the tap water samples (e.g., 6:2 fluorotelomers could be present while shorter or longer-chain homologs may not). A second in-house script (also programmed with Anaconda) was used to conduct an automated library search of features remaining after the filtering strategy, using 9 Excel databases including the Norman Network PFAS Suspect List, the OECD's New Comprehensive Global Database for PFASs, PFAS KEMI (List from the Swedish Chemicals Agency), the USEPA Comptox Chemistry Dashboard, and lists of AFFF- and surfactant-derived PFAS from literature (Barzen-Hanson et al. 2017; Nickerson et al. 2020) and patents (e.g., US5616273A, 1997). For identity confirmation of positive hits, retention times were visually inspected and structural information was acquired by reinjecting extracts using high-resolution MS/MS (**Figures S1-S26**). The additional compounds identified through suspect screening were then retrospectively searched in the LC-HRMS chromatograms of all 463 tap water samples and semi-quantified using a reference calibrant and internal standard (Mejia-Avendaño et al. 2017).

2.6. Statistics and GIS

Statistical analyses were performed with the R statistical software version 4.0.4 (R Core Team 2021, Vienna, Austria). Statistical significance was set at $p < 0.05$. Quantum GIS (QGIS 3.6 Noosa) was used as a geographic information system. Base maps were retrieved from Natural Earth (vector and raster map data available at naturalearthdata.com).

3. Results and discussion

3.1. Preliminary tests

A previous drinking water method using automated off-line SPE was evaluated in HPLC water, mineral bottled water, and dechlorinated tap water; the original sample loading volume was decreased from 1000 mL (Kaboré et al. 2018) to 500 mL (present study) for improved turnaround times.

In dechlorinated tap water, 23 of 44 tested PFAS had spike recoveries between 80-100% and 12 PFAS between 50-80% (**Figure S27**). The 6:2 FTAB was near-quantitatively recovered (95%) using the initial method. Recoveries of C5-C14 PFCAs approximately followed an inverted sigmoid with increasing carbon chain length, with the minimum at ~40% for PFTrDA and PFTeDA. Interestingly, higher recoveries were observed for C16-C18 than for C12-C14 PFCAs. The molecular mechanism responsible for this is unclear, but this may be due to perfluoroalkyl chain folding of very long-chain PFCAs in the aqueous medium, resulting in lower hydrophobicity.

The absolute recovery of ultra-short chain PFPrA (C3) greatly varied with matrix type (**Figure S27**), ranging from acceptable in HPLC-water (69±14 %) to unacceptable in mineral water (MW+$Na_2S_2O_3$: 10.0±0.8 %) or tap water (<2%). Short-chain PFBA (C4) also had much higher SPE recoveries in HPLC water (78±14 %) compared to tap water (25±8 %). The higher pH of tap water amended with sodium thiosulfate (pH ~ 8.3) was likely responsible for the lower PFPrA and PFBA recovery.

A weak acid could be amended to water samples to attain a slightly acidic pH and thus better recoveries of short-chain PFCAs (Method 533; Janda et al. 2019). The absolute recoveries of hydrophobic PFAS could possibly be improved by extracting the HDPE bottles with organic solvent after SPE. This was tested in our following spike-recovery experiments.

3.2. Factors influencing analytical method performance

Influence of sample pH. Short-chain PFCAs present analytical challenges due to limited retention on SPE sorbents and reverse-phase liquid chromatography columns (Janda et al. 2019; Yeung et al. 2017). A tap water matrix (pH ~ 8) was amended with acetic acid to investigate the influence of lowering sample pH on recoveries of short-chain PFCAs and other targeted PFAS (**Figure 2**). Lowering the sample pH had a strong positive impact on the recoveries of PFPrA (C3) and PFBA (C4). The absolute recovery of PFPrA increased from 3.3±0.2% at pH 8 to 90±5% at pH 6, with marginal variations at lower pH values. A pH range of 4–7 was found to yield suitable recovery of PFBA in tap water matrix.

Strata X-AW yielded satisfactory recoveries for zwitterionic betaine-based PFAS (6:2 FTAB, 5:3 FtB, 5:1:2 FtB). No influence of pH on recovery was noted for these compounds within the tested pH range, which agrees with their predicted speciation—i.e., predominately in the neutral form under environmental pH conditions (Mejia-Avendaño et al. 2020). As the pH was lowered, certain types of PFAS had decreased recoveries. The absolute recovery of FOSA, for instance, dropped from 90±6% (pH 8) to 40±5% (pH 4). The lower recoveries of long-chain FOSA are assumed to be due to speciation, with the neutral form having increased hydrophobicity (and volatility).

Influence of organic solvent rinse. For mass balance purposes, the HDPE bottles were submitted to a rinse step with 3 x 4 mL of MeOH after the SPE loading step. The MeOH rinse fraction was kept separately and transferred to PP tubes for extract concentration (N_2, 40-45 °C) prior to LC-MS analysis of the sorption artefact (**Figure 3**). Solvent extracting the HDPE bottles did not yield

quantifiable PFAS amounts for C4-C9 PFCAs or C3-C5 PFSAs, and the sorption loss was also negligible for C6-C8 PFSAs (e.g., ~1.2% for PFOS). PFAAs between 12 and 15 perfluorinated carbon atoms showed substantial sorption artefact (10-20%), especially under low pH conditions. Apart from FOSA and MeFOSAA, the tested precursors exhibited limited sorption to the HDPE material.

Influence of storage holding time. A preliminary test conducted in AFFF-amended tap water suggested no impact of reductant type on the recovery of PFAAs or their precursors over a 28-day storage period (unpublished data). As storage stability data are already available for drinking water samples amended with Trizma or ammonium acetate (EPA Methods 533 and 537), we have focused on testing sodium thiosulfate.

Storage stability trials were conducted on non-spiked tap water containing low but detectable PFAS levels (17 compounds characterized at T_0 with concentrations between 0.04 and 2.2 ng/L). The 500-mL chlorinated tap water samples were collected from a tap in downtown Montreal and amended with 100 mg/L $Na_2S_2O_3$ before immediate extraction (T_0) or storage at 4 °C for variable durations (**Table 1**). After 60 days of storage, recovery % (relative to T_0) was within 85.1% (FBSA) and 110.5% (PFBA), which was deemed acceptable. Our results agree with Taniyasu et al. (2022), who also observed suitable stability of 31 PFAS in drinking water stored for 45 days at ± 3 °C.

Influence of sample preservatives on matrix effects. Though analytical validation was essentially focused on tap water samples amended with sodium thiosulfate as the chlorine quenching reagent, other reductants relevant to EPA methods were also considered, including 5 g/L Tris HCl/Tris (15.5:1 w/w) (EPA Methods 537 and 537.1) and 1 g/L ammonium acetate (EPA Method 533). The 500-mL tap water samples were acidified prior to automated off-line SPE as previously described, and matrix effects were derived using a matrix-free reference.

Raw matrix effects evaluated based on the IS absolute area generally remained within a ±50% acceptance range (**Figure S29**). Short-chain PFCAs showed moderate signal suppression (-25%), while signal enhancement was noted for long-chain PFCAs. Limited influence of the reductants was noted between the tested conditions. For instance, raw matrix effects for $^{13}C_8$-PFOS ranged between +19% (tap water + ammonium acetate) and +21% (tap water + sodium thiosulfate).

As the method derives a large sample volume of tap water (500 mL), observing *raw* matrix effects is not unexpected. However, as internal standards are used for matrix compensation of target analytes, the *effective* (IS-corrected) matrix effect should thus be considered. The instrumental accuracy (based on the analyte to internal standard area ratio) is shown in **Figure S30** for tap water with or without reductants. For PFCAs and PFSAs, for which a broad suite of internal standards is available, accuracy was typically within the range of 80-120% (i.e., an effective matrix effect within ± 20%) with few exceptions. Even for zwitterionic and cationic precursors without matched IS, accuracy was within 70-130% in most cases, independently of reductant type.

Lessons learned and recommendations. In the modified method, we suggest adjusting tap water pH to ~ 6.5 (with acetic acid) prior to submitting the samples to SPE. The pH condition was selected considering the improved recovery for PFBA/PFPrA but avoiding lower pH values to maintain acceptable recoveries for FOSA and its related homologs. The selected pH condition is also within a reasonable range of pH conditions of EPA Methods 537.1 (the Tris-HCl/Tris blend targeting to produce a pH near 7.0), 533 (targeting a pH between 6 and 8), and 1633 (targeting a pH of 6.5 ± 0.5). A rinse step of bottle materials with organic solvent post-SPE is also advised for improved recoveries of long-chain PFAS, although these compounds are probably more relevant to sediments and biotic tissues than water samples.

Stability assays suggested suitable storage hold times for a broad range of PFAS in dechlorinated tap water. Our results indicate that the reductant type is unlikely to exert a strong influence on analytical method performance. However, as only one drinking water source was tested, we cannot

over-generalize these results. The tested matrix is representative of finished Montreal tap water (produced from the St. Lawrence River), available to consumers at public distribution points. It is not necessarily representative of a 'freshly treated' water matrix from the DWTP facility, where higher amounts of residual oxidants may be present. In other localities, tap water may also be produced from groundwater and have higher amounts of inorganic elements, which could imply different trends.

Absolute SPE recoveries or accuracies were lower than the performance objective of 70-130% for several of the long-chain ESI+ PFAS. Due to the lack of available isotope-labelled internal standards for ESI+ PFAS, this could have implied an underestimation of sample concentrations if using a solvent-based, nonextracted calibration curve (iCAL). For this reason, we recommend using a matrix-matched calibration curve (mCAL) constructed in tap water, wherein calibration levels are submitted to SPE.

3.3. PFAS classes identified by target and nontarget screening

The analytical method was applied to 463 tap water samples collected at a large spatial scale in Québec. Overall, 54 PFAS were detected, representing 24 distinct classes (**Figure 4**). Of these, 23 compounds (13 classes) would have been missed by our targeted list of 42 PFAS. Detection frequency and concentration ranges are summarized in **Table 2**. Of the 463 samples, 99.3% were positive for at least one PFAS. Summed PFAS ranged from below detection limits (<0.001 ng/L) to a maximum of 108 ng/L (average ΣPFAS: 4.8 ng/L; median ΣPFAS: 2.0 ng/L; 95% percentile of ΣPFAS: 13 ng/L). The 95th percentile of ΣPFAS is a good indicator of what can be considered above background, long-range contamination and we surmise that water samples containing more than 13 ng/L for the ΣPFAS are actually affected by a local source of contamination.

Negative ion mode PFAS. Ten PFCA (C4-C12, C14) and eight PFSA (C2-C8, C10) were detected in tap water samples. PFOA and PFOS were frequently detected (89 and 81%, respectively) but

remained at low concentrations (PFOA: median 0.27 ng/L, maximum 8.1 ng/L; PFOS: median 0.15 ng/L, maximum 13 ng/L). Boxplots are presented in SI (**Figure S31**). These median values are well below the current drinking water guidelines of Health Canada (200 and 600 ng/L for PFOA and PFOS, respectively) as well as those of the USEPA (70 ng/L for PFOA, PFOS, and their sum) but would be higher than the recent USEPA interim drinking water health advisory of 0.004 ng PFOA/L and 0.02 ng PFOS/L (USEPA 2022). The median PFOS at 0.15 ng/L is also lower than medians from US drinking water treatment plants (1.6 ng/L; n = 25) and public supply tap water from Australia (0.76 ng/L; n = 109) and South Korea (0.69 ng/L; n = 44) (Boone et al. 2019; Park et al. 2018; Thomson & Mueller 2011).

Perfluoroethyl cyclohexane sulfonate (PFECHS), a cyclic PFAS found to bioaccumulate in aquatic ecosystems (Wang et al. 2016), was detected in 32% of tap water samples from the present survey with a maximum of 7.1 ng/L. Chromatographic peak shapes and MS/MS evidence (**Figures S1-S2**) suggest that closely eluting PFECHS isomers were also present (Stefanac et al. 2018). Two additional cyclic PFAS, perfluoromethyl cyclohexane sulfonate (PFMeCHS) and perfluoromethyl cyclopentane sulfonate (PFMeCPeS), were detected in about 12-14% of tap water samples at sub ng/L levels. Identification confidence remained at level 3 only (**Figures S3-S4**) due to the possible ambiguity with the isomeric class of unsaturated-PFSA.

A series of short-chain (C3-C6) perfluoroalkyl sulfonamides (**Figures S5-S8**) was recurrently found in tap water, although at low concentration levels (maximum concentrations of 0.07–0.62 ng/L). Short-chain perfluoroalkyl sulfonamides are not currently included in EPA Methods 533, 537.1 and 1633. However, their detection in tap water agrees with previous reports for US and Canadian drinking water samples (Kaboré et al. 2018; McDonough et al. 2021). The most frequent homolog was the C4 perfluorobutane sulfonamide (FBSA), which was also identified in surface water and fish of the Laurentian Great Lakes and the St. Lawrence River (Chu et al. 2016; Munoz et al. 2022).

Several electrochemical fluorination (ECF)-derived precursors with large nonfluorinated head groups (**Figure 4**; classes N-SPAmP-FASA, N-SPAmP-FASAA, N-SPAmP-FASAPS, and N-SHOAmP-FASAHOPS) were detected by nontarget screening as probable structures or tentative candidates (**Figures S10-S15**). These chemicals were discovered in 3M AFFFs or AFFF-impacted groundwater (Barzen-Hanson et al. 2017), and this is the first report of their detection in treated tap water. N-sulfopropyl dimethylammoniopropyl perfluorohexane sulfonamidopropyl sulfonate (N-SPAmP-FHxSAPS; a possible precursor to PFHxS) was detected in 4.3% of tap water samples (concentration range of 0.003-0.64 ng/L); whereas other related compounds were infrequent. Fluorotelomer sulfonates (included in EPA Methods 533 and 1633) were occasionally detected in tap water, particularly the 6:2 FtS homolog (detection rate of 22%; maximum of 20 ng/L). In addition, a series of hydroxy-X:2 FtS (X = 4, 5, 6; **Figures S17-S19**) was also detected in a few samples, with MS/MS spectra in agreement with the fragmentation pattern expected for this class (Barzen-Hanson et al. 2017). The 6:2 fluorotelomer thioether amido sulfonate (6:2 FTSAS, also referred to as 6:2 FtTAoS and 6:2 FTTh-PrAd-DiMeEtS) and three related classes (6:2 FTSAS-sulfoxide, 6:2 FTSAS-sulfone, and 6:2 FTSO2PA) are reported for the first time in tap water samples (**Figures S20-S22**). The most frequent was 6:2 FTSAS-sulfone (detection rate of 8%), which also occurred at the greatest semi-quantified concentrations (maximum of 15 ng/L).

Positive ion mode PFAS. Only a few positive ion mode PFAS were detected in tap water samples from the present survey. The most notable were 6:2 FTAB (6:2 FTSA-PrB) (detection rate: 5.4%; maximum: 2.1 ng/L), 5:3 fluorotelomer betaine (5:3 FtB; detection rate: 3.5%; maximum: 0.58 ng/L) and 5:1:2 FtB (detection rate: 9.9%; maximum: 2.7 ng/L) (Figures S23-S25). Trimethyl ammonio propyl PFHxSAmS (TAmPr-FHxSA) and PFOSAmS (TAmPr-FOSA) were detected in less than 0.5% of samples.

3.4. Geographical trends of PFAS in Quebec tap water

A geographical mapping of PFAS in Quebec tap water is presented in **Figure 5** (for geographical reference to some of the raw water sources rivers discussed here, see also **Figure S32**). Relatively higher levels were found for sites located along a densely populated axis in the St. Lawrence valley. In contrast, very low PFAS levels were found for sites located in the eastern parts of the province (e.g., Bas-Saint-Laurent, Cote Nord, Gaspésie, Saguenay – Lac-Sant-Jean). Considering all data together, the mean abundance profile of PFAS was dominated by short-chain (C4-C7) PFCAs (accounting each between 8-21% of ΣPFAS), PFOA (16% of ΣPFAS), PFOS (10% of ΣPFAS), PFBS (5.4% of ΣPFAS), and PFHxS (3.4% of ΣPFAS). Some deviations to this average profile were, however, noted and linked to specific watersheds.

In tap water samples produced from the St. Lawrence River (**Figure S33**), profiles were consistently dominated by PFBA, PFOA, and PFOS (altogether representing 52 ± 2 % of ΣPFAS). These samples also had 100% detection rates for PFECHS (mean of 0.40 ± 0.17 ng/L), an important distinction with other watersheds where it was seldom detected. PFECHS was previously reported in surface waters of the Laurentian Great Lakes and the St. Lawrence River (De Silva et al. 2011; Munoz et al. 2022), and presumably originates from aircraft corrosion inhibitors. Its presence may thus be linked to long-range aquatic transport from the Great Lakes, as well as some local inputs to the St. Lawrence River.

Tap water samples produced from the Richelieu River (Montérégie) were relatively similar to the average global profile, except for unusually high contributions of FBSA (4.4% of ΣPFAS, or 8 times higher) and FHxSA (0.55% of ΣPFAS, or 4 times higher). FBSA is a known metabolite of fluorinated surfactants used in fabric protectors, while FHxSA is a potential degradation product of C6 precursors present in ECF-based AFFFs (Chu et al. 2016; Liu et al. 2022). As the concentrations of FBSA/FHxSA were not found to increase from upstream to downstream along the Richelieu River, we assume that the contamination source may be in the upper reaches—in Lake Champlain or further south.

Tap water samples produced from the Mille Iles River (north of Laval) had occasional detections of fluorotelomers linked to AFFF formulations (e.g., 6:2 FTAB and 5:1:2 FtB) and/or wastewater (e.g., 6:2 FtS and 6:2 FTAB). This agrees well with previous characterization of fire-training grounds in the area and the presence of wastewater effluents (Goeury et al. 2022; Liu et al. 2022). Interestingly, the 6:2 FTAB and X:1:2 FtB were also detected at low levels in another watershed (a few tap water samples produced from the Chaudière River), likely reflecting residual contamination from the emergency use of AFFFs earlier in 2013 (Mejia-Avendaño et al. 2017).

Data were collated regarding production sources (**Figure S34**). Overall, tap water produced from surface water was relatively more contaminated than that produced from groundwater (**Figure 6**). For instance, the summed PFAS was 12 times lower (median) in tap water produced from groundwater sources. However, 6 of the top ten contaminated locations were groundwater based and the two particular outlier sites (Figure 5) with the highest ΣPFAS were also related to groundwater contamination.

Outlier site #1 (Abitibi region) had unusually high abundances of PFHxS (18-29% of ΣPFAS) and PFPeA (28-35% of ΣPFAS), and PFAS profiles were consistent for the three consecutive years of sampling (**Figure S35**). Several ECF-derived precursors were found, predominately C5-C6 homologs (e.g., N-SPAmP-FHxSAPS). The unusual PFAS profile, together with the relatively high ΣPFAS (up to 108 ng/L), might be related to local emissions from surfactants used in mining/ore extraction processes historically performed in the area.

Outlier site #2 (Lanaudière region) presented relatively high ΣPFAS (68-82 ng/L) and unusually high contributions of PFPeA, 6:2 FtS, and 6:2 fluorotelomer thioether amido sulfonate (FTSAS-) related compounds; profiles were consistent for all three samples collected there between 2019 and 2020 (**Figure S36**). At this site, semi-quantified concentrations of 6:2 FTSAS-sulfone and 6:2 FTSAS-sulfoxide were each ~10 times greater than PFOS or PFOA. Though the contamination source remains to be clarified, the contamination profile is reminiscent of some current-use PFAS

formulations (AFFFs and industrial cleaning products) based on 6:2 fluorotelomer chemistry (D'Agostino & Mabury 2014; Field & Seow 2017).

4. Conclusions

An analytical method was developed to screen an expanded suite of PFAS in drinking water, with limits of detection of 0.001–0.082 ng/L. Sample acidification improved the SPE recoveries of short-chain perfluorocarboxylates but decreased those of perfluoroalkyl sulfonamides. Storage time (up to 2 months) had a limited influence on analytical performance. Targeted analyses revealed the presence of 31 PFAS in tap water samples from Québec province, and an additional 23 PFAS were identified by nontarget screening. This study is the first to report the presence of HO-X:2 FtS, FTSAS-related compounds, N-SPAmP-FASA related compounds, TAmPr-FASA, X:3 FtB, and X:1:2 FtB in tap water. None of these compounds are currently included in EPA methods for drinking water. Some of the emerging PFAS, such as 6:2 FTSAS-sulfone and 5:1:2 FtB, were locally present at concentrations >1 ng/L but were not widespread. In contrast, short-chain (C3-C6) perfluoroalkyl sulfonamides were frequently detected, in agreement with previous detections in the US and Canadian drinking water samples. The gathered database contributes to the current efforts toward expanding the lists of PFAS for monitoring. We also suggest that this large survey of nearly 400 sites allows us to use the 95th percentile as an estimate of maximum concentrations of PFAS occurring from large scale diffusion. This suggests that drinking water (and surface water) containing more than 13 ng/L for the ΣPFAS may have a local source of PFAS contamination. The 95th percentile concentration is 2.1 ng/L for PFOA and 2.6 ng/l for PFOS; these values are much significantly higher than the interim drinking water advisory being proposed by the USEPA. The 10th percentile for PFOA and PFOS are both at 0.026 ng/L, indicating that the vast majority of such water samples would not meet the interim drinking water health advisory for PFOA (0.004 ng/L) but the cleanest samples would almost meet the value for PFOS (0.02 ng/L).

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Tables and Figures

Table 1. *Recovery % relative to T_0 concentrations of PFAS detected in a non-spiked tap water sample (amended with 100 mg/L sodium thiosulfate upon collection at the Université de Montréal) and stored at 4°C for variable durations before sample preparation and analysis.*

		Recovery % relative to T_0				
	T_0 (ng/L)	2d	7d	14d	28d	60d
PFBA	2.17	101.2	105.4	99.7	110.6	110.5
PFPeA	1.01	102.8	89.7	89.3	90.4	102.3
PFHxA	1.45	96.5	96.7	98.7	94.9	96.4
PFHpA	0.75	103.6	97.9	97.7	102.1	103.3
PFOA	1.29	98.0	99.4	100.7	98.7	103.8
PFNA	0.36	96.3	96.9	101.0	93.9	104.8
PFDA	0.16	85.0	98.1	100.8	96.8	103.9
PFPrS	0.10	102.4	99.5	93.8	89.1	93.2
PFBS	0.54	102.5	96.2	102.9	101.9	102.2
PFPeS	0.12	98.0	100.8	99.6	101.0	101.1
PFHxS	0.77	98.0	100.2	100.0	100.3	102.7
PFHpS	0.04	94.3	102.2	98.6	88.5	94.6
PFOS	1.51	90.7	95.3	102.9	96.4	102.5
PFECHS	0.48	99.6	103.9	100.2	99.8	103.6
FBSA	0.20	100.5	100.0	114.4	98.0	85.1
FHxSA	0.08	93.1	102.0	123.6	103.4	98.8

Table 2. *Summary of PFAS occurrence data in Quebec tap water (2018-2020; N = 463).*

	Analyte type	Limit of detection (ng/L)	Detection frequency (%)	Min (ng/L)	Max (ng/L)
PFBA	Qn	0.044	73.9	0.044	8.54
PFPeA	Qn	0.006	75.6	0.007	30.7
PFHxA	Qn	0.007	74.3	0.009	19.2
PFHpA	Qn	0.004	81.6	0.004	6.88
PFOA	Qn	0.005	89.4	0.005	8.07
PFNA	Qn	0.003	51.4	0.006	1.12
PFDA	Qn	0.008	48.4	0.008	0.82
PFUnA	Qn	0.006	12.3	0.006	0.07
PFDoA	Qn	0.009	0.6	0.011	0.03
PFTrDA	Qn	0.009	0	-	-
PFTeDA	Qn	0.013	0.2	-	0.03
PFHxDA	Qn	0.012	0	-	-
PFOcDA	Qn	0.015	0	-	-
PFPrS	Qn	0.003	51.6	0.004	0.58
PFBS	Qn	0.005	85.7	0.005	14.8
PFPeS	Qn	0.002	59.0	0.002	1.25
PFHxS	Qn	0.004	78.4	0.004	31.2
PFHpS	Qn	0.004	34.1	0.005	0.61
PFOS	Qn	0.006	81.4	0.007	12.8
PFNS	Qn	0.005	0	-	-
PFDS	Qn	0.006	1.1	0.007	2.24
PFDoS	Qn	0.015	0	-	-
FBSA	Qn	0.001	49.7	0.003	0.62
FHxSA	Qn	0.005	25.5	0.006	0.40
FOSA	Qn	0.005	58.1	0.007	1.01
MeFOSA	Qn	0.017	0	-	-
EtFOSA	Qn	0.020	0.4	0.040	0.10
MeFOSAA	Qn	0.021	0.4	0.035	0.57
EtFOSAA	Qn	0.015	3.7	0.018	0.35
3:3 acid	Qn	0.082	0	-	-
5:3 acid	Qn	0.050	0.6	0.074	0.15
7:3 acid	Qn	0.077	0	-	-
4:2 FtS	Qn	0.005	1.3	0.008	0.02
6:2 FtS	Qn	0.010	22.5	0.011	19.7
8:2 FtS	Qn	0.005	2.2	0.024	0.27
10:2 FtS	Qn	0.012	0	-	-
PFECHS	Qn	0.003	32.4	0.003	7.11
PFHxSAm	Qn	0.003	0	-	-
PFOSAm	Qn	0.012	0	-	-
PFHxSAmS	Qn	0.004	0.4	0.009	0.02
PFOSAmS	Qn	0.014	0.4	0.015	0.02
6:2 FTAB	Qn	0.016	5.4	0.021	2.06
PFEtS	sQ	n/a	3.2	0.004	0.02
N-SPAmP-FPeSAPS	sQ	n/a	0.9	0.005	0.04
N-SPAmP-FHxSAPS	sQ	n/a	4.3	0.003	0.64
N-SHOPAmP-FHxSAHOPS	sQ	n/a	1.1	0.003	0.18
N-SPAmP-FPeSA	sQ	n/a	0.9	0.007	0.20
N-SPAmP-FHxSA	sQ	n/a	1.3	0.005	0.11
N-SPAmP-FHxSAA	sQ	n/a	0.6	0.003	0.07
FPrSA	sQ	n/a	18.6	0.002	0.07
FPeSA	sQ	n/a	21.8	0.003	0.46
H-U-PFOS	sQ	n/a	1.9	0.010	0.20
PFMeCPeS	sQ	n/a	12.7	0.003	0.9
PFMeCHS	sQ	n/a	14.0	0.006	0.3
HO-4:2-FtS	sQ	n/a	1.3	0.014	0.17
HO-5:2-FtS	sQ	n/a	1.5	0.016	0.04
HO-6:2-FtS	sQ	n/a	0.4	0.075	0.09
6:2-FTSAS	sQ	n/a	0.4	0.018	0.06
6:2-FTSAS-sulfoxide	sQ	n/a	0.9	0.024	14.28
6:2-FTSAS-sulfone	sQ	n/a	8.0	0.010	15.06
6:2 FTSO2PA	sQ	n/a	0.6	0.036	0.06
5:3 FtB	sQ	0.007	3.5	0.012	0.58
5:1:2 FtB	sQ	0.007	9.9	0.023	2.71
7:3 FtB	sQ	n/a	0.4	0.096	0.10
7:1:2 FtB	sQ	n/a	0.9	0.091	0.84

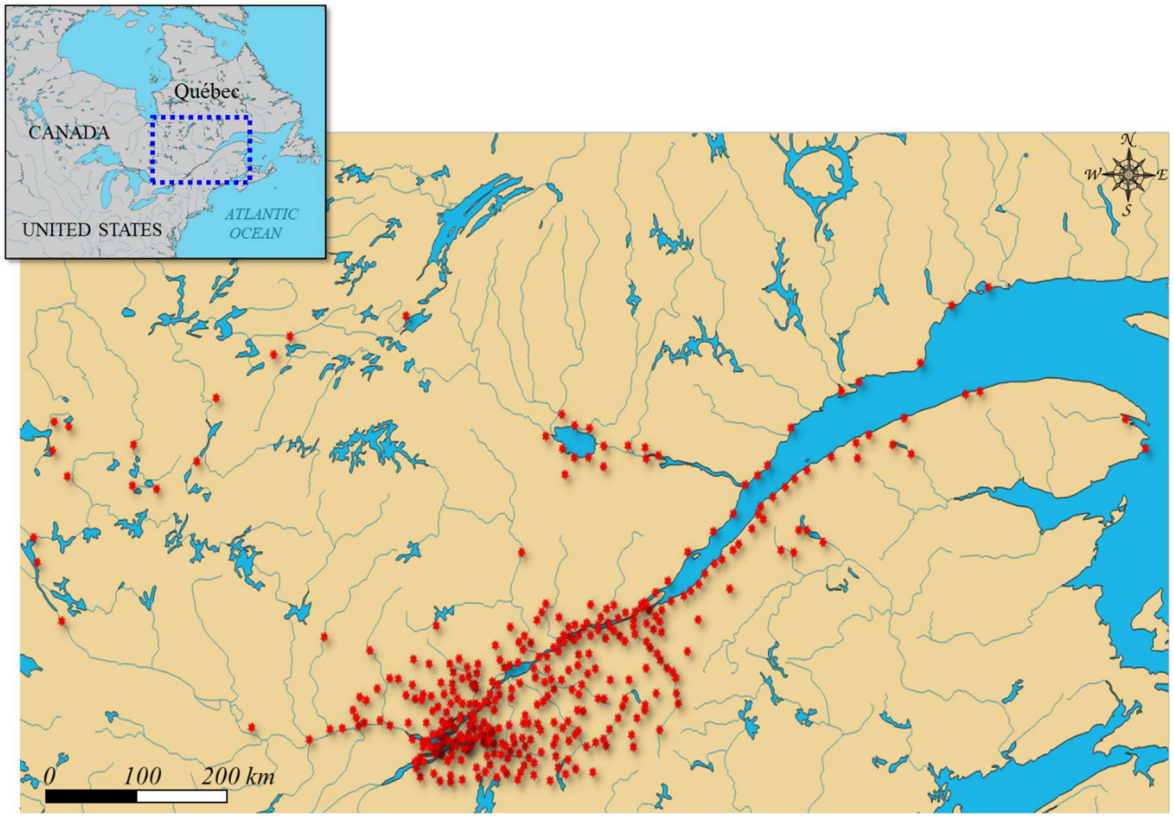

Figure 1. *Geographical distribution of tap water sampling sites including 376 municipalities of Québec, Canada.*

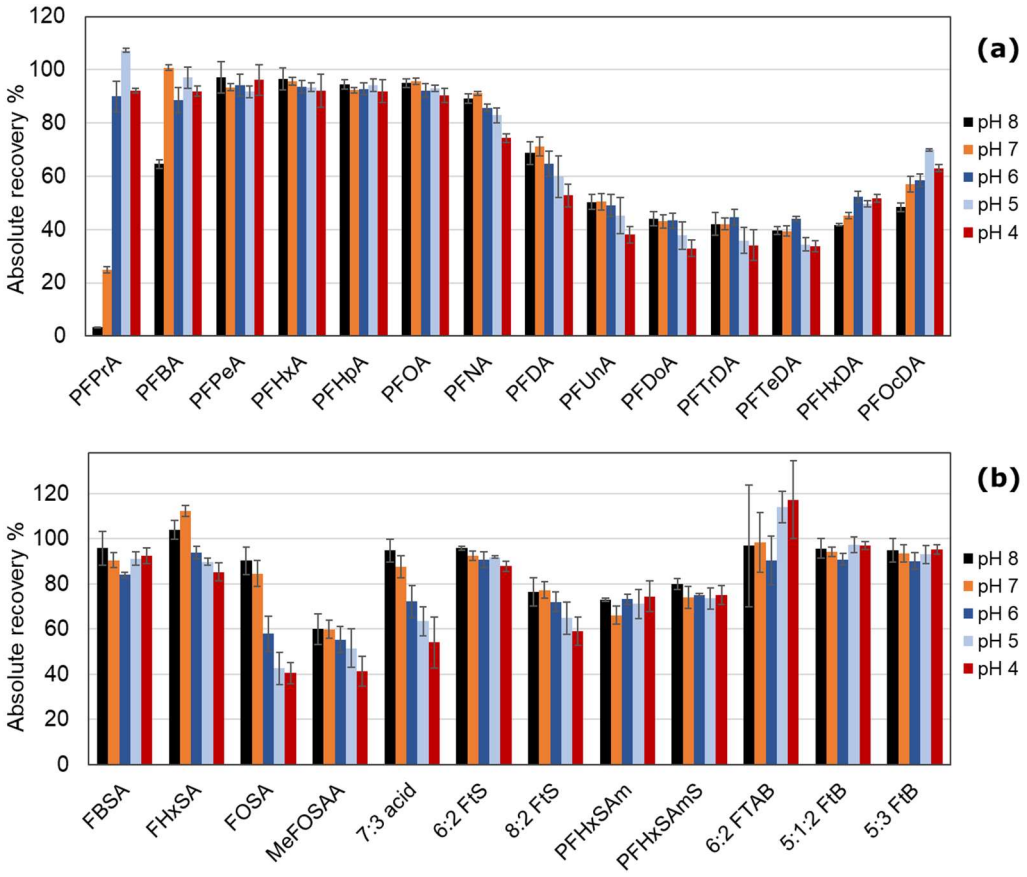

Figure 2. *Influence of lowering tap water sample pH (using acetic acid) on absolute SPE recovery %, illustrated for perfluoroalkyl carboxylates (**2.a**) and selected precursors (**2.b**). Native PFAS were spiked at 5 ng/L (except PFPrA: 20 ng/L) to 500-mL water samples (HDPE bottles) and submitted to Automated off-line SPE (Strata X-AW, 200 mg/6 mL). Error bars refer to standard deviations (n = 3 sample preparation replicates per condition).*

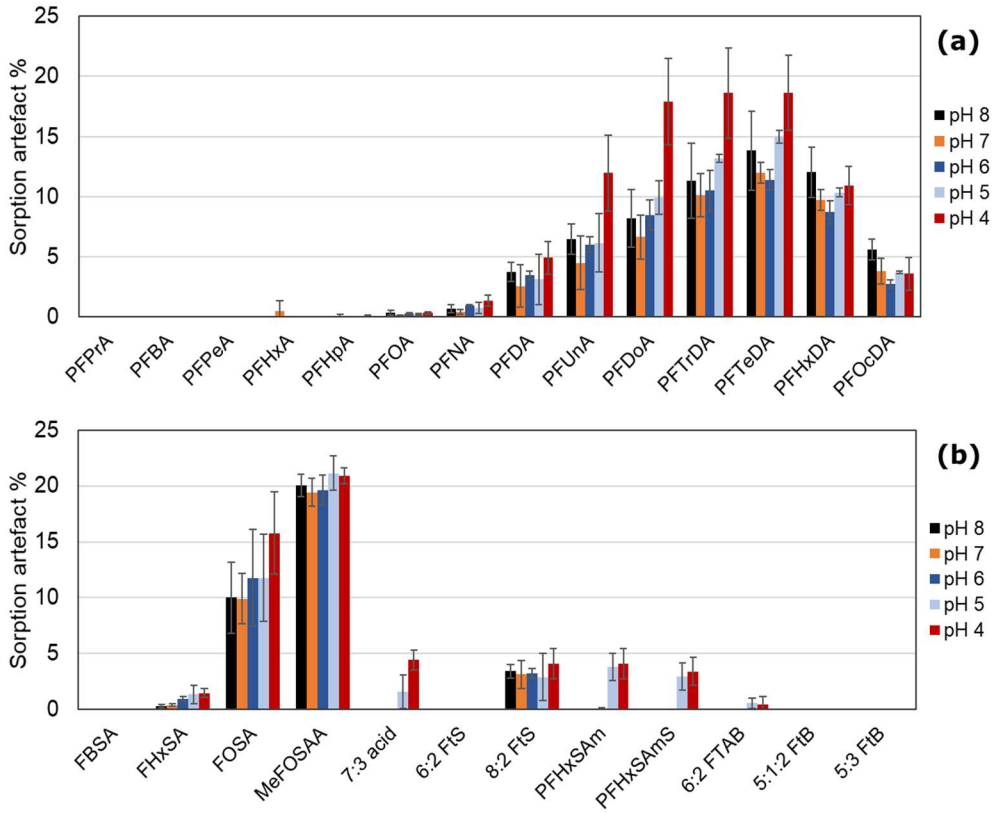

Figure 3. *Influence of lowering tap water sample pH (using acetic acid) on the fraction of PFAS recovered from HDPE bottles (sorption artefact %), illustrated for perfluoroalkyl carboxylates (**3.a**) and selected precursors (**3.b**). Native PFAS were spiked at 5 ng/L (except PFPrA: 20 ng/L) to 500-mL water samples (HDPE bottles) and submitted to Automated SPE (Strata X-AW, 200 mg/6 mL). Following SPE loading, HDPE bottles were rinsed with methanol, and this rinse fraction was kept separately from the SPE eluate for analysis. Error bars refer to standard deviations (n = 3 sample preparation replicates per condition).*

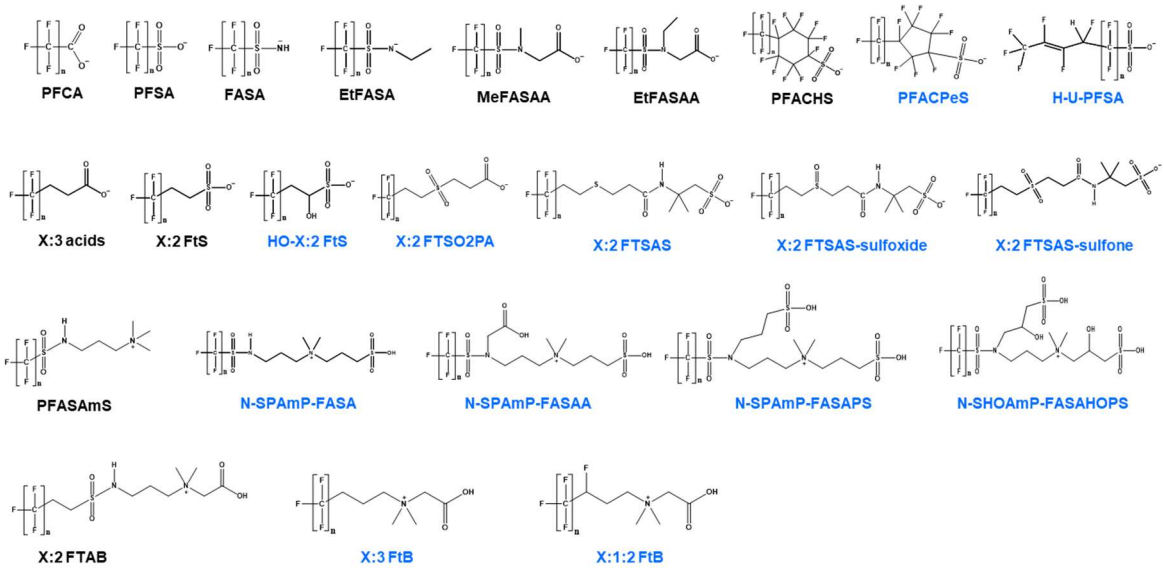

Figure 4. *Structures of the 24 PFAS classes that were identified by target and nontarget screening in tap water samples from the present survey. The blue font is for those classes that would otherwise have been missed by our targeted method (42 PFAS). Class acronyms: PFCA (perfluorocarboxylic acids), PFSA (perfluoroalkane sulfonates), FASA (perfluoroalkyl sulfonamides), EtFASA (N-ethyl perfluoroalkyl sulfonamides), MeFASAA (N-methyl perfluoroalkyl sulfonamido acetic acids), EtFASAA (N-ethyl perfluoroalkyl sulfonamido acetic acids), PFACHS (perfluoroalkyl cyclohexane sulfonates), PFACPeS (perfluoroalkyl cyclopentane sulfonates), H-U-PFSA (hydrido-unsaturated perfluoroalkane sulfonates), X:3 acids (X:3 fluorotelomer carboxylic acids), X:2 FtS (X:2 fluorotelomer sulfonates), HO-X:2 FtS (hydroxy-X:2 fluorotelomer sulfonates), X:2 FTSO2PA (X:2 fluorotelomer sulfonyl propanoic acids), X:2 FTSAS (X:2 fluorotelomer thioether amido sulfonates), X:2 FTSAS-sulfoxide (Sulfinyl analogues of X:2 FTSAS), X:2 FTSAS-sulfone (Sulfonyl analogues of X:2 FTSAS), PFASAmS (or TAmPr-FASA; trimethylammoniopropyl perfluoroalkyl sulfonamides), N-SPAmP-FASA (N-sulfopropyl dimethylammoniopropyl perfluoroalkyl sulfonamides), N-SPAmP-FASAA (N-sulfopropyl dimethylammoniopropyl perfluoroalkyl sulfonamido acetic acids), N-SPAmP-FASAPS (N-sulfopropyl dimethylammoniopropyl perfluoroalkyl sulfonamidopropyl sulfonates), N-SHOAmP-FASAHOPS (N-sulfohydroxypropyl dimethylammoniopropyl perfluoroalkyl sulfonamidohydroxypropyl sulfonates), X:2 FTAB (or X:2 FTSA-PrB; X:2 fluorotelomer sulfonamidopropyl betaines), X:3 FtB (X:3 fluorotelomer betaines), X:1:2 FtB (X:1:2 fluorotelomer betaines).*

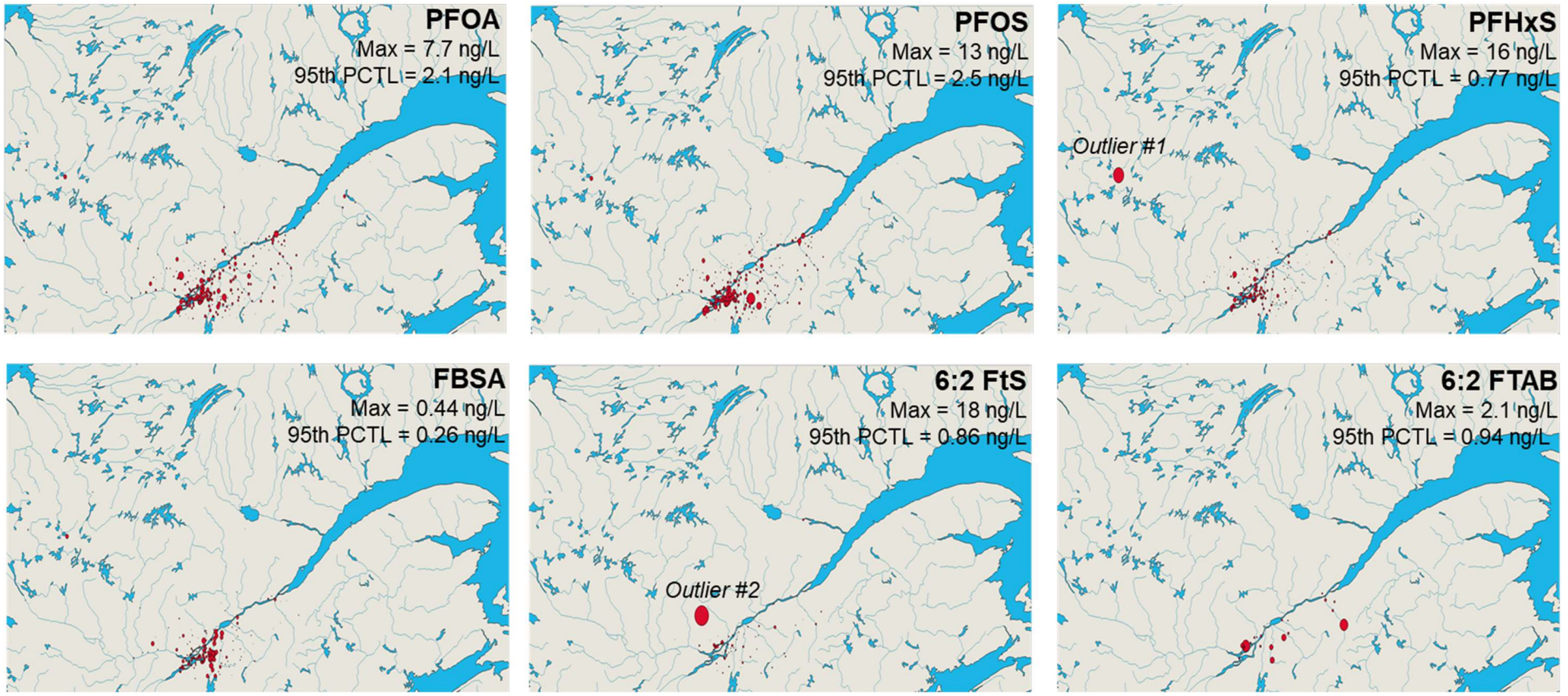

Figure 5. *Geographical distribution of PFAS levels (ng/L, mean per site) in Québec tap water (376 localities assayed), illustrated for perfluorooctanoic acid (PFOA), perfluoroctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonamide (FBSA), 6:2 fluorotelomer sulfonate (6:2 FtS), and 6:2 fluorotelomer sulfonamido propyl betaine (6:2 FTAB). Note that different scales are applied between each map. For each compound, the maximum observed concentration (Max, ng/L) and 95th percentile (95th PCTL, ng/L) are also indicated.*

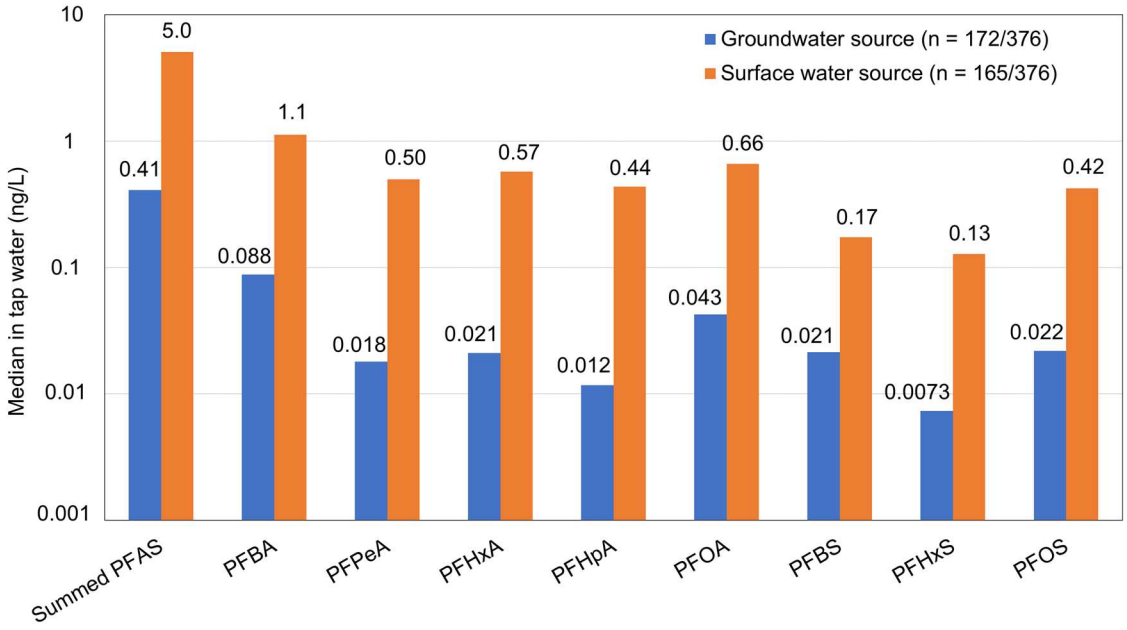

Figure 6. *Influence of the drinking water production source (produced from groundwater, n = 172, or surface water, n = 165) on median PFAS levels (ng/L) in tap water samples from Québec.*