



Worldwide drinking water occurrence and levels of newly-identified perfluoroalkyl and polyfluoroalkyl substances

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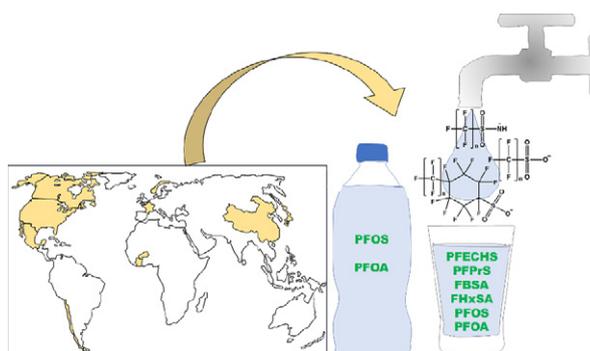
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HIGHLIGHTS

- 133 PFASs from different chemical classes were screened in drinking water samples.
- Detection frequencies in tap water were high (64–92%) for short-chain PFCAs/PFSAs.
- PFOS and PFOA did not exceed 5 ng L⁻¹ across the 97 samples surveyed.
- 2 tap water samples from Burkina Faso showed high 5:3FTCA levels (landfill sources).
- First report of a cyclic PFSA (PFECHS) and C₄–C₆ FASAs (FBSA, FHxSA) in drinking water.

GRAPHICAL ABSTRACT



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ABSTRACT

In the last decade or so, concerns have arisen with respect to the widespread occurrence of perfluoroalkyl acids (PFAAs) in the environment, food, drinking water, and humans. In this study, the occurrence and levels of a large range of perfluoroalkyl and polyfluoroalkyl substances (PFASs) were investigated in drinking water (bottled and tap water samples) from various locations around the world. Automated off-line solid phase extraction followed by ultra-high-performance liquid chromatography coupled to high-resolution mass spectrometry was used to analyze PFASs of various chain lengths and functional groups. In total, 29 target and 104 suspect-target PFASs were screened in drinking water samples (n = 97) from Canada and other countries (Burkina Faso, Chile, Ivory Coast, France, Japan, Mexico, Norway, and the USA) in 2015–2016. Out of the 29 PFASs quantitatively analyzed, perfluorocarboxylates (PFCAs: C_{4/14}), perfluoroalkane sulfonates (PFSAs: C₄, C₆, C₈), and perfluoroalkyl acid precursors (e.g., 5:3 fluorotelomer carboxylate (5:3 FTCA)) were recurrently detected in drinking water samples (concentration range: <LOD to 39 ng L⁻¹). Tap water samples from Canada showed noteworthy differences depending on their source; for instance, $\sum_{29} \text{PFASs}$ was significantly greater in those produced from the Great Lakes/St. Lawrence River ecosystem than those produced from other types of sources (14 versus 5.3 ng L⁻¹, respectively). A suspect-target screening approach indicated that other perfluoroalkane sulfonamides (FBSA, FHxSA), perfluoroethyl cyclohexane sulfonate (PFECHS), ultrashort chain (C₂–C₃) PFSAs (PFtS, PFPrS), and two additional PFASs (PFPeS (C₅) and PFHpS (C₇)) were repeatedly present in tap water samples (concentration ranges: <LOD to 4.0 ng L⁻¹). To the authors' best knowledge, this constitutes the first observation of a cyclic

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perfluoroalkane sulfonate (PFECBS) and C₄–C₆ perfluoroalkane sulfonamides (FBSA, FHxSA) in drinking water. According to the newly updated US EPA health advisory for PFOS and PFOA (70 ng L⁻¹), the drinking water samples collected in the present monitoring would not pose a health risk to consumers as regards PFAA levels.

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1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been recognized as environmental contaminants of emerging concern (Renner, 2001; Kannan et al., 2004; Sauvé and Desrosiers, 2014). PFASs have been used in a large variety of applications such as processing aids for fluoropolymer manufacturing, as well as in the formulation of paints, adhesives, fire-fighting foams, and grease-proof coating for food packaging (Buck et al., 2011; Backe et al., 2013; Schaidler et al., 2017). Due to this widespread use for >60 years and their physicochemical properties (i.e., water solubility, resistance to heat or degradation, sorption, bioaccumulation potential), PFASs are now ubiquitous and occurring at a global scale. PFASs have been reported in aquatic environments, including surface water, groundwater, and tap water (Ahrens, 2011; Gonzalez-Gaya et al., 2014; Munoz et al., 2015a; Sammut et al., 2017), as well as in biota (Hansen et al., 2016; Babut et al., 2017). Sources of perfluoroalkyl acid (PFAA) contamination to surface water (which may in turn be used to produce drinking water) include industrial facilities, firefighting training sites, military bases and airports, municipal landfills, and wastewater treatment plants (Hu et al., 2016; Zhang et al., 2016; Lang et al., 2017). Several PFAAs including perfluoroalkyl carboxylic acids (PFCAs, C₄–C₆) and perfluoroalkane sulfonates (PFSAs, C₄, C₆, C₈) have been included in US EPA and/or Health Canada nationwide drinking water monitoring programmes (US EPA, 2012; Health Canada, 2016). PFAAs are globally distributed in human populations at µg L⁻¹ levels (Lau et al., 2007; Fisher et al., 2013; Wu et al., 2015). Temporal trends in blood serum from the USA (2000–2010) and Sweden (1996–2010) (Glynn et al., 2012; Olsen et al., 2012) as well as data from the two cycles (2007–2009 and 2009–2011) of the Canadian Health Measures Survey (Health Canada, 2013) showed that, despite the gradual implementation of phase-out since the early 2000s, levels of long-chain PFAAs tended to be stable from 2006 to 2010. While both short-chain and long-chain PFSAs are persistent, the long-chain analogues are poorly eliminated once ingested, as evidenced in the elevated human serum half-lives of PFHxS and PFOS (>5 years) (Rahman et al., 2014). Dietary uptake, indoor and outdoor air intake (Fromme et al., 2009; Shoeib et al., 2011), and drinking water consumption (Shoeib et al., 2011; Gyllenhammar et al., 2015) are the main pathways of PFAS exposure to general human populations. Experiments conducted under controlled laboratory conditions indicate that exposure to long-chain PFAAs (such as PFOS and PFOA) may result in various adverse health effects (US EPA, 2016) and immune system effects (DeWitt et al., 2012). Therefore, it should come as no surprise that several environmental protection agencies and the scientific community propose drinking water guidelines for both PFOS and PFOA: 70 ng L⁻¹ and 1 ng L⁻¹, respectively for the US EPA updated health advisory lifetime levels and suggested drinking water limit to preserve children from immune adverse effects (Grandjean and Budtz-Jørgensen, 2013; US EPA, 2016).

From 2003 to 2017, multiple studies reported the presence of PFOS and PFOA in tap water from Japan (Harada et al., 2003; Takagi et al., 2008), as well as other PFAAs in drinking water from China (Mak et al., 2009; Zhang et al., 2011), Brazil (Quinete et al., 2009; Schwanz et al., 2016), Norway (Haug et al., 2010), Australia (Thompson et al., 2011), the European Union (Exner and Färber, 2006; Loos et al., 2007; Ericson et al., 2009; Domingo et al., 2012; Gellrich et al., 2013; Schwanz et al., 2016; Le Coadou et al., 2017), South Korea (Kim et al., 2011), Vietnam (Lam et al., 2017), and the USA (Dasu et al., 2017). To

date, the aforementioned surveys have essentially focused on PFCAs (C_{4/14} and C₁₆, C₁₈), PFSAs (C₄, C₆, C₈, C₁₀) and very few precursors (e.g., perfluorooctane sulfonamide (FOSA)). Additionally, the occurrence data of PFAAs in drinking water from Canada, Burkina Faso and Ivory Coast are scarce, if not non-existent (Mak et al., 2009; Munoz et al., 2015b). In addition, a large breadth of PFASs bear the potential to generate PFAAs through degradation (Liu and Avendaño, 2013). A wide range of newly-identified anionic, zwitterionic, and cationic PFASs were recently reported in aqueous film forming foams (AFFFs) and environmental samples (Place and Field, 2012; D'Agostino and Mabury, 2014; Backe et al., 2013; Barzen-Hanson and Field, 2015; Chu et al., 2016; Mejia-Avendaño et al., 2017b; Munoz et al., 2017a; Xiao, 2017), some of which were shown to generate fluorotelomer sulfonates and/or PFAAs upon transformation (Moe et al., 2012; Mejia-Avendaño et al., 2016; D'Agostino and Mabury, 2017). Yeung et al. (2017) reported that ultrashort chain (C₂–C₃) PFAAs could represent over 40% of the total target PFAS in rainwater samples; however, such compounds have been rarely monitored in the previous literature (Mak et al., 2009; Barzen-Hanson and Field, 2015). Other PFASs recently identified in environmental samples include perfluoroalkane sulfonamides such as perfluorobutane sulfonamide (FBSA, C₄) –identified in fish species from multiple Canadian lakes (Chu et al., 2016)– and perfluorohexane sulfonamide (FHxSA, C₆) –reported to occur at an AFFF-impacted site (McGuire et al., 2014). Additionally, previous studies have reported the occurrence of perfluoroethyl cyclohexane sulfonate (PFECBS) in fish, sediment, and surface water (De Silva et al., 2011; Wang et al., 2016). Hitherto, newly-identified PFASs have not yet been investigated in drinking water. Integrated assessment of legacy and newly-identified PFASs is needed to assess the risk associated with PFAS human exposure through drinking water consumption. As such, it appears essential to monitor both short-chain and long-chain legacy PFASs (e.g.: PFAAs), but also fluorotelomer-based compounds and newly-identified PFASs that may be precursors to PFAAs.

In this context, the objective of the present survey was to analyze a large breadth of quantitatively targeted PFASs, including legacy PFAAs, FOSA, fluorotelomer carboxylates and sulfonates, and cationic and zwitterionic PFASs representing various newly-identified PFAS classes, in bottled and tap water samples from Canada and several other countries (Burkina Faso, Chile, China, France, Ivory Coast, Japan, Mexico, Norway, and the USA). Profiles of legacy PFASs in bottled water from different sources, i.e., natural spring water, natural mineral water and treated water from Abidjan (Ivory Coast), Beijing (China), Montreal (Canada), Mexico City (Mexico), and Ouagadougou (Burkina Faso) cities were documented. The occurrence and levels of 29 target PFASs in tap water from 41 cities from 9 different countries were examined. A suspect-target screening was performed in this study to evaluate whether newly identified compounds would occur in drinking water. A preliminary health risk assessment of PFOS and PFOA was also conducted.

2. Materials and methods

2.1. Sample collection

Tap water samples (n = 59) were collected between February 2015 and June 2015 in Canadian cities, in the USA, Japan, China, France, Norway, Chile and in December 2016 in Burkina Faso, Ivory Coast, Guadeloupe (French West Indies), and China. Commercial bottled water samples (n = 38) were purchased from retail shops in the cities of

Abidjan (Ivory Coast), Beijing (China), Montreal (Canada), Mexico City (Mexico) and Ouagadougou (Burkina Faso) in 2015–2016. Drinking water sampling locations are presented in Fig. 1 and full details on sampling sites, including associated internal laboratory code, are provided in Table S1 of the Supporting information (SI).

2.2. Chemical analysis

2.2.1. Chemicals and materials

PFAAs and fluorotelomer carboxylic acids (5:3 FTCA and 7:3 FTCA) standards and isotope-labelled internal standards (IS) were purchased from Wellington Laboratories, Inc. (Guelph, ON, Canada) and had chemical purities > 98% and IS isotopic purities > 99% per ^{13}C and > 94% per ^{18}O . Fluorotelomer unsaturated acids (6:2 FTUA, 8:2 FTUA) were donated by DuPont USA (Wilmington, DE, USA). Perfluorooctane sulfonamide (FOSA) and sodium 1H, 1H, 2H, 2H perfluorooctane sulfonate (6:2 FTSA) were purchased from Wellington Laboratories, Inc., and were provided at 50 and 47.4 $\mu\text{g mL}^{-1}$ in methanol, respectively. Seven novel PFASs with chemical purities >95% were custom-synthesized at the Beijing Surfactant Institute (Beijing, China) and were provided

at 2 $\mu\text{g mL}^{-1}$ in methanol (Munoz et al., 2016; Mejia-Avendaño et al., 2017a). Details on analyte name and corresponding acronym, chemical formula, measured exact mass and corresponding IS are all supplied in the SI (Table S2).

HPLC-grade water, HPLC-grade water containing 0.1% formic acid (HCOOH), methanol (MeOH) and acetonitrile (ACN) were obtained from Fisher Scientific (Whitby, ON, Canada), as was ammonium hydroxide (NH_4OH , purity 28–30% in water). Nitrogen (N_2) (purity 99.998%) was from MEGS, Inc. (Montréal QC, Canada). Strata-X-AW cartridges (200 mg/6 mL) were obtained from Phenomenex (Torrance, CA, USA).

2.2.2. Solid-phase extraction and instrumental analysis

Water samples (1 L) were spiked with internal standards (ISs, see Table S2 for details) at the start of the extraction procedure (60 μL of a 50 ng mL^{-1} IS mixture). Sample enrichment was conducted by off-line automated solid phase extraction (SPE) using a Dionex/Thermo Autotrace 280 system. Strata X-AW cartridges were conditioned with 2 \times 4 mL of 0.2% NH_4OH in methanol and 2 \times 4 mL of HPLC-grade water. Samples were then loaded onto the cartridges at a flow rate of 10 mL min^{-1} . Cartridges were finally dried for 30 min with nitrogen

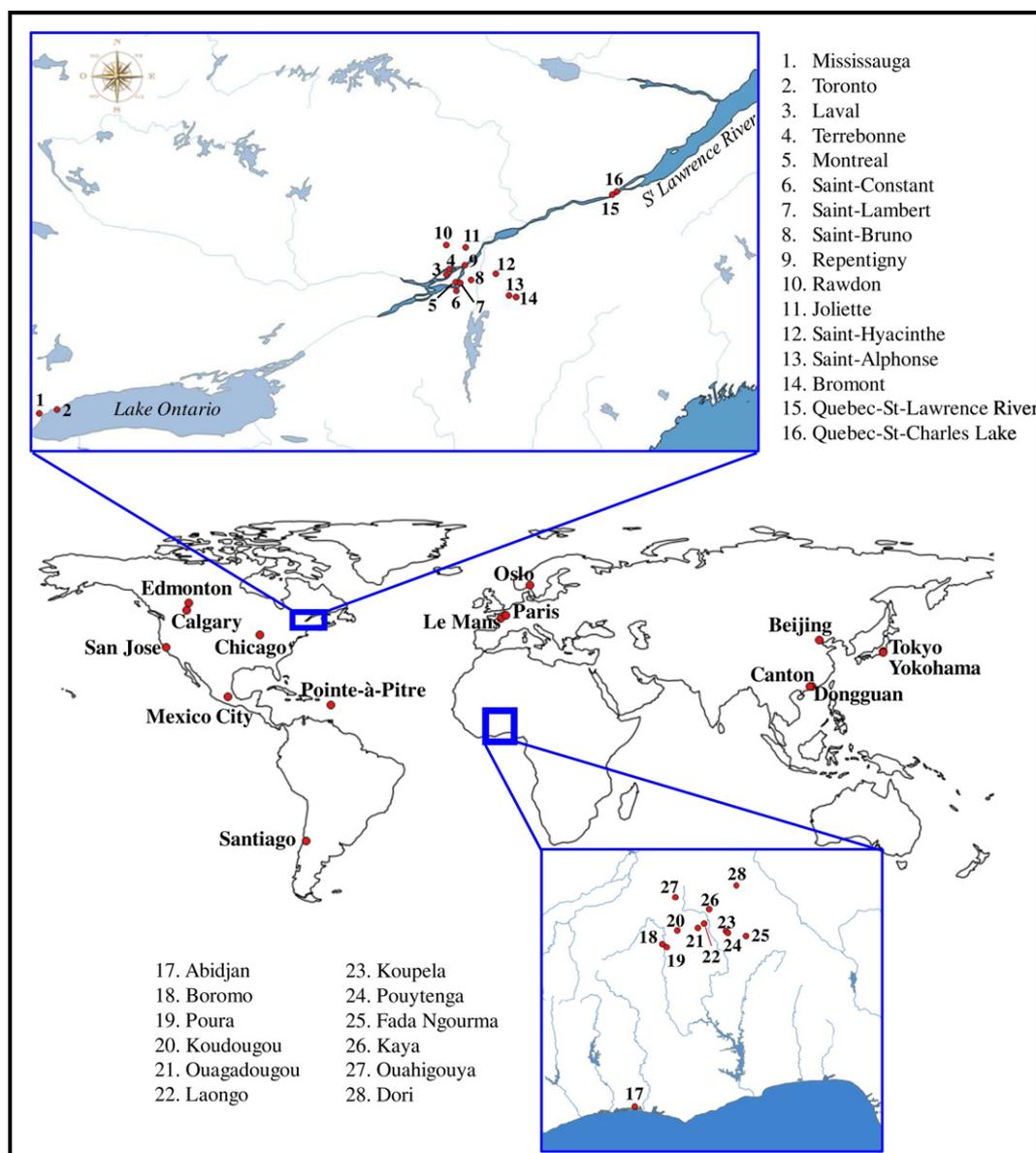


Fig. 1. Spatial distribution of tap water samples investigated in the present study.

(N₂) and eluted twice with 4 mL of 0.2% NH₄OH in methanol. All extracts were reduced to 400 µL under a gentle stream of N₂ at 40 °C and stored at –20 °C until analysis.

The separation of PFASs was performed with a Thermo Hypersil Gold C18 column (100 mm × 2.1 mm; 1.9 µm particle size). The Dionex Ultimate 3000 LC chain was interfaced with a Q-Exactive Orbitrap mass spectrometer controlled via the Xcalibur 2.3 software (Thermo Fisher Scientific, Waltham, MA, USA). The mass scan range was set at 150–1000 *m/z* (full scan MS, fast polarity switching mode). The optimization of chromatographic operating conditions, as well as mass spectrometry parameters, is fully described elsewhere (Munoz et al., 2016).

2.3. Quality assurance and quality control

The analytical results generated should give an ultimately correct value and acceptable spread of data in order to legitimate a rigorous comparison between samples (Munoz et al., 2017b). In the present study, specific measures were implemented in order to integrate procedural blank contamination at ultra-trace level, and evaluate the performance of the method including whole-method recovery, instrumental accuracy, and precision. In order to minimize the risk of unintended contamination, samples were collected using HDPE bottles thoroughly pre-cleaned in the laboratory with distilled water followed by ultrapure water and methanol. Procedural blanks (*n* = 7, multibatch replicates) followed the same preparation steps as the drinking water samples. Detectable PFAS levels in such procedural blanks were found only in the case of particular PFCAs. Overall, the PFCAs levels in procedural blanks were moderate (<0.15 ng L⁻¹ for most analytes) and reproducible (full details provided in Table S3 of the SI). Each sample batch was therefore blank-corrected. The quantification procedure relied on a matrix-matched calibration curve approach with isotope-labelled internal standard correction. Method recovery was evaluated at two levels (in triplicate) by spiking 2 ng or 10 ng of each target analyte to 1 L of a tap water matrix at the beginning of the preparation procedure and comparing to the post-extraction spiked reference (in both cases, subtracting the contribution of the non-spiked sample initial contribution). Mean recoveries (*n* = 3) were in the range 70–110% for most analytes, regardless of the spike level (see SI, Table S4). The lower recoveries (36–53%) observed for long-chain (C₁₁–C₁₈) PFCAs and PFDS are consistent with previous reports and likely reflect sorption losses due to the higher hydrophobicity of these compounds (Munoz et al., 2015a, 2015b). To control appropriate quantification performance of the instrumental analysis, precision and accuracy were also evaluated at two concentration levels (low: 0.2 ng L⁻¹ and high: 4 ng L⁻¹). Instrumental accuracy and precision were determined in tap water by spiking native analytes along with IS post-extraction. Accuracies in the range 80–110% could be obtained for nearly all analytes (see also SI Fig. S1). The variability between replicate measurements was also acceptable, the intra-day relative standard deviation being always lower than 11%, and inter-day precision generally lower than 25% (see also SI Table S4).

2.4. Suspect screening strategies

Suspect-target screening of 50 positive- and 54 negative- ionization mode compounds was performed through extracted ion chromatograms of high-resolution full scan MS data using the Xcalibur 2.3 software (Thermo Fisher Scientific, Waltham, MA, USA) with a mass window of ± 5 ppm, and an intensity threshold level (absolute height) ≥ 10⁴. Table S9 shows the list of PFAS suspects investigated in the present study. These suspect compounds were discovered in the recent literature (Place and Field, 2012; D'Agostino and Mabury, 2014; Rotander et al., 2015; Ruan et al., 2015; Munoz et al., 2016). When the exact mass of a PFAS suspect was detected within a ± 5 ppm window and the retention time was in agreement with the elution order, the corresponding drinking water extracts were analyzed in high-resolution parallel reaction monitoring (PRM) mode as described elsewhere (Mejia-Avenidaño

et al., 2017b; Munoz et al., 2017a) and the confidence levels in the identification of these compounds were assigned based on published criteria (Schymanski et al., 2014). Elution order refers to the agreement in the retention time of a given suspect with an available reference compound, when applicable (for instance, FHxSA < FOSA when considering the reversed-phase liquid chromatography separation implemented in the present study). Of note, elution order was not the only criterion examined, and the observation of a logical retention time pattern with regard to -CF₂ units was further enlisted for identification at a higher confidence level (see also Munoz et al., 2017a). The classification proposed by Schymanski et al. (2014) was used to provide an associated level of confidence in the identification of suspects, which is briefly summarized hereafter. At Level 1 (Confirmed structure), the proposed structure has been confirmed via appropriate measurement of the reference native standard with MS, MS/MS, and retention time matching. At Level 2 (Probable structure), no reference standard is used but the exact mass accuracy fits with the specified threshold while the full scan MS and MS/MS spectrum match unambiguously with library spectrum data. The exact structure remains speculative at Level 3 (tentative candidate) where evidence exists for possible structure but insufficient information for one exact structure (e.g., positional isomers). The lowest levels of confidence are Level 4 (Unequivocal molecular formula), for which MS/MS spectra either cannot be generated or are uninformative but a molecular formula can be proposed, and Level 5 wherein the sole information that can be provided is the exact mass of interest (Schymanski et al., 2014).

For quantification purposes, the PFAS suspects detected were classified into two different levels: i) Quantitative analytes (Qn): those for which true reference standards were available; ii) Semi-quantitative analytes (sQ): those for which a true standard was not available, but an analogue with different chain length was used. For instance, the calibration curve of FOSA (C₈) was used to estimate the concentrations of the shorter-chain analogues FBSA (C₄) and FHxSA (C₆), which were therefore classified at the sQ level. At the onset of the present study, only 29 target analytes were quantitatively assessed. Since additional suspects were detected in the samples, reference standards were acquired (if available) to improve the identification confidence (at level 1) and the quantification confidence (at the Qn level). This approach was used for PFPrS, PFECs, PFPeS, and PFHpS, the reference standards being obtained from Wellington Laboratories, Inc. (Guelph, ON, Canada). Note that the PFPrS (C₃) standard was also used to semi-quantify the C₂ analogue (PFETs). In the identification and the quantification strategies, procedural blank measurements were used to ensure that the substance does not arise from sample preparation and instrumental analysis.

2.5. Statistical analyses

Principal component analysis (PCA) and K-means clustering were used to discriminate statistically distinct PFAS composition profiles between samples. One-way ANOVA or Kruskal-Wallis rank sum tests were used (depending on whether the application conditions were fulfilled) with a view to comparing means of individual PFASs and ∑₂₉PFAS of different groups yielded by the clustering analysis, as well as mean PFAS levels in drinking water samples according to their source. Statistical analyses were conducted with the R statistical software (R-Core-Team, 2016). Tukey's HSD test was used as a post-hoc test if the null hypothesis (H₀) of ANOVA was rejected. Statistical significance was set at *p* < 0.05.

3. Results and discussion

3.1. PFAS occurrence and levels in bottled water

Table 1 shows the occurrence and levels of PFASs in bottled waters (*n* = 38) purchased from Ivory Coast (Abidjan, *n* = 11), China (Beijing,

Table 1
Summary of PFAS occurrence in bottled (n = 38) and tap (n = 59) water from Canada, and other countries.

Unit	LOD ng L ⁻¹	LOQ	Bottled water (n = 38)						Tap water (n = 59)					
			DF %	QF	Abundance % ∑ PFAS	Max ng L ⁻¹	Median	Mean	DF %	QF	Abundance % ∑ PFAS	Max ng L ⁻¹	Median	Mean
PFBA	0.020	0.070	58	45	26	1.3	<LOQ	0.20	92	90	30	3.6	1.3	1.5
PFPeA	0.060	0.17	32	24	7.1	1.1	<LOQ	<LOQ	68	54	5.9	2.7	0.10	0.44
PFHxA	0.080	0.23	50	24	7.4	0.58	<LOQ	<LOQ	64	39	7.4	4.5	<LOQ	0.59
PFHpA	0.040	0.13	42	26	6.4	1.1	<LOD	<LOQ	90	61	9.3	3.2	0.15	0.33
PFOA	0.070	0.20	34	21	9.4	3.0	<LOD	<LOQ	86	64	8.6	4.9	0.31	0.67
PFNA	0.030	0.10	18	0	0.7	0.050	<LOD	<LOQ	64	56	2.5	4.5	0.15	0.22
PFDA	0.010	0.030	8	3	0.5	0.69	<LOD	<LOQ	66	47	0.8	1.0	<LOQ	0.060
PFUnDA	0.010	0.030	3	3	0.2	0.39	<LOD	<LOQ	14	14	0.4	1.6	<LOD	<LOD
PFDoDA	0.010	0.030	11	5	1.7	2.9	<LOD	0.10	12	7	0.3	1.1	<LOD	<LOD
PFTTrDA	0.010	0.030	5	5	0.1	0.17	<LOD	<LOQ	8	5	0.3	0.94	<LOD	<LOD
PFTeDA	0.010	0.030	11	8	0.5	0.080	<LOD	<LOQ	8	5	0.2	0.62	<LOD	<LOD
∑ PFCAs						2.0	0.48	0.62				22	2.9	4.1
PFBS	0.020	0.070	47	29	16	1.6	<LOD	0.10	88	75	4.1	1.1	0.16	0.24
PFHxS	0.020	0.070	32	18	8.2	0.67	<LOD	0.10	78	66	6.9	1.0	0.16	0.30
PFOS	0.030	0.10	18	8	3.5	0.67	<LOD	<LOQ	85	83	16	4.1	0.64	1.0
PFDS	0.010	0.030	0	0	0.0	–	<LOD	<LOQ	5	5	0.3	1.5	<LOD	0.030
∑ PFSA						2.0	–	0.50				5.6	0.94	1.6
FOSA	0.020	0.070	3	0	0.0	<LOQ	<LOD	<LOQ	24	5	0.4	1.1	<LOD	<LOQ
6:2FTSA	0.010	0.030	21	18	7.4	1.3	<LOD	0.20	36	36	3.3	6.3	<LOD	0.30
6:2FTUA	0.010	0.030	5	5	0.1	0.050	<LOD	<LOQ	0	0	0.0	<LOD	<LOD	<LOD
8:2FTUA	0.010	0.030	5	5	0.1	0.080	<LOD	<LOQ	5	2	0.0	0.19	<LOD	<LOD
5:3FTCA	0.020	0.070	3	3	0.0	0.090	<LOD	<LOQ	10	7	3.1	39	<LOD	1.2
PFOAB	0.045	0.15	11	8	3.1	0.15	<LOD	<LOQ	0	0	0.0	<LOD	<LOD	<LOD
∑ ₂₉ PFAS						5.1	0.59	1.1				44	3.7	7.1

LOD: limit of detection (ng L⁻¹); LOQ: limit of quantification (ng L⁻¹); DF: detection frequency (% of samples ≥LOD); QF: quantification frequency (% of samples ≥LOQ); Abundance: mean relative abundance (% of ∑₂₉PFAS); Max: maximum concentration observed (ng L⁻¹); Median: median concentration (ng L⁻¹); Mean: average concentration (ng L⁻¹).

$n = 2$), Canada (Montreal, $n = 11$), Mexico (Mexico City, $n = 1$) and Burkina Faso (Ouagadougou, $n = 13$). Long-chain (C_{16} , C_{18}) PFCAs, 7:3 FTCA, quaternary ammonium PFASs (PFOSAmS, PFOAAmS), amine oxide PFASs (PFOANO, PFOSNO) and perfluorooctane sulfonamide betaine (PFOSB) were not found in any of the samples analyzed in the present survey. Eighteen of the 29 quantitatively measured PFASs were variously detected at levels above the LOQs (LOQ range = 0.030 – 0.23 ng L^{-1}) (see also Table 1). The quantification frequencies for compounds occurring in bottled waters were all below 50%. PFBA was found in 45% of the samples, while PFBS (29%), PFHpA (26%), PFHxA (24%), PFPeA (24%), PFOA (21%), PFHxS (18%) and 6:2 FTSA (18%) were found in a relatively minor number of samples. Quantifiable levels of PFOS, PFTeDA, and perfluorooctane amide betaine (PFOAB) were found in only 8% of the bottled water samples from the present survey while other compounds such as PFDA, PFUnDA, PFTrDA and some precursors (5:3 FTCA, 6:2 FTUA, and 8:2 FTUA) were found in <5% of the bottled water samples. The median and mean levels of most individual PFASs –including PFOS and PFOA– reported in bottled water were lower than their corresponding LOQ. Maximum observed concentrations amounted to 1.3, 1.6, 3.0, and 0.67 ng L^{-1} for PFBA, PFBS, PFOA, and PFHxS, respectively. PFAS composition profiles were generally dominated by C_4 perfluoroalkyl acids (PFBA and PFBS representing on average 26% and 16% of the $\sum_{29}\text{PFAS}$, respectively), while PFOA and PFHxS also accounted for a significant proportion of the total target PFAS levels (9.4 and 8.4% of the $\sum_{29}\text{PFAS}$, respectively). Levels of PFOA in bottled water purchased from Canada, Ivory Coast, China, Burkina Faso, and Mexico ranged from a high of 3 ng L^{-1} in Ivory Coast to below LOQ in Canada. The mean $\sum_{29}\text{PFAS}$ in bottled water samples was 0.72 , 1.5 , and 1.4 ng L^{-1} for natural spring water, natural mineral water, and treated water, respectively. When examining all bottled water samples ($n = 38$) according to their source (i.e., natural spring water versus natural mineral source versus treated water), the Kruskal-Wallis rank sum test indicated no significant difference in means of individual PFASs and $\sum_{29}\text{PFAS}$ concentrations from the different types. The maximum $\sum_{29}\text{PFAS}$ concentrations in bottled water samples from the present study amounted to 6.3 ng L^{-1} . Albeit it is difficult to compare PFAS sums across studies because of possible differences among lists of target analytes and reporting limits, this value is about 20-fold lower than those observed by Schwanz et al. (2016) in bottled water samples from Brazil and western Europe, but in the same order of magnitude as values (1.4 to 9.5 ng L^{-1}) reported by Le Coadou et al. (2017) in bottled water samples from France.

3.2. PFAS occurrence and levels in tap water from Canada, Burkina Faso, Chile, China, EU, Ivory Coast, Japan, and the USA

Tap water samples from Canada, Burkina Faso, Chile, China, EU, Ivory Coast, Japan and the USA presented overall similar PFAS profiles to bottled water samples. PFCAs (i.e., $C_{4/14}$), PFSAs (C_4 , C_6 , C_8 , C_{10}) and precursors (FOSA, 6:2FTSA, 6:2FTUA, 5:3FTCA) were variously detected in these tap water samples.

Tables S5 and S6 show the descriptive statistics of 15/29 quantitative PFASs that were recurrently detected in tap water samples produced from the Great Lake/St. Lawrence River surface water ($n = 8$) and the rest of Canada, i.e., lakes and other small rivers ($n = 11$), based on different source location. We attribute the increased presence of PFASs in the Great Lakes/St. Lawrence River hydrosystem to its role as a vital waterway in North America and to its exposure to a multitude of anthropogenic stresses. Nearly 70% of Quebec's population (~5.5 million people) lives on the shores of the St. Lawrence River along with 75% of all industry in the province (Desrosiers et al., 2008). Consequently, it should come as no surprise that PFASs were mainly detected and quantified in tap water samples produced from the Great Lakes/St. Lawrence River surface water sources. Seven PFCAs ($C_{4/10}$), three PFSAs (C_4 , C_6 , C_8) and one precursor (FOSA) were found in all the tap water samples produced from the Great Lakes/St. Lawrence river while another

precursor (6:2 FTSA) was found in 63% of such samples. However, PFBA (92%), PFPeA (73%), PFHxA (100%), PFHpA (73%), PFOA (73%), PFNA (73%), PFDA (73%), PFBS (73%), PFHxS (82%), PFOS (82%), FOSA (8%) and 6:2 FTSA (18%) were also found in Canadian tap water produced from other sources. Additionally, PFUnDA (9%), PFDoDA (18%), and 5:3FTCA (9%) occurred in tap water produced from the rest of Canada while these compounds were not found in tap water produced from Great Lakes/St. Lawrence River surface water.

Fig. 2 shows the $\sum_{29}\text{PFAS}$ (ng L^{-1}) in tap water samples collected from Canada, gathered according to different tap water source, as well as the corresponding relative abundance for the predominant PFASs quantified in such samples. Tap water produced from the Great Lakes/St. Lawrence River surface water typically displayed higher PFAS concentrations comparatively to tap water produced from other sources, which is not surprising since the Great Lakes/St. Lawrence River flows through major metropolitan areas and may be exposed to a multitude of anthropogenic stresses including urban and industrial pressures.

Tap water produced from the Great Lakes/St. Lawrence River ($n = 8$) presented a mean $\sum_{29}\text{PFAS}$ of 14 ng L^{-1} , while the mean for the rest of Canada ($n = 11$) was 5.3 ng L^{-1} (see also Tables S5–S6 of the SI). A Kruskal-Wallis rank sum test suggested a significant difference between the mean $\sum_{29}\text{PFAS}$ in tap water from the Great Lakes/St. Lawrence River and other sources. The mean and median of $\sum_{29}\text{PFAS}$ in tap water from the Great Lakes/St. Lawrence River source were about 3 to 4 times higher than those found in tap water from the rest of Canada where other lakes and small rivers surface water were used as a source for tap water production. These results are in agreement with Scott et al. (2009) who observed that PFAA levels in surface water samples from the St. Lawrence River were generally higher than those from its tributaries. For instance, it was previously shown that St. Lawrence River surface water samples displayed higher PFOS (4.4 to 7.8 ng L^{-1}) and PFOA (1.6 to 5.5 ng L^{-1}) concentrations than several large rivers from Canada (0.584 to 1.94 ng L^{-1} for PFOS and 1.04 to 2.3 ng L^{-1} for PFOA) (Scott et al., 2009).

In general, the relationship between Canadian tap water production sources and the relative abundance is different for PFSAs and PFCAs, as shown in Fig. 2. The relative abundances for individual PFSAs were generally different in tap waters produced from the Great Lakes/St. Lawrence River and those produced from the rest of Canada while the relative abundances for individuals PFCAs were relatively similar in the two types of samples (Fig. 2). In this study, the predominant (Fig. 2, Tables S5 and S6) long-chain congeners in tap water from the Great Lakes/St. Lawrence River were PFOS and PFOA with mean concentrations of 3.4 ng L^{-1} and 1.8 ng L^{-1} , respectively, while tap water samples produced from the rest of Canada surface water displayed mean PFOS and PFOA concentrations of 0.4 and 0.7 ng L^{-1} , respectively. Interestingly, the maximum levels of PFOS (4.1 ng L^{-1}) and PFOA (4.9 ng L^{-1}) observed in tap water produced from the Great Lakes/St. Lawrence River in this study are similar with the concentrations found earlier in surface water samples from the St. Lawrence River (Scott et al., 2009). This could indicate that PFASs are not efficiently removed by conventional drinking water treatment systems.

When considering all tap water samples from Canada ($n = 19$ sites, 3 replicates per sample), PFHxA was the only compound detected in all samples followed by PFBA (95%), PFHxS and PFOS (89%), while PFPeA, PFHpA, PFOA, PFNA, PFDA and PFBS were detected in at least 84% of the samples. FOSA (53%), 6:2 FTSA (37%), and 5:3 FTCA (11%) were also found in Canadian tap water, while PFUnDA, PFDoDA and 7:3 FTCA were less recurrent ($DF < 10\%$). These detection frequency values are comparable to those reported by Mak et al. (2009) in a survey on tap water across Chinese cities, where PFOS and PFCAs bearing between 5 and 7 perfluoroalkyl carbon atoms were the most recurrent PFASs in Chinese tap water ($DF > 83\%$). In Canadian tap water measured in the present study, PFBA (30% of $\sum_{29}\text{PFAS}$), PFOS (15%), PFHxA (12%) and PFOA (11%) dominated globally the PFAS profile, with maximum

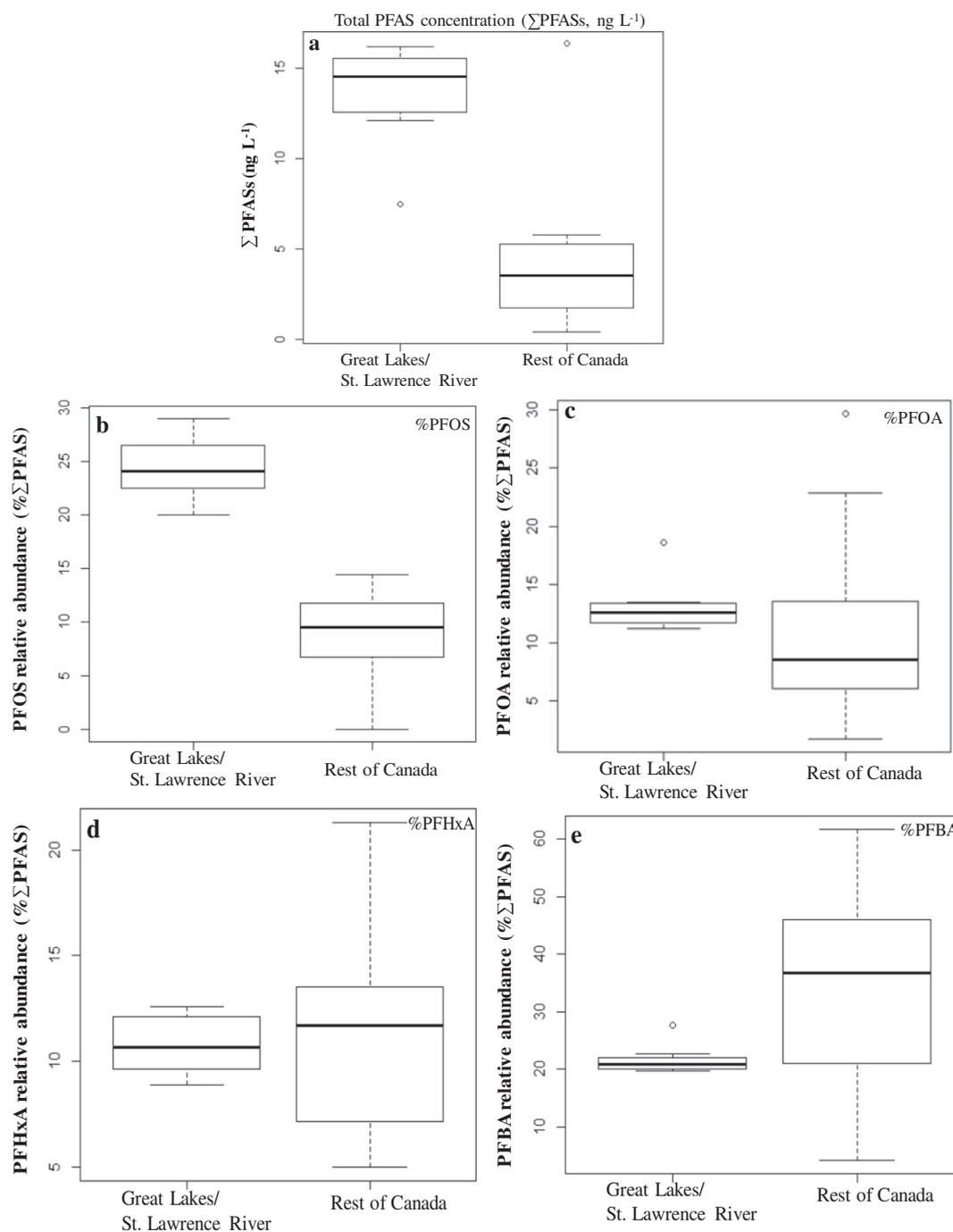


Fig. 2. Box plots of \sum_{29} PFAS (ng L⁻¹) (box plot showing minimum, 25th, median values, 75th, and maximum percentiles) in the tap water samples collected from Canada, grouped according to production source (2.a), and corresponding relative abundance (% of \sum_{29} PFAS) for PFOS (2.b), PFOA (2.c), PFHxA (2.d) and PFBA (2.e), the predominant target PFASs in such samples.

concentrations of 3.6, 4.1, 3.5, and 4.9 ng L⁻¹, respectively. The mean PFOS concentration observed in the present study for Canadian tap waters produced from the St. Lawrence River (3.4 ng L⁻¹) was in the same order of magnitude as that found in Chinese tap waters (3.9 ng L⁻¹) (Mak et al., 2009).

Table S7 presents the mean concentration of individual PFASs in all drinking water samples from Burkina Faso, Canada, Chile, China, Ivory Coast, Japan, EU, and the USA. The PFAS data from other countries in this study were used to provide a comparison to those collected from Canada. This exercise will also be informative in documenting the global distribution of these compounds in drinking water from various

locations around the world. Similar to the Canadian tap water samples already discussed, only 15/29 target compounds were detected in tap water samples from other countries, including PFCAs (C_{4/12}), PFASs (C₄, C₆ and C₈), and some precursors (FOSA, and two fluorotelomer-based compounds (6:2 FTSA and 5:3 FTCA)). Mean concentrations of PFASs and PFCAs were in the range < LOD to 3.9 ng L⁻¹ in China (n = 3), USA (n = 2), EU (n = 4), Japan (n = 2), Ivory Coast (n = 11) and Burkina Faso (n = 16) tap waters.

Fig. 3 shows a K-means clustering on the PCA of tap water data collected from Burkina Faso, Canada, Chile, China, EU, Ivory Coast, Japan and the USA related to their PFAS composition. Five distinct groups

(totaling 52 out of 59 sampling sites) were identified (see also SI Table S8) and 7 samples are identified as outliers, i.e., two samples from China (CH01, CH02), one from Canada (Can08), two from the European Union (EU01, EU02), one from the USA (US01), and one from Japan (J01). These outliers presented either much higher total PFAS concentrations (at 26 ng L⁻¹ for a tap water sample from Japan, J01), or higher concentrations of certain individual PFASs (such as US01, a sample from the USA with 6:2 FTSA at 6.8 ng L⁻¹). As can be seen in Fig. 3, the two principal components together explain around 73% of the variance in PFAS composition. In order of decreasing importance, PFOA, PFHpA, PFHxA, PFOS, PFPeA, PFNA, PFBS and PFBA are correlated to the first principal component (PC1) and PFDA, 5:3FTCA, PFHxS, and PFBA to the second principal component (PC2). The compounds that correlated to PC1 explained the target PFAS composition (57.1% of variance) of most samples from Canadian tap water produced from Great Lakes/St. Lawrence River (Group2) while 15.7% of variance from PC2 explained the target PFAS composition of some tap water samples from Burkina Faso and Canada (see Fig. 3 for details). In general, the PFAS contamination in tap water sampling sites as a group was in the following order: Group1 > Group2 > Group3 and Group5 > Group4 when considering \sum_{29} PFAS concentration (see also SI Table S8 for group composition). The highest \sum_{29} PFAS concentration was measured in tap water from Group1, i.e., BER3 and BER3" (samples from Burkina Faso, at 44 ng L⁻¹), while the lowest \sum_{29} PFAS (<LOQ) was observed for Group4. As indicated in Fig. 3, the contamination of the two tap water samples from Burkina Faso was mainly due to 5:3 FTCA (32 and 39 ng L⁻¹), probably due to nearby municipal landfills that could contribute to the contamination of the reservoir surface water used as tap water source. Fluorotelomer carboxylates were recently demonstrated to be major PFAS components in landfill leachates (Lang et al., 2017), which seems to corroborate this hypothesis. In contrast, tap water samples in Group4 showed low levels of PFAS contamination. BER3" and the 12 samples from Ivory Coast, for example, were collected from tap water with groundwater as the source. When considering all tap water samples including all groups and outliers (Table 1, n = 59), short-chain PFCAs (C_{4/7}) and long-chain PFCAs (C_{8/10}) were detected

at frequencies >64%. Detection frequencies for PFASs (C₄, C₆ and C₈) were higher than 78%.

The PFAS concentrations in tap water samples from the present study are comparable to those reported in other studies. Fig. 4 shows PFOS (A) and PFOA (B) mean confidence intervals (95% of confidence level) in different countries around the world. The mean PFOS concentration in tap water from Canada observed in this study was 3.4 ng L⁻¹, comparable to 4.7 ng L⁻¹ in Germany (Gellrich et al., 2013), 3.9 ng L⁻¹ in China (Mak et al., 2009), and 6.7 ng L⁻¹ in Brazil (Schwanz et al., 2016). Similar levels of PFOA were also found across different countries. The average PFOA concentration in Canada was 1.8 ng L⁻¹ (present study) versus 2.7 ng L⁻¹ in Brazil (Schwanz et al., 2016), 10 ng L⁻¹ in China ((Mak et al., 2009), and 6.1 ng L⁻¹ in Germany (Gellrich et al., 2013).

3.3. Screening of anionic, cationic and zwitterionic PFAS suspects

Seven compounds, including perfluorobutane sulfonamide (FBSA), perfluorohexane sulfonamide (FHxSA), perfluoroethane sulfonate (PFETs), perfluoropropane sulfonate (PFPrS), perfluoropentane sulfonate (PFPeS), perfluoroheptane sulfonate (PFHpS), and perfluoroethyl cyclohexane sulfonate (PFECCHS) were qualitatively identified in various tap water samples as shown in Table 2. Four compounds (PFPrS, PFPeS, PFHpS, and PFECCHS) were identified at Level 1, where the proposed structure was confirmed via appropriate measurement of MS, MS/MS and retention time matching in both a reference standard acquired for this purpose and the particular sample (see also Section 2.4, and full details in Figs. S2a, S2b, S2c, and S2d of the SI). FBSA and FHxSA retention times matched with their expected elution order when comparing with an analogous target analyte (e.g.: FBSA < FHxSA < FOSA), and the exact mass accuracy fitted our ± 5 ppm threshold. Additionally, the characteristic 77.9 m/z fragment ion (SO₂N⁻) was observed in both FBSA and FHxSA high resolution MS/MS spectra (see also Figs. S2e and S2f of the SI). However, a slight discrepancy in the retention time pattern was noted. The difference between the retention times of FBSA (C₄) and FHxSA (C₆) was 1.18 min (tantamount to a + 0.59 min for each

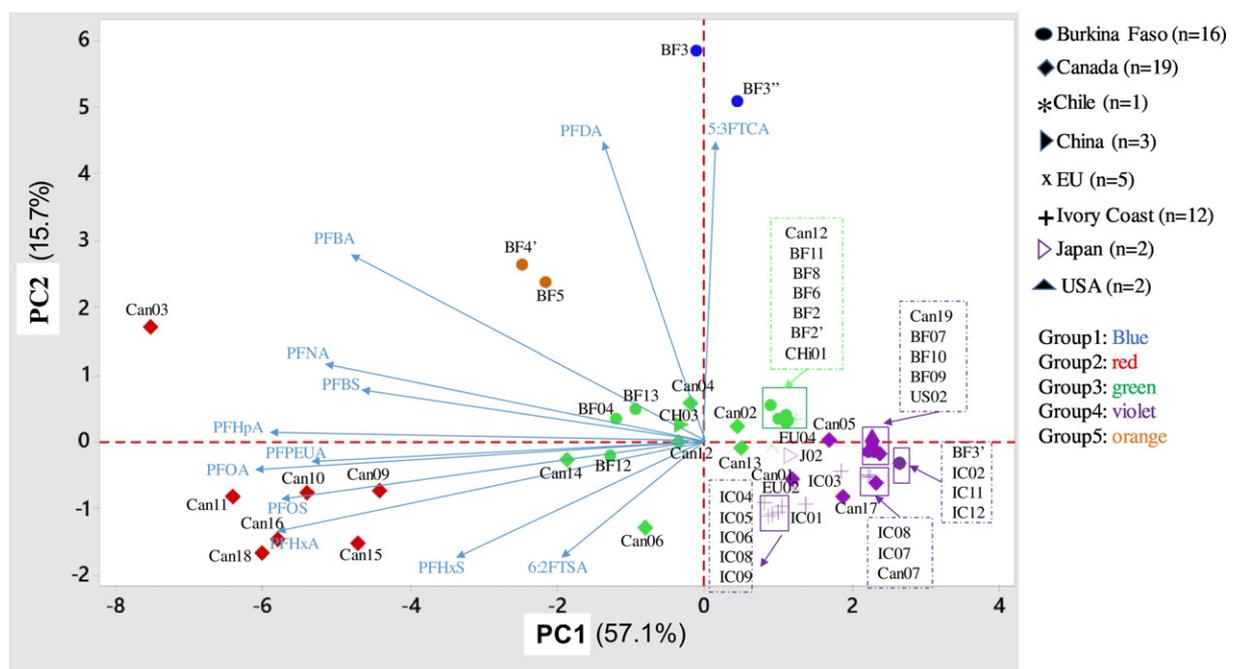


Fig. 3. Multivariate statistical analysis of tap water data collected from Burkina Faso (n = 16), Canada (n = 19), Chile (n = 1), China (n = 3), EU (n = 5), Ivory Coast (n = 12), Japan (n = 2), USA (n = 2); K-means clustering on principal component analysis (PCA) of different sites, color-coded according to their classification into five distinct groups based on their PFAS composition.

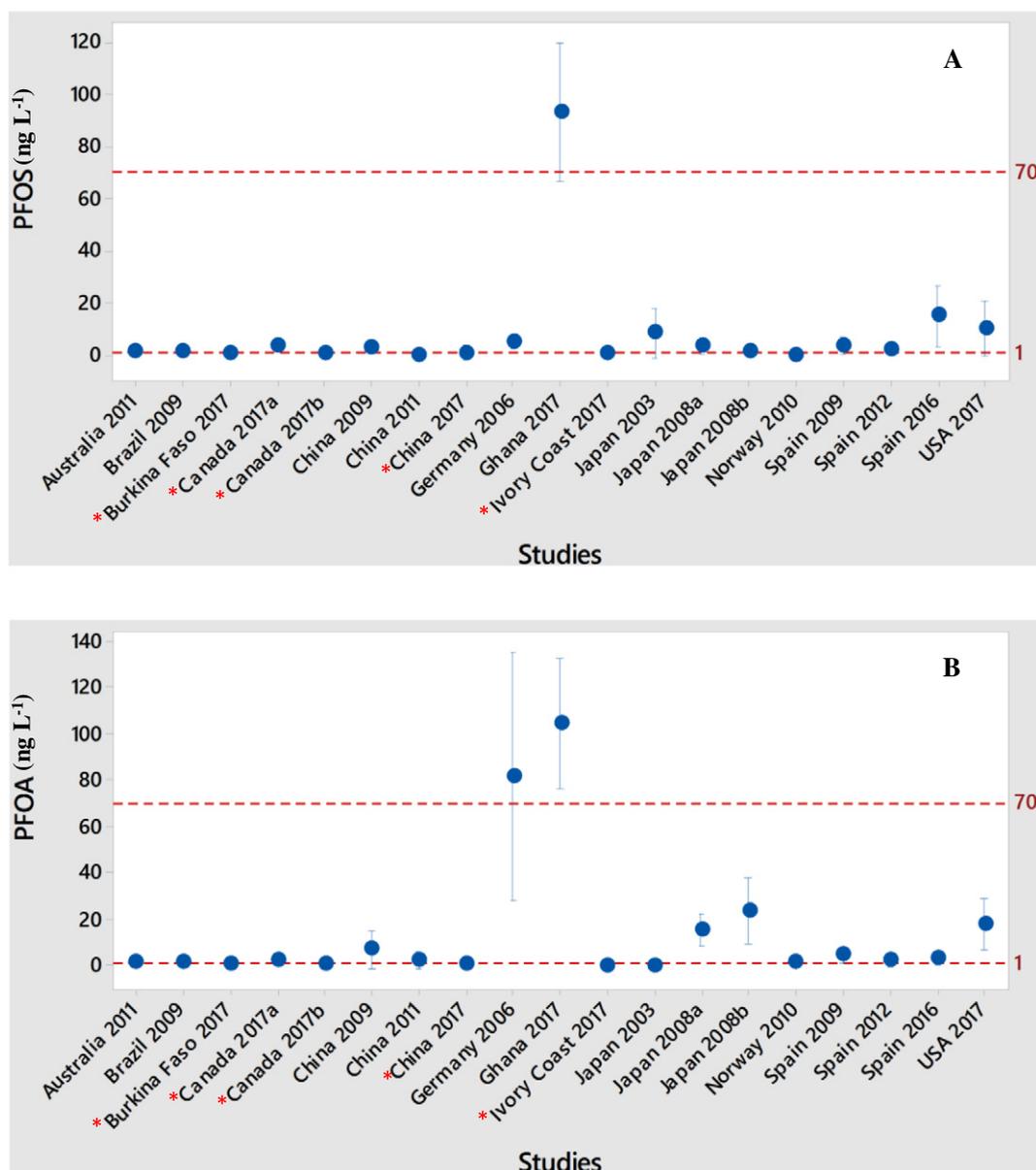


Fig. 4. PFOS (A) and PFOA (B) mean confidence intervals (95%) in tap water of different countries around the world (Harada et al., 2003; Exner and Färber, 2006; Takagi et al., 2008; Ericson et al., 2009; Mak et al., 2009; Quinete et al., 2009; Haug et al., 2010; Thompson et al., 2011; Zhang et al., 2011; Domingo et al., 2012; Schwanz et al., 2016; Essumang et al., 2017). Red asterisks (*) indicate data from the present survey. The red dashed line at 70 ng L^{-1} represents the updated US EPA life time health advisory level (US EPA, 2016) and the 1 ng L^{-1} is the suggested benchmark concentration for immunotoxicity in children (Grandjean and Budtz-Jørgensen, 2013).

additional $-\text{CF}_2$ moiety), while the difference between the retention times of FHxSA and the FOSA (C_8) native reference was 1.38 min (+ 0.69 min for each additional $-\text{CF}_2$ moiety). This observation somewhat differs with retention time chain length patterns commonly observed within other classes of PFASs (see also SI Table S2), wherein the magnitude of the retention time differences tends to decrease with increasing chain length; our observation could be explained by the presence of the branched, rather than linear isomer of the perfluoroalkane sulfonamide suspects. In view of the aforementioned, FBSA and FHxSA could only be identified at Level 3 (SI Figs. S2e and S2f). The seven identified suspects were screened in instrumental blanks and procedural blanks; they were not detected in any of these blanks. The quantified and semi-quantified concentrations are shown in Table 2. The highest concentrations were observed for FHxSA (4.0 ng L^{-1}) from China, PFPeS (3.9 ng L^{-1}) from Ivory Coast, and PFECHS (1.2 ng L^{-1}) from Canada.

C_4 -based (FBSA) and C_6 -based (FHxSA) perfluoroalkane sulfonamides have been recently reported in groundwater and biota (McGuire et al., 2014; Chu et al., 2016). To the knowledge of the authors, this is the first study to report on the occurrence of these short-chain perfluoroalkane sulfonamides in tap water. These results would also tend to confirm current monitoring findings toward the increasing prevalence of short-chain PFASs in environmental samples (Ahrens and Bundschuh, 2014; Valsecchi et al., 2015).

PFECHS is a cyclic perfluoroalkane sulfonate reportedly used in aircraft hydraulic fluids. It was previously identified in the Great Lakes surface waters and biota (De Silva et al., 2011) as well as in biota from the St. Lawrence River downstream from a WWTP outfall (Houde et al., 2013); it is, however, the first time that this compound has been reported in drinking water used for human consumption.

Ultrashort-chain (C_2 – C_3) perfluoroalkane sulfonates (PFES, PFPRS) have been recently identified in 3 M aqueous film-forming foams

Table 2
Concentration (ng L⁻¹) of suspects based on different source locations. Quantification confidence levels: sQ: semi-quantitative; Qn: quantitative.

		FBSA	FHxSA	PFECHS	PFETs	PFPrS	PFPeS	PFHpS
		sQ	sQ	Qn	sQ	Qn	Qn	Qn
Great Lakes/St. Lawrence River	Can03	<LOQ	0.09	1.2	<LOD	<LOD	<LOD	<LOQ
	Can09	<LOD	0.070	<LOD	<LOD	<LOD	<LOD	<LOQ
	Can11	0.15	0.090	1.0	<LOD	<LOD	0.14	<LOQ
	Can16	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOQ
	Can18	<LOD	0.070	<LOD	<LOD	<LOD	<LOD	<LOD
Rest of Canada	Can08	<LOD	<LOD	<LOQ	<LOD	<LOD	0.12	<LOD
EU	EU03	<LOD	0.070	<LOD	<LOD	<LOD	<LOD	<LOD
USA	US01	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chile	CHi01	0.27	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Burkina Faso	BF10	<LOD	<LOD	<LOD	0.16	0.15	<LOD	<LOD
	BF11	<LOD	<LOD	<LOD	0.49	0.33	<LOQ	<LOD
	BF12	<LOD	<LOD	<LOD	0.41	0.51	0.35	0.33
	BF2	<LOD	<LOD	<LOD	0.082	0.13	<LOD	<LOD
	BF2'	<LOD	<LOD	<LOD	0.10	0.093	<LOQ	<LOD
	BF3'	<LOD	<LOD	<LOD	0.43	0.14	<LOD	<LOD
	BF3	<LOD	<LOD	<LOD	<LOQ	0.082	<LOD	<LOD
	BF3''	<LOD	<LOD	<LOD	<LOQ	0.082	<LOD	<LOD
	BF4	0.080	<LOD	<LOD	0.14	0.66	0.19	<LOQ
	BF4'	0.090	<LOD	<LOD	0.20	0.52	0.19	<LOQ
	BF5	0.080	<LOD	<LOD	0.26	0.69	0.16	0.082
	BF6	<LOQ	<LOD	<LOD	0.13	0.14	<LOQ	<LOD
	BF7	<LOD	<LOD	<LOD	0.23	0.082	<LOD	<LOD
	BF8	<LOD	<LOD	<LOD	0.19	0.14	<LOQ	<LOQ
BF9	<LOD	<LOD	<LOD	0.51	0.21	<LOD	<LOD	
Ivory Coast	IC1	0.38	0.12	<LOD	0.21	0.94	3.9	1.2
	IC10	0.16	<LOD	<LOD	<LOD	0.31	0.75	0.31
	IC3	<LOQ	<LOD	<LOD	<LOD	0.15	0.28	<LOD
	IC4	0.080	0.15	<LOD	<LOD	0.58	0.86	0.57
	IC5	LOQ	0.09	<LOD	<LOD	0.23	0.36	0.16
	IC6	LOQ	0.13	<LOD	<LOD	0.36	0.54	0.27
	IC7	LOQ	<LOD	<LOD	<LOD	0.29	0.36	<LOD
	IC8	0.14	<LOD	<LOD	<LOD	0.12	0.25	<LOD
	IC9	0.14	<LOQ	<LOD	<LOD	0.30	0.82	0.36
China	CH01	<LOD	4.0	<LOD	0.093	<LOD	<LOD	<LOD
Estimated LOD		0.020	0.020	0.030	0.020	0.020	0.020	0.020
Estimated LOQ		0.070	0.070	0.10	0.070	0.070	0.070	0.070

(AFFFs) from the USA (Barzen-Hanson and Field, 2015). In the formulations, these compounds were generally present in a mixture with other co-occurring PFASs such as C₄, C₆, C₈, and C₁₀ analogues. Due to their expectedly high water solubility and mobility, PFETs and PFPrS were quantified for the first time in groundwater samples from US military bases (Barzen-Hanson and Field, 2015). In the present study, PFETs and PFPrS were repeatedly detected in tap water samples from various countries. For instance, PFPrS was systematically reported in tap water samples from the two West African countries (i.e. Burkina Faso and Ivory Coast) as well as from one tap water sample from China (Table 2). PFETs was occasionally detected in these samples. The highest concentrations observed for PFETs and PFPrS were, however, lower than 1.0 ng L⁻¹ in all samples from Burkina Faso, Ivory Coast, and China.

3.4. Risk assessment of PFOS and PFOA for drinking water consumers

In this section, we assessed the human health risk for PFOS and PFOA via drinking water since these compounds were present at variable concentrations as indicated in Table 1 and may present a risk of resultant adverse effects on some human populations. Many government agencies throughout the world have proposed chronic drinking water or provisional advisory health guidelines or screening values for most PFASs and PFCAs (German Ministry of Health, 2006; Drinking Water Inspectorate, 2009; Livsmidelsverket, 2014; Danish EPA, 2015; Health Canada, 2016; US EPA, 2016), i.e., drinking water Sweden (90 ng L⁻¹, sum of seven PFASs), US EPA health advisory for PFOS and PFOA (70 ng L⁻¹ for individual or combined), drinking water screening values of Canada for PFOS and PFOA (600 and 200 ng L⁻¹, respectively),

drinking waters of Germany for PFOS and PFOA (300 ng L⁻¹ for individual), and Denmark (100 ng L⁻¹ for PFOS). In addition to these values, a previous study proposed a benchmark dose for immunotoxicity in children and suggested a drinking water limit of approximately 1 ng L⁻¹ for individual or combined PFOS and PFOA (Grandjean and Budtz-Jorgensen, 2013). The latter benchmark and the recently updated US EPA lifetime advisory for PFOS and PFOA were used to evaluate the protective health scenario of drinking water analyzed in the present study. As can be inferred from Table 1, the PFOS and PFOA maximum concentrations for all drinking water samples ($n = 97$) (respectively 4.9 and 4.1 ng L⁻¹) would fall below (4 to 14 times lower) the US EPA lifetime health advisory level of 70 ng L⁻¹ (see also Fig. 4). This indicates that PFOS and PFOA levels in this study should not cause significant adverse effects on the general human population. However, the situation may be critical for subgroups of the human population that are more sensitive, such as children. According to the immunotoxicity benchmark considered, the maximum PFOS and PFOA levels in the drinking water samples from this study may still be of concern for the most sensitive individuals.

4. Conclusion

In summary, legacy and newly-identified PFASs were analyzed in 97 drinking water samples from Canada and several other countries around the world. Canadian tap water samples showed relatively higher concentrations for the samples produced from the Great Lakes/St Lawrence River than those produced from the other examined sources. However, the overall PFAS concentrations found in drinking water samples from Canada were similar to those found from other countries in this study as well as in other studies around the world. Although the direct emissions of PFOS and PFOA may be declining, they were still predominantly detected in tap water samples around the world due to global dissemination, their persistence in the environment, and the possible contribution of precursors. A suspect-target screening indicated that FBSA, FHxSA, PFECHS, PFETs, PFPrS, PFPeS and PFHpS were occasionally present in tap water from Canada and other countries (concentration range: <LOD–4 ng L⁻¹). A risk assessment approach suggested that the concentrations of PFOA and PFOS analyzed in this study should not pose a health risk for drinking water consumers.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2017.10.210>.

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