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Bioaccumulation and trophic magnification of emerging and legacy per- and polyfluoroalkyl substances (PFAS) in a St. Lawrence River food web☆

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ABSTRACT

Research on per- and polyfluoroalkyl substances (PFAS) in freshwater ecosystems has focused primarily on legacy compounds and little is still known on the presence of emerging PFAS. Here, we investigated the occurrence of 60 anionic, zwitterionic, and cationic PFAS in a food web of the St. Lawrence River (Quebec, Canada) near a major metropolitan area. Water, sediments, aquatic vegetation, invertebrates, and 14 fish species were targeted for analysis. Levels of perfluorobutanoic acid (PFBA) in river water exceeded those of perfluorooctanoic acid (PFOA) or perfluorooctane sulfonate (PFOS), and a zwitterionic betaine was observed for the first time in the St. Lawrence River. The highest mean PFAS concentrations were observed for the benthopelagic top predator Smallmouth bass (*Micropterus dolomieu*, Σ_{60}PFAS ~ 92 ± 34 ng/g wet weight whole-body) and the lowest for aquatic plants (0.52–2.3 ng/g). Up to 33 PFAS were detected in biotic samples, with frequent occurrences of emerging PFAS such as perfluorobutane sulfonamide (FBSA) and perfluoroethyl cyclohexane sulfonate (PFECHS), while targeted ether-PFAS all remained undetected. PFOS and long-chain perfluorocarboxylates (C10–C13 PFCAs) dominated the contamination profiles in biota except for insects where PFBA was predominant. Gammarids, molluscs, and insects also had frequent detections of PFOA and fluorotelomer sulfonates, an important distinction with fish and presumably due to different metabolism. Based on bioaccumulation factors >5000 and trophic magnification factors >1, long-chain (C10–C13) PFCAs, PFOS, perfluorodecane sulfonate, and perfluorooctane sulfonamide qualified as very bioaccumulative and biomagnifying. Newly monitored PFAS such as FBSA and PFECHS were biomagnified but moderately bioaccumulative, while PFOA was biodiluted.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have been used in varied applications, including the fluoropolymer industry (processing aids), aqueous film-forming foams (AFFFs) for firefighting, and domestic products (Glüge et al., 2020). Concerns over toxicity, bioaccumulation potential, and widespread dissemination of PFAS led the historic U.S. manufacturer to enact the phase-out of perfluorooctane sulfonyl fluoride and derivatives, such as perfluorooctane sulfonic acid (PFOS, C8), around 2002. In 2009, the Conference of the Parties to the Stockholm Convention listed PFOS and certain related compounds in Annex B to the Convention (Decision SC-4/17). In 2019, following recommendations of the Persistent Organic Pollutants Review Committee, perfluorooctanoic acid (PFOA, C8) and related compounds were added in Annex A to the Stockholm Convention (Decision SC-9/12). As a result of international actions, downward or plateauing time trends of legacy PFAS have been reported in some biomonitoring studies (Barrett et al., 2021; Kratzer et al., 2011).

The bioaccumulation of legacy PFAS has been well documented in aquatic biota (Burkhard, 2021; Cousins et al., 2020; Houde et al., 2011). Bioaccumulation factors (BAF) correlate positively with fluoroalkyl chain length for perfluoroalkyl acids (PFAAs) of C7–C12, with typically higher values for sulfonates compared with carboxylates of an equivalent number of $-CF_2$ units (Labadie & Chevreuil, 2011). The

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bioaccumulation of emerging PFAS has also been reported. A short-chain sulfonamide of high current concern, perfluorobutane sulfonamide (FBSA, C4), was detected as a metabolic product of proprietary precursors present in post-2002 3M's Scotchgard formulations (Chu & Letcher, 2014). FBSA was recently reported in fish, polar bears, and cetaceans, including species from remote regions, indicating bioaccumulation and potential for long-range transport (Boisvert et al., 2019; Chu et al., 2016). Current-use alternatives to PFOS and PFOA include PFAS with fluoroalkylether linkages (–CF_2–O–CF_2–), under trade names such as Gen-X (HFPO-DA; Chemours' alternative to PFOA), ADONA (a 3M's processing aid in the polymerization of fluoropolymers), or F–53B (metal plating), and Solvay's chloroperfluoropolyether carboxylates and the short-chain perfluoropolyether C6O4 (Galloway et al., 2020; Morganti et al., 2021; Pan et al., 2018; Washington et al., 2020). Fluoroalkylether compounds were variously detected in wastewater, river water, and soils in the United States and China, while fewer reports are available for biota (Li et al. 2022; Xiao, 2017). For example, bioaccumulation factors higher than PFOS were reported for X:2 chlorinated polyfluoroalkyl ether sulfonates (F–53B components, 6:2 Cl-PFESA and 8:2 Cl-PFESA) in amphibians (e.g., *Pelophylax nigromaculatus*) and fish (e.g., *Carassius carassius*) from Chinese freshwater ecosystems (Cui et al., 2018; Shi et al., 2015). Another PFAS superclass of high current concern is the fluorotelomer substances with large nonfluorinated organic head groups. The zwitterionic 6:2 fluorotelomer sulfonamidopropyl betaine (6:2 FTAB), for instance, is predominant in some contemporary AFFFs (D'Agostino & Mabury, 2014; Dauchy et al., 2017; Ruyle et al., 2021). Long-chain homologues of 6:2 FTAB were reported in benthopelagic fish *Micropterus dolomieu* and benthic fish *Catostomus commersonii* following firefighting emergency response at Lac-Mégantic, QC, Canada (Munoz et al., 2017a; Kaboré et al., 2022). They were also detected in the omnivorous cyprinid *Squalius cephalus* of the Seine River near Paris, France, impacted by industries and municipal wastewater treatment plants (Macorps et al., 2022).

The transfer of legacy PFAS has been characterized over entire aquatic food webs, for instance, through field-derived biomagnification factors (BMF) and trophic magnification factors (TMF). Most studies have focused on lake or marine environments (e.g., Fang et al., 2014; Kelly et al., 2009), with fewer data for river food webs (Penland et al., 2020; Simonnet-Laprade et al., 2019a, b). A recent review article tabulated PFAS biomagnification data for 25 studies, with only 5 studies for riverine systems (Miranda et al., 2022). BMF and TMF significantly greater than 1.0 are viewed as good indicators for classification under the B (bioaccumulative) status; however, different ecological variables, study designs, and methodological issues may yield conflicting conclusions between studies (Borgå et al., 2012). A meta-analysis of literature for aquatic studies (Franklin, 2016) showed that the TMF_{PFOA} could range from 0.58 (biodiluted) to 13 (biomagnified), and the TMF_{PFOS} from ~1.0 (non-significantly biomagnified) to 19.6 (biomagnified). Kidd et al. (2019) recently provided practical advice for the design and execution of TMF studies. The authors highlighted several criteria, among which: (1) a minimum trophic level (TL) range of 2.0, selecting organisms known to be linked by diet (predator-prey interactions); (2) analysis of contaminants and stable isotopes ($\delta^{15}N$ and $\delta^{13}C$) with appropriate analytical quality data; (3) preferential use of whole-body residue measurements; (4) inclusion of several low TL non-vertebrate taxa; and (5) collection of all organisms within the same time frame (Kidd et al., 2019). The need for larger dataset sizes (preferentially >60) and balanced designs (adequate number of samples collected at different TLs) are also critical to reduce TMF uncertainty (Borgå et al., 2012; Kidd et al., 2019).

The present study set out to provide an up-to-date portrait of the PFAS contamination status in a freshwater food web from the St. Lawrence River (QC, Canada). The sampling design followed practical guidance for TMF determination (Kidd et al., 2019). Water, sediment, and a large number of biotic samples (n = 110) were characterized for 60 PFAS, including legacy PFAAs, electrochemical fluorination (ECF)-derived precursors, fluorotelomer precursors, ether-PFAS, and other miscellaneous compounds. To the best of our knowledge, this is the first study to investigate the trophodynamics of a wide range of emerging PFAS, also the first report of PFAS biomagnification in the St. Lawrence River.

2. Materials and methods

2.1. Chemicals and materials

The isotope-labelled internal standards (ILIS), including 22 surrogate ILIS and 8 injection ILIS, were obtained from Wellington Laboratories (Guelph, ON, Canada). Certified standards of 49 PFAS analyzed using negative ion mode were obtained from Wellington Laboratories (Guelph, ON, Canada), DuPont (Wilmington, DE, USA), or Synquest Laboratories (Alachua, FL, USA). Standards of 11 cationic/zwitterionic PFAS were procured from Wellington Laboratories (Guelph, ON, Canada) or the Fluobon Surfactant Institute (Beijing, China). Further details are supplied in the Supporting Information (Supporting Information, SI; Text S1 and Tables S1–S2).

2.2. Study site and sample collection

With a mean annual discharge of ~12000 m^3/s at Quebec City, the St. Lawrence is one of the largest rivers in North America. It flows nearly 1500 km, connecting the Laurentian Great Lakes to the Atlantic Ocean. The freshwater section (Kingston, ON, to Quebec City, QC) is impacted by discharges of wastewater systems serving over 4 million people (Marcogliese et al., 2015). Samples of river water (n = 5), sediment (n = 5) and biota (a total of 21 species of aquatic plants, aquatic invertebrates, and fish) were collected in September 2019 in the St. Lawrence River near the Montréal archipelago, QC, Canada (Text S2 and Fig. S1).

Richardson's pondweed (*Potamogeton richardsonii*, n = 5), water stargrass (*Heteranthera dubia*, n = 5), and water sedge (*Carex* spp., n = 5) were the aquatic plants sampled. Invertebrates (pools of multiple individuals per site) included aquatic insects (Insecta, n = 5), aquatic snails (Gastropoda, n = 5), gammarids (Gammaridae, n = 5), and crayfish (Astacoidea, n = 5). Species of fish, collected using a beach seine or a gillnet, were sand shiner/mimic shiner (*Notropis stramineus*/*Notropis volucellus*, n = 8), sicklefin redhorse (*Moxostoma* spp., n = 4), bluntnose minnow (*Pimephales notatus*, n = 5), emerald shiner (*Notropis atherinoides*, n = 5), white sucker (*Catostomus commersonii*, n = 2), gold shiner (*Notemigonus crysoleucas*, n = 7), rock bass (*Ambloplites rupestris*, n = 6), pumpkinseed (*Lepomis gibbosus*, n = 5), yellow perch (*Perca flavescens*, n = 11), northern pike (*Esox lucius*, n = 7), and smallmouth bass (*Micropterus dolomieu*, n = 6). Being invasive species and having to be euthanized when captured, round goby (*Neogobius melanostomus*, n = 7) and tench (*Tinca tinca*, n = 2) were kept for analysis. Length and weight of fish, for which information is available, are provided in Table S3. Sampling protocols for fish were approved by Environment Climate Change Canada's Animal Care Committee, working under the Canadian Council on Animal Care.

2.3. PFAS analytical methods

2.3.1. Surface water

Following the addition of surrogate ILIS, river water (500 mL) was concentrated by automated off-line solid-phase extraction (Thermo Dionex Autotrace 280) using Strata X-AW SPE cartridges (200 mg/6 mL) (Picard et al. 2021). Cartridges were eluted using 15 mM NH_4OH in MeOH, and the eluates were spiked with injection ILIS and concentrated to 320 μL. A 120-μL aliquot of extract was introduced in a 250-μL polypropylene (PP) LC-MS vial with 30 μL of HPLC-grade water.

2.3.2. Sediment

Sediment samples were submitted to a sequential extraction procedure adapted from previous studies (Chen et al., 2020; Nickerson et al., 2020). After sample homogenization with a mortar and pestle, a 1-g dry weight aliquot (freeze-dried) was introduced in a 15-mL PP tube and spiked with surrogate ILIS. A 1-h wait time was applied, and the samples subsequently underwent three extraction cycles, each involving the addition of 4 mL of extraction solvent, high-speed vortexing (3200 rpm, 0.5 min), ultrasonication (10 min), centrifugation (6000 rpm, 5 min), and transfer of the supernatant. The first two cycles were conducted with 10 mM NH_4OH in MeOH as the extractant, and the third cycle with 100 mM ammonium acetate in MeOH (Chen et al., 2020; Munoz et al., 2018). The extracts were concentrated to <2 mL and submitted to cleanup through Supelclean ENVI-Carb cartridges (250 mg/6 mL). Samples were spiked with injection ILIS and concentrated to 200 μL. After the addition of 50 μL of HPLC-grade water, the samples were centrifuged and aliquoted for analysis.

2.3.3. Biota samples

Whole-body of organisms, including fish, were crushed and freeze-dried. Upon receipt at the analytical facilities, the samples were further homogenized with a mortar and pestle prior to aliquoting for PFAS analysis. A 100-mg dry weight aliquot (freeze-dried) was introduced in a 15-mL PP tube and spiked with surrogate ILIS. A 1-h wait time was applied, and the samples subsequently underwent two extraction cycles, each involving the addition of 4 mL of extraction solvent (10 mM NH_4OH in MeOH) (Munoz et al., 2017a), high-speed vortexing (3200 rpm, 0.5 min), ultrasonication in an ice-cold water bath (10 min), centrifugation (6000 rpm, 5 min), and transfer of the supernatant. The extracts were concentrated to <2 mL and submitted to the same cleanup procedure as the sediment. Next, samples were spiked with injection ILIS and concentrated to 300 μL. After brief vortexing, the samples were centrifuged and aliquoted for analysis.

2.3.4. LC-MS analysis

Instrumental analysis was carried out at Université de Montréal and involved ultra-high-performance liquid chromatography high-resolution mass spectrometry (UHPLC-HRMS Q-Exactive Orbitrap, Thermo Scientific, Waltham, MA, USA). The scan range was *m/z* 150–1000 (full scan mode), with a resolution setting of 70,000 FWHM at *m/z* 200. Details on method settings are provided in Table S4.

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

QA/QC elements were inserted in each analytical batch sequence (see also Text S3), with performance criteria derived from EPA methods (Shoemaker & Tettenhorst, 2018) and consolidated quality system manuals (DoD QSM version 5.3). Determination coefficients (R^2) of nonextracted solvent-based calibration curves (iCAL) and extracted matrix-matched calibration curves (mCAL) were ≥0.9900 (Table S5). Method blanks were performed using mineral bottled water (for water) and commercial Ottawa sand (for solids) (Text S3). Method limits of detection were in the range of 0.003–0.34 ng/L for river water, 0.0006–0.15 ng/g dry weight (d.w.) for sediment, and 0.004–0.59 ng/g wet weight (w.w.) for biota (Table S6). Matrix spike accuracies in river water, sediment, and fish were in the overall range of 73.6–121.3% with suitable precision (Table S7). Absolute recoveries were also verified for a subset of the biota samples (including 3 aquatic plants, 1 invertebrate, and 3 fish species) by performing standard additions (Table S8). A standard reference material from the National Institute of Standards and Technology (NIST SRM 1947 Lake Michigan fish tissue) was also analyzed to control whole-method trueness (Table S9).

2.5. Stable isotopes and proteins

Biotic samples (aliquots of whole-body homogenates) were dried at 45 °C for at least 48h until a constant weight was achieved and ground into a fine homogeneous powder. Analyses of carbon and nitrogen stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) were performed at the University of Waterloo on a Thermo Finnigan Mat Delta Plus Isotope Ratio Mass Spectrometer with a Carlo Erba Elemental Analyzer (EA – IRMS). Carbon and nitrogen isotope compositions were expressed as per mil (‰) relative to Vienna PeeDee Belemnite limestone and atmospheric nitrogen, respectively. Details on protein quantification are provided in SI (Text S4).

2.6. Data treatment and statistical analyses

The R statistical software was used to conduct data analyses (R version 4.0.5, R Core Team, 2022). Statistical significance was set at $p < 0.05$. For calculation of summed PFAS or depiction of percent compositions, non-detect data were treated as 0 × LOD. Calculation procedures of trophic levels and bioaccumulation metrics (Conder et al., 2012), including BAFs, biota-sediment accumulation factors (BSAFs), BMFs and TMFs, are described in SI (Text S5). TMFs were only calculated for PFAS of detection rates higher than 30%, representing between 33 and 110 uncensored data points. The 30% censoring threshold was selected as an intermediate value used in previous studies (threshold detection rates of 20–40%), also considering dataset size (Miranda et al., 2021; Munoz et al., 2017b; Simonnet-Laprade et al., 2019a). Log-transformed concentrations of contaminants (whole-body basis, n = 110 biotic samples) were plotted as a function of trophic levels, and the TMF was derived as the antilog of the regression slope. The tested regression models included parametric (Pearson's) linear regressions either based on all data (**Method 1**) or geometric means per taxa (**Method 2**) (Madgett et al., 2021), nonparametric linear regression (**Method 3**) (Kendall–-Theil Sen Siegel line, R-package mblm: *Median-Based Linear Models*), nonparametric linear regression accounting for < LOD data (**Method 4**) (Akritas–Theil–Sen line for censored data, *cenken* command of the R-package NADA: *Non-detects And Data Analysis*) (Helsel, 2006; Helsel, 2012), and generalized linear mixed-effect model (GLMM) also accounting for < LOD data (**Method 5**) (GLMM/LMEC, R-package LMEC: *Linear Mixed-Effect Models with Censored Responses*) (Munoz et al., 2017b; Simonnet-Laprade et al., 2019a). The GLMM/LMEC approach was also tested on protein-normalized PFAS data for a subset of 95 biotic samples; the vegetation samples were excluded from this regression due to their very low protein content.

3. Results and discussion

3.1. Stable isotopes and food web description

The stable isotope signature (biplot of $\delta^{15}N$ *vs.* $\delta^{13}C$) of the investigated freshwater food web is shown in Fig. 1. The $\delta^{13}C$ signature reflects the general diet while $\delta^{15}N$ reflects the trophic position, i.e., enrichment of ^{15}N relative to ^{14}N in organisms relative to their food due to preferential excretion of the lighter isotope (Cabana and Rasmussen, 1994; Kiriluk et al., 1995). Mean $\delta^{13}C$ values ranged between −23.3‰ and −12.8‰ for invertebrates and between −24.7‰ and −18.8‰ for fishes, with much lower intraspecific variations in fishes than invertebrates. For a given $\delta^{15}N$ value (or trophic position), overall ranges of $\delta^{13}C$ were progressively narrower with increasing trophic level with the $\delta^{13}C$ of top predators being in the mid-range of their preys, due to greater omnivorous feeding habit (Kidd et al., 1998).

Mean $\delta^{15}N$ values varied between 3.8 and 14.5‰ and ranked as follows: aquatic plants (3.8–6.7‰) < invertebrates (6.1–9.2‰) < minnows (10.0–10.7‰) ~ juvenile Yellow perch (10.5‰) ~ suckers (10.2–10.6‰) < Tench (11.6‰) ~ sunfishes (11.6–13.0‰) ~ Round goby (12.1‰) ~ adult Yellow Perch (13.2‰) < Northern pike (14.4‰) ~ Smallmouth bass (14.5‰). A $\delta^{15}N$ span of ~10‰ between primary producers and top predators is consistent with previous reports for temperate and subarctic freshwater ecosystems (Kidd et al., 1998).

Trophic levels (TL) ranged between ~1 (aquatic plants) and 3.7 for

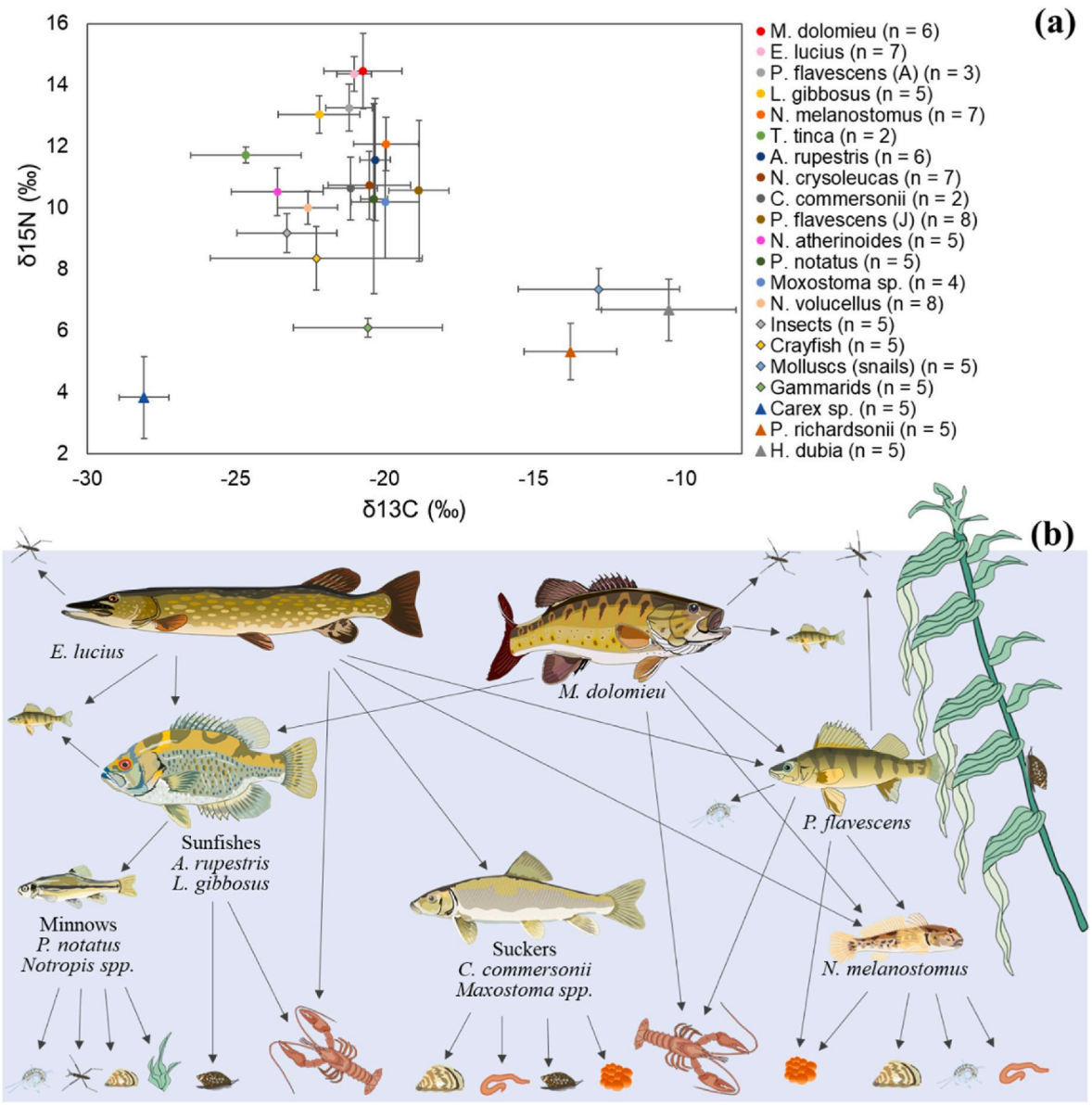

Fig. 1. Stable isotopes and food web schematic. (a) Stable isotope signature of biotic samples collected in the St. Lawrence River. Circles correspond to fish, diamonds to invertebrates, and triangles to aquatic plants. Error bars represent standard deviations. (b) Predator-prey interactions in the aquatic food web investigated in this study, dominated by Northern pike (*Esox lucius*) and Smallmouth bass (*Micropterus dolomieu*) (Boivin et al., 2021; Gouvernement du Québec, 2007; Lapointe et al., 2020). (Note that not all predator-prey couples are represented, and not all preys were available for analysis).

the largest collected specimen of *E. lucius* (75 cm, 2.3 kg). The trophic positions (on the basis of ^{15}N enrichment) agree with the feeding ecology of the fish species of interest (Fig. 1b and Table S10). Prey-size fish include benthopelagic invertivores/detritivores/herbivores (minnows - *N. atherinoides*, *N. crysoleucas*, *N. stramineus/volucellus*), benthopelagic planktivores (minnow - *P. notatus*), benthopelagic invertivores/piscivores (*P. flavescens* and sunfishes - *A. rupestris*, *L. gibbosus*), and benthic invertivores (*N. melanostomus* and suckers - *C. commersonii*, *Moxostoma* spp.). At the top of the food chain, pike (*E. lucius*) are benthopelagic carnivorous omnivores consuming *P. flavescens* and *N. melanostomus* (Boivin et al., 2021), while also feeding on other fishes (suckers, crappies, and cyprinids), crustaceans, amphibians, small mammals, and young waterfowl. Smallmouth bass (*M. dolomieu*) was the other benthopelagic top predator collected for analysis; its diet was predominately based on crayfish and Yellow perch but increasingly shifted to invasive Round goby (*N. melanostomus*) as a major prey item, based on stomach content analyses (Boivin et al., 2021). Small and intermediate-size fishes are also preyed upon by piscivorous mammals (e.g., River otter *Lontra canadensis*) and piscivorous birds (Lapointe et al., 2020), including Great blue heron (*Ardea herodias*), Ring-billed gulls (*Larus delawarensis*), and Herring gulls (*Larus argentatus*).

3.2. PFAS in river water and sediment

In river water, 25 of 60 targeted PFAS were detected (Table 1), and their summed concentration (Σ_{60}PFAS) ranged between 18 and 26 ng/L except for site #1 (Fig. S1), which was detected to be 99 ng/L due to higher PFBA level. Compounds detected in all water samples included C4–C10 PFCAs, C3–C8 perfluoroalkane sulfonates (PFSAs), PFECHS, short-chain sulfonamides (FBSA and perfluorohexane sulfonamide (FHxSA)), and 6:2 FTSA. At least two other isomers of PFECHS (Stefanac et al., 2018) were also detected in river water (Figs. S2–S3). None of the target fluoroalkyl ethers (DONA, Gen-X, and F–53B) were detected in surface water.

Table 1
Descriptive statistics including PFAS detection frequency (DF, % of samples > LOD) and concentration ranges (min-max) in river water (ng/L), sediments (ng/g dw), aquatic plants (ng/g ww), invertebrates (ng/g ww), and fish (ng/g ww) from the investigated St. Lawrence River food web (nd: <LOD).

	River water (n = 5)		Sediments (n = 5)		Aquatic plants (n = 15)		Invertebrates (n = 20)		Fish (n = 75)	
	DF %	Range (ng/L)	DF %	Range (ng/g)	DF %	Range (ng/g)	DF %	Range (ng/g)	DF %	Range (ng/g)
PFBA	100	3.6–87	20	nd-0.12	40	nd-0.25	25	nd-29	22.7	nd-0.31
PFPeA	100	1.2–1.4	60	nd-0.059	0	nd	10	nd-0.050	0	nd
PFHxA	100	1.6–2.7	80	nd-0.028	0	nd	20	nd-2.9	4	nd-0.33
PFHpA	100	0.81–0.92	80	nd-0.021	13.3	nd-0.074	15	nd-0.17	0	nd
PFOA	100	2.0–2.5	100	0.0075–0.092	66.7	nd-0.19	95	nd-3.7	30.7	nd-1.6
PFNA	100	0.39–0.56	80	nd-0.042	80	nd-0.46	100	0.084–5.7	94.7	nd-8.2
PFDA	100	0.060–0.079	80	nd-0.031	73.3	nd-0.33	100	0.16–4.1	100	0.62–7.3
PFUnDA	60	nd-0.018	80	nd-0.071	80	nd-0.12	100	0.21–3.5	100	0.45–6.8
PFDoDA	0	nd	80	nd-0.048	73.3	nd-0.50	100	0.12–1.2	100	0.094–2.8
PFTrDA	20	nd-0.012	80	nd-0.045	40	nd-0.036	100	0.067–1.4	98.7	nd-2.9
PFTeDA	0	nd	20	nd-0.017	20	nd-0.069	75	nd-0.56	96	nd-1.3
PFHxDA	0	nd	0	nd	0	nd	0	nd	0	nd
PFPrS	100	0.066–0.12	0	nd	0	nd	0	nd	0	nd
PFBS	100	0.42–0.52	100	0.0011–0.0085	0	nd	25	nd-0.22	1.3	nd-0.020
PFPeS	100	0.098–0.13	80	nd-0.0035	0	nd	5	nd-0.045	0	nd
PFHxS	100	0.72–0.86	100	0.0019–0.043	6.7	nd-0.0068	55	nd-3.1	42.7	nd-0.16
PFHpS	100	0.040–0.058	80	nd-0.0054	0	nd	30	nd-0.10	45.3	nd-0.15
PFOS	100	2.80–4.4	100	0.037–0.72	100	0.058–3.3	100	0.93–61	100	12–140
PFNS	0	nd	20	nd-0.0015	0	nd	0	nd	18.7	nd-0.046
PFDS	20	nd-0.025	100	0.0020–0.045	20	nd-0.021	100	0.013–0.51	100	0.11–1.8
PFDoS	0	nd	0	nd	0	nd	0	nd	0	nd
FBSA	100	0.25–0.35	0	nd	0	nd	40	nd-0.078	68	nd-0.85
FHxSA	100	0.020–0.046	40	nd-0.0029	0	nd	15	nd-0.078	32	nd-0.42
FOSA	40	nd-0.029	100	0.0017–0.021	0	nd	50	nd-0.44	33.3	nd-0.69
MeFBSA	0	nd	0	nd	0	nd	0	nd	0	nd
MeFOSA	0	nd	0	nd	0	nd	0	nd	0	nd
EtFOSA	0	nd	60	nd-0.0061	0	nd	0	nd	0	nd
FOSAA	0	nd	60	nd-0.014	0	nd	0	nd	6.7	nd-2.7
MeFOSAA	0	nd	60	nd-0.028	0	nd	35	nd-0.25	12	nd-0.15
EtFOSAA	40	nd-0.039	80	nd-0.062	20	nd-0.014	65	nd-0.27	28	nd-0.22
3:3 Acid	0	nd	0	nd	13.3	nd-0.23	0	nd	0	nd
5:3 Acid	0	nd	40	nd-0.023	0	nd	0	nd	0	nd
7:3 Acid	0	nd	60	nd-0.022	0	nd	5	nd-0.094	0	nd
6:2 FTCA	0	nd	0	nd	0	nd	0	nd	0	nd
8:2 FTCA	0	nd	0	nd	0	nd	0	nd	0	nd
10:2 FTCA	0	nd	0	nd	0	nd	0	nd	0	nd
4:2 FTSA	0	nd	0	nd	0	nd	0	nd	0	nd
6:2 FTSA	100	0.092–0.31	0	nd	0	nd	5	nd-0.71	4	nd-0.22
8:2 FTSA	60	nd-0.029	0	nd	0	nd	30	nd-0.24	0	nd
10:2 FTSA	0	nd	20	nd-0.0039	0	nd	0	nd	0	nd
Gen-X	0	nd	0	nd	0	nd	0	nd	0	nd
DONA	0	nd	0	nd	0	nd	0	nd	0	nd
6:2 Cl-PFESA	0	nd	0	nd	0	nd	0	nd	0	nd
8:2 Cl-PFESA	0	nd	0	nd	0	nd	0	nd	0	nd
Cl-PFOS	0	nd	0	nd	0	nd	0	nd	0	nd
PFECHS	100	0.57–0.78	100	0.0015–0.036	0	nd	35	nd-0.83	45.3	nd-0.20
PFHxPA	0	nd	0	nd	0	nd	0	nd	0	nd
PFOPA	0	nd	0	nd	0	nd	0	nd	0	nd
6:2 diPAP	20	nd-0.36	40	nd-0.047	6.7	nd-0.017	25	nd-0.11	36	nd-0.50
PFHxSAm	0	nd	0	nd	0	nd	0	nd	2.7	nd-0.055
PFOSAm	0	nd	40	nd-0.0044	0	nd	0	nd	0	nd
PFHxSAmS	0	nd	0	nd	0	nd	0	nd	1.3	nd-0.11
PFOSAmS	0	nd	80	nd-0.016	0	nd	0	nd	0	nd
PFOANO	0	nd	0	nd	0	nd	0	nd	0	nd
PFOSNO	0	nd	0	nd	0	nd	0	nd	0	nd
PFOAB	0	nd	0	nd	0	nd	0	nd	0	nd
PFOSB	0	nd	0	nd	0	nd	0	nd	0	nd
5:3 FTB	0	nd	0	nd	0	nd	0	nd	0	nd
5:1:2 FTB	0	nd	0	nd	0	nd	5	nd-0.040	0	nd
6:2 FTAB	100	0.050–0.13	20	nd-0.015	0	nd	0	nd	0	nd

The three most abundant PFAS in river water were PFBA (3.6–87 ng/L), PFOS (2.8–4.4 ng/L), and PFOA (2.0–2.6 ng/L). The low variability of PFOS and PFOA could be due to the legacy status of these compounds. A recent study also found greater variability of PFBA in the Great Lakes watershed, with increasing water concentrations in the easternmost lakes, Erie and Ontario (Gewurtz et al., 2019). Houde et al. (2014) reported similar concentration ranges for PFOS (2.5–2.8 ng/L) and PFOA (2.4–2.8 ng/L) in St. Lawrence River water collected in 2012 from the same area; at that time, PFBA was already slightly dominant (4.2–4.8 ng/L). Though present at relatively low concentrations (0.05–0.13 ng/L), the zwitterion 6:2 FTAB was found in all water samples of the present study. It was recently reported in Ontario watersheds (Canada) impacted by AFFFs and urban wastewaters (D'Agostino and Mabury, 2017). This is the first study to report its occurrence in the St. Lawrence River.

Of 60 target PFAS, 32 were variously detected in sediment samples (Table 1). Summed PFAS ranged between 0.05 and 1.4 ng/g (dry weight basis). PFOS (0.04–0.72 ng/g) was the most abundant compound,

representing *circa* 53% of Σ_{60}PFAS. The dominance of PFOS over other PFAAs in sediments agrees with profiles reported in other Canadian hydrosystems with anthropogenic impacts, including Lake Erie and Lake Ontario (Gewurtz et al., 2013; Guo et al., 2016). PFOS was also often the dominant PFAS in river and lake sediments elsewhere, including nationwide surveys in France, Vietnam, and South Korea (Lam et al., 2014, 2017; Munoz et al., 2015). Apart from PFOS, compounds with high detection rates in sediments included C6–C14 PFCAs, perfluorodecane sulfonate (PFDS), C8 sulfonamides, 7:3 fluorotelomer acid, and PFECHS. Two ECF-based zwitterionic precursors to PFOS (Liu et al., 2021), dimethylammoniopropyl perfluorooctane sulfonamide (PFOSAm) and trimethylammoniopropyl perfluorooctane sulfonamide (PFOSAmS), are reported for the first time in St. Lawrence sediments.

3.3. PFAS in aquatic biota

Detection frequencies. Overall, 33 PFAS were detected in biotic samples (Table 1; see also the Supporting Excel database for individual results). Mean values of Σ_{60}PFAS across species generally ranked as aquatic plants (0.52–2.3 ng/g) < molluscs/crustaceans (7.4–18 ng/g) < insects (70 ng/g) ~ fish (21–92 ng/g), with the highest values reported for Smallmouth bass *M. dolomieu* (Fig. 2). Aquatic plants had only a few compounds with high detection rates (Table 1), including PFOS (detected in 100% of samples), C8–C13 PFCAs (40–80%), and PFBA (40%). Detection rates higher than 40% were observed for 13/60 PFAS in invertebrates and 12/60 PFAS in fish (Table 1). Five compounds were found in 100% of invertebrates (n = 20) and fish (n = 75): perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), PFOS, and PFDS.

Regarding PFAS of emerging concern, FBSA was found in 40% of invertebrate samples (<0.006–0.078 ng/g) and 68% of fish samples (<0.006–0.85 ng/g) from the St. Lawrence (Table 1). This chemical has also been reported in benthopelagic fishes from lakes and rivers in Alberta, Northwest Territories, Ontario, Québec, and Yukon Territory (Chu et al., 2016; Kaboré et al., 2022). FBSA was also detected in flounder (*Platichthys flesus*) from Western Europe (Chu et al., 2016). The C6 homolog, FHxSA, was occasionally detected in invertebrates and fish of the present study (detection rates of 15% and 32%, respectively). F–53B's major component, 6:2 Cl-PFESA, was not detected in any biota sample from our study; this is in stark contrast with elevated levels in ecosystems from China due to local emissions of the hard chrome plating industry (Shi et al., 2015; Pan et al., 2021). PFECHS was found in 35% of

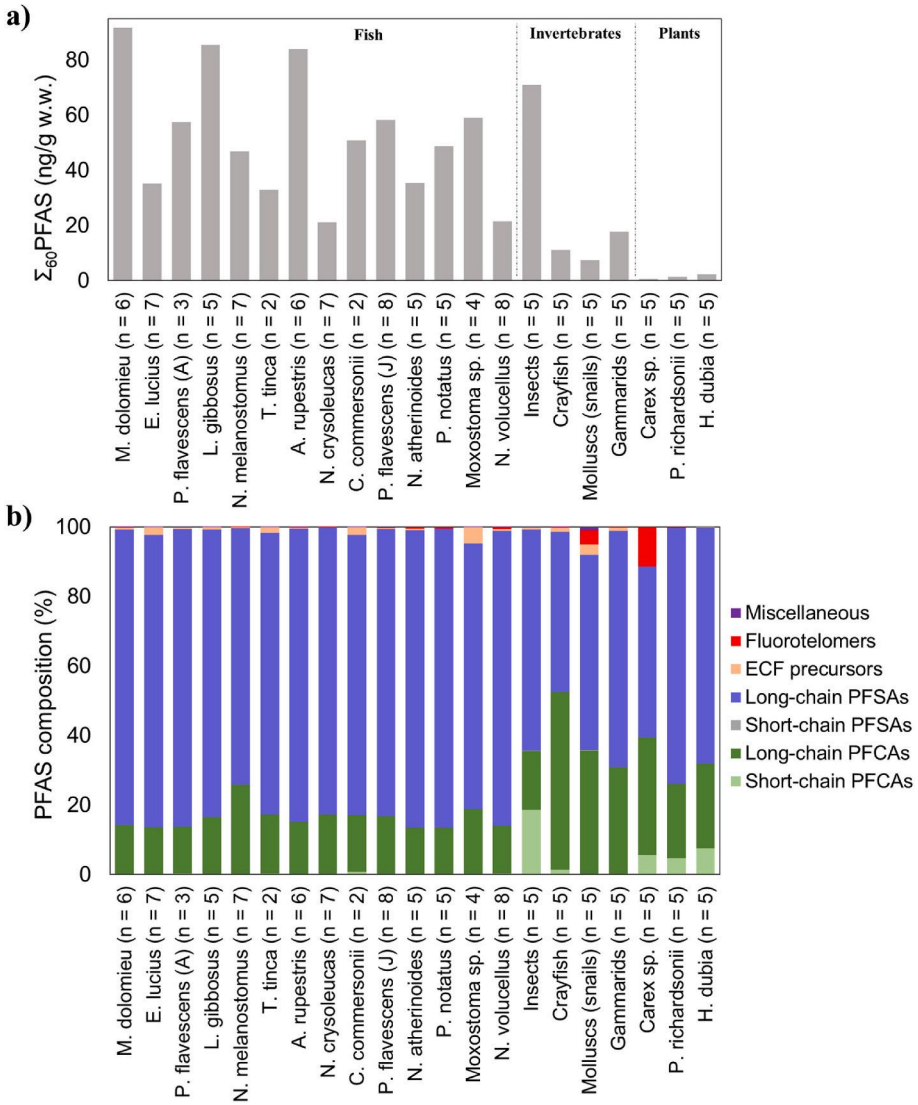

Fig. 2. a) average PFAS concentrations (ng/g wet weight whole-body) in aquatic biota from the St. Lawrence River and b) abundance profiles (% of $\sum_{60}$PFAS) for each species. In the x-axis, organisms are generally arranged from higher to lower trophic level, subdivided by groups (fish, invertebrates, and plants), from left to right.

invertebrates and 45% of fish at relatively low levels (<0.009–0.83 ng/g and <0.009–0.20 ng/g, respectively). Very few studies have investigated the occurrence of PFECHS at low trophic levels (Lescord et al., 2015). PFECHS concentrations in fish from the present study were lower than levels previously reported for fish homogenates from Lake Erie and Lake Ontario (0.7–4.4 ng/g ww whole-body; collected in 2006–2008) (De Silva et al., 2011) but in the same range as Northern pike (0.54 ng/g ww liver, or ~0.14 ng/g ww converted on a whole-body basis; collected in 2011) and Yellow perch (<0.21 ng/g ww whole-body; collected in 2012) from the St. Lawrence River (Houde et al., 2013, 2014).

PFOS predominance in fish and compliance with guidelines. In fish, PFOS (12–140 ng/g) was largely predominant, accounting for ~81 ± 5% of Σ_{60}PFAS. The other four major PFAS were PFDA (4.8% of Σ_{60}PFAS), PFUnDA (4.8%), PFDoDA (2.1%) and perfluorotridecanoic acid (PFTrDA, 2.0%). Previously, Lin et al. (2021) also observed that PFOS was the most abundant PFAS (representing 73% of Σ_{11}PFAS) in 139 fish samples from the Great Lakes; concentrations and abundance increased from west to east, with the highest levels for Lake Ontario. PFOS was also by far the most abundant PFAS in Northern pike and Yellow Perch specimens collected in 2011–2012 in the St. Lawrence, with PFUnDA the second most abundant (Houde et al., 2013, 2014). PFOS was typically the most abundant PFAA in fish from lakes and rivers with urban influences elsewhere, including European chub (*Leuciscus cephalus*) near Paris, France, perch (*Perca fluviatilis*) from German freshwaters, and crucian carp (*Carassius carassius*) from South Korea freshwaters (Labadie & Chevreuil, 2011; Lam et al., 2014; Rüdel et al., 2022). PFOS was also often the predominant PFAS in fish from more pristine environments, including semi-remote Canadian lakes and subalpine European lakes (Kaboré et al., 2022; Valsecchi et al., 2021). Differing profiles have been noted for sites influenced by the fluorochemical industry, where long-chain (C9–C13) PFCAs or ether-PFAS can be dominant in fish (Babut et al., 2017; Pan et al., 2017).

In Canada, Environment and Climate Change Canada has developed Federal Environmental Quality Guidelines (FEQGs) for PFOS (ECCC, 2017), including a Federal Fish Tissue Guideline (FFTG, 8300 ng/g) and Federal Wildlife Diet Guidelines (FWiDGs, 4.6 and 8.2 ng/g for mammals and birds, respectively). The European Union Water Framework Directive also set a PFOS ecological benchmark for the secondary poisoning of top predators (EU, 2014), with a Quality Standard ($QS_{biota,\ sec.\ poison.}$) of 33 ng/g. These guidelines are all expressed on a whole-body, wet weight basis. The fish samples from the present survey were all below the Canadian FFTG—the maximum PFOS measured in fish from our series was 66 times lower than the FFTG, and the median, 260 times lower. However, Canadian FWiDGs would be exceeded for fish-eating mammals by 2.6–30 times (median: 7.9 times) and fish-eating birds by 1.5–17 times (median: 4.4 times). The findings are consistent with a Pan-Canadian survey of PFOS in fishes (2006–2011), where near-systematic exceedances to the wildlife FEQGs were reported in fishes from the easternmost Great Lakes (Erie and Ontario) and the St. Lawrence (Gewurtz et al., 2013). Half of the fish samples from the present study (38 of 75) were also above the $QS_{biota,sec.\ poison.}$ of the European Union (EU, 2014).

Changes in PFAS profiles between invertebrates and vertebrates. There were limited differences across fish species in terms of PFAS profiles (Fig. 2). Peculiar profiles were, however, noted for the invertebrates. For instance, the mean relative abundance in invertebrates was 4.4% for PFOA (67 times higher than in fish). The median PFOA/PFOS ratio was 50 times higher in invertebrates than in fish (Mann-Whitney test, p-value $<10^{-10}$), and the same was observed for the median PFNA/PFOS ratio (5.6 times higher in invertebrates, p-value $<10^{-10}$). This may be due to differences in life traits, with strictly benthic organisms showing higher PFOA- and PFNA-to-PFOS ratios than benthopelagic ones (Nakata et al., 2006). Invertebrates could also have a much lower depuration capacity of PFCAs than fishes (Simonnet-Laprade et al., 2019a). PFBA occurrence and concentrations were particularly high in aquatic insects (4/5 samples with detections, maximum of 29 ng/g or 44% of Σ_{60}PFAS), contrasting with relatively low levels in all other organisms. Aquatic insects could be exposed by distinct pathways due to feeding near the air-water interface, where PFAS accumulation phenomena have been reported (Ju et al., 2008). 8:2 FTSA was also relatively frequent in invertebrates (30% detection rate) but not found in fish. The two species that had higher percent compositions of fluorotelomers (snails and wetland aquatic plant, Fig. 2) may also be related to the terrestrial food chain, which could be a reason for their distinct PFAS profile.

The relatively higher abundance of PFOA and short-chain homologues in invertebrates than in fish agrees, for instance, with patterns reported for gastropods, polychaetes, and crabs from the west coast of South Korea (Hong et al., 2015) and gammarids from the Barents Sea (Haukås et al., 2007). Simonnet-Laprade et al. (2019a) also found systematically higher relative abundances of PFOA and Σprecursors in invertebrates than in fish from five river ecosystems of France. Langberg et al. (2019) observed higher (1.5–5.6 times) abundances of fluorotelomer sulfonates in benthic/epibenthic invertebrates than in teleost fish. Using a total oxidizable precursor (TOP) assay, Simonnet-Laprade et al. (2019b) noted that the relative contribution of total unknown precursors decreased in the following order in a riverine food web: aquatic vegetation (biofilm, macrophytes) > invertebrates (gammarids) > fish. Different elimination rates and enzymatic biotransformation between trophic levels could explain the distinct occurrence of precursors along aquatic food webs (Langberg et al., 2019; Simonnet-Laprade et al., 2019a, b).

3.4. Bioaccumulation and biomagnification factors

The mean BAFs of C4–C8 PFCAs, PFBS, and PFHxS were higher for invertebrates than for fish, while the reverse was true for the longer chain homologues (Table S11). A similar trend was found when examining field BAF data from two aquatic food webs of France and Korea (Hong et al., 2015; Munoz et al., 2017b). This may reflect higher elimination rates in aquatic vertebrates than in invertebrates. Biotransformation at higher trophic levels could also explain the lower BAF of 6:2 FTSA in fish than invertebrates from our study and others (Langberg et al., 2019; Simonnet-Laprade et al., 2019a).

In fish, BAFs (overall means) were low for C4–C8 PFCAs (13–86 L/kg) and C4–C6 PFSAs (38–44 L/kg), intermediate for PFHpS (850 L/kg), PFECHS (95 L/kg) and FBSA (1010 L/kg), and high for C9–C13 PFCAs (2400–150,000 L/kg), C8–C10 PFSAs (14,000–25,000 L/kg) and C8 sulfonamides (4200–7900 L/kg). The BAF of long-chain PFCAs (C8–C13) increased with fluoroalkyl chain length, with the highest value often found for PFUnDA (C11). The relatively lower BAF of >C11 PFCAs (e.g., PFTrDA) may reflect lower bioavailability due to the increased molecular size and stronger affinity for suspended particulate matter (Fang et al., 2014).

Several compounds had Log BAFs systematically above 3.7 (or BAF ≥5000, the REACH criterion for very bioaccumulative chemicals) across all fish species: PFDA, PFUnDA, PFTrDA, PFOS (except for *N. crysoleucas*) and PFDS. Mean Log BAF ≥3.7 were also reported for PFDA, PFUnDA, and PFOS in top predator fishes from the Laurentian Great Lakes (De Silva et al., 2011). The median Log BAF of PFOS across all fish samples was 4.05 (n = 75), higher than the meta-analysis value compiled from 84 teleost fish studies (median Log BAF = 3.55, whole-body basis, Burkhard, 2021) but similar to the value of 4.1 determined by De Silva et al. (2011) in the Great Lakes.

Biota-sediment accumulation factors of PFAS in benthic species were near-systematically above unity (Table S12). BSAFs of long-chain PFCAs did not follow the same trend with fluoroalkyl chains as BAFs. Rather, BSAFs tended to decrease with chain length, with maximum values for PFNA or PFDA *vs.* lower BSAFs for PFTrDA or PFTeDA (by 1.5–14 times). The findings agree with observations in benthic food webs in China and Europe (Li et al., 2022; Munoz et al., 2017b) and could reflect the lower bioavailability of C13–C14 PFCAs strongly adsorbed onto sediment

organic matter.

Biomagnification factors are compiled in SI for key predator-prey couples (Table S13). BMFs were generally <1 (biodiluted) for C4–C9 PFCAs and C6–C7 PFSAs, and >1 (biomagnified) for their long-chain homologues (C10–C14 PFCAs, PFOS, and PFDS). The highest BMF values of C10–C14 PFCAs were observed for prey-size fish to molluscs, for instance for Yellow perch (BMF~5.6–9.6), Pumpkinseed (BMF~8.7–15), and suckers (BMF~4.1–8.9). The highest BMF values of PFOS and PFDS were for top predators (Northern pike and Smallmouth bass) to crayfish prey (BMF~6.1–33) and sunfishes to invertebrate preys, e.g., Pumpkinseed/molluscs (BMF~17–22) and Rock bass/crayfish (BMF~15–32).

3.5. Trophic magnification factors (TMFs)

Biomagnification integrated along the food chain is evaluated through TMFs; this metric may be more robust than BMFs relying on single predator-prey relationships (Borgå et al., 2012). The analysis of liver alone or fillet alone for fish (where PFAS tend to accumulate to a greater and lower extent, respectively) *vs.* whole-body for invertebrates could also bias results, resulting in artificially higher or artificially lower TMFs, respectively. Hence, whole-body homogenates were used for all trophic levels following guidance in Kidd et al. (2019) and as a more realistic scenario, since predators can consume prey as a whole.

Different statistical approaches, such as the choice of regression model and treatment of non-detects, could exert a large influence on the generated TMF values - although the overall conclusion regarding biomagnification potential (TMF >1 or <1) was generally unaffected (Fig. 3). Depending on the model, and despite the relatively large dataset size (n = 110), TMFs could vary by 1.2–11 times between the 5 tested statistical methods (Fig. 3). Parametric regressions with substitution of non-detects by a default value (0.5 × LOD) (Methods 1, 2) resulted in higher TMF estimates than a nonparametric Kendall–Theil Sen Siegel regression (Method 3). The latter model would be less susceptible to the influence of outliers, though still influenced by the substitution of <LOD data. The difference may also be due to the data distribution, which deviated from normality.

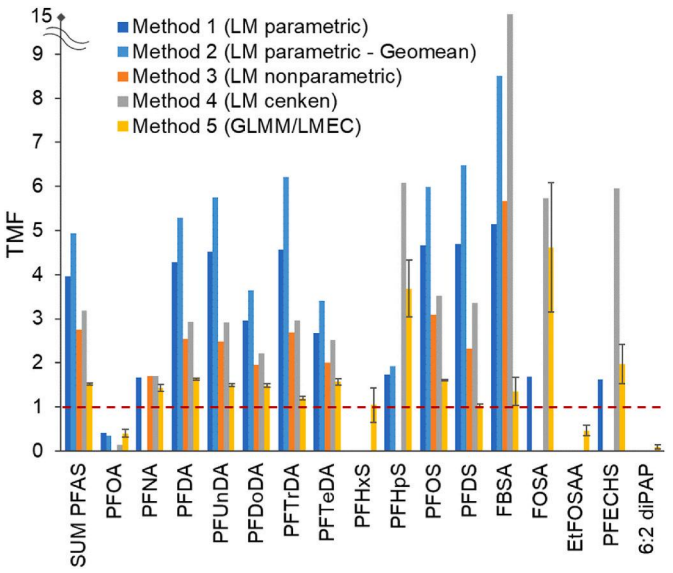

Fig. 3. Trophic magnification factors (TMF) determined for those PFAS of detection frequencies >30% by 5 different regression methods based on linear models (LM). The red dashed line refers to the threshold for trophic magnification (TMF >1: biomagnified; TMF <1: biodiluted). Method 1: Simple parametric linear regression (LM parametric; n = 110); Method 2: Parametric linear regression on geometric means rather than individual data points (LM parametric - Geomean; n = 21); Method 3: Nonparametric Kendall–Theil Sen Siegel linear regression (LM nonparametric; n = 110); Method 4: Nonparametric linear regression accounting for nondetect data (LM cenken; n = 110); Method 5: Generalized linear mixed effect model also accounting for nondetect data, interspecific variability (random effects) and different number of specimens per taxa (GLMM/LMEC; n = 110). In Method 5, error bars refer to the TMF 95% confidence interval returned by the model. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Among the two tested censored methods (imputation), Method 4 (cenken) provided TMF estimates systematically above the 95% CI upper bound of Method 5 (GLMM/LMEC), in agreement with Simonnet-Laprade et al. (2019a). Method 5 was selected as combining the advantages of non-detect handling and use of a generalized linear mixed model with random effect on species (Munoz et al., 2017b; Simonnet-Laprade et al., 2019a), thus reducing the risk of TMF distortion with different *n* per taxa available for analysis (Kidd et al., 2019).

TMFs based on the GLMM/LMEC model with censored responses are presented in Table 2. Normalization of PFAS concentrations to protein content (Kelly et al., 2009) also did not affect the conclusions (TMFs >1) except for FBSA whose TMF was no longer significantly >1 after applying protein normalization (Table S14). TMFs (not protein normalized) were significantly >1 (biomagnified) for long-chain (C9–C14) PFCAs (TMF range: 1.20–1.63), long-chain (C7, C8, C10) PFSAs (1.03–3.68), sulfonamides (FBSA: 1.35; FOSA: 4.62), and PFECHS (1.98). This is the first study to demonstrate biomagnification of the cyclic fluorinated surfactant PFECHS, to the best of our knowledge. A review of PFAS TMFs in food webs of lakes, rivers, and estuaries is presented in Table 2. TMFs >1 for long-chain PFCAs/PFSAs, as observed in our study, agree with data from the literature. The geomeans derived from TMF literature data (Table 2) were higher for C9–C11 PFCAs (TMF of 2–2.4) than their shorter (<C9) or longer (>C12) chain homologues. The geomean TMF of PFOS was 2.3, slightly higher than the value found in this study (1.60).

The TMF of PFOA was significantly lower than unity (i.e., biodiluted), in line with findings from at least three other studies in lake or river food webs (Martin et al., 2004; Penland et al., 2020; Simonnet-Laprade et al., 2019a). The other compounds with low TMF values were N-ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA: 0.46) and 6:2 polyfluoroalkyl phosphate diester (6:2 diPAP: 0.09). These precursors and others (N-methyl perfluorooctane sulfonamidoacetic acid (MeFOSAA), 6:2 FTSA) were previously reported to have TMFs lower than unity (Munoz et al., 2017b; Simonnet-Laprade et al., 2019a), likely reflecting enhanced biotransformation and elimination occurring at higher trophic levels.

4. Conclusions

In the present study, we documented PFAS levels in a food web of the St. Lawrence River. The PFAS data of the year 2019 could inform future time trends following ongoing shifts in fluorochemical manufacture, regulations, or improvements in wastewater treatment technology. Overall, forty PFAS were detected in river water, sediment, and the aquatic biota. Precursors were found in water and sediments, and this is the first report of the zwitterion 6:2 FTAB in the St. Lawrence River. PFBA, PFOA, and anionic precursors (e.g., 8:2 FTSA) were found at high frequency and relative abundance in gammarids, insects, and molluscs, an important distinction from teleost fish. This could be due to different detoxification pathways between invertebrates and vertebrates, e.g., different expressions of enzymes involved in the redox reactions of xenobiotics (and endogenous molecules), such as cytochromes P450 (Langberg et al., 2019). PFOS was largely dominant in aquatic organisms, with maximum levels observed for the benthopelagic top predator Smallmouth bass. Federal guidelines were frequently exceeded, indicating that PFOS may represent ecotoxicological risks to mammalian and avian consumers. It is possible that the situation would improve in the long term, as PFOS concentrations were reported to stabilize or decline in the upstream Laurentian Great Lakes (Gewurtz et al., 2013,

Table 2
Trophic magnification factors (TMF) of PFAS determined in the present study (GLMM/LMEC method; estimate and [95% confidence interval]) and TMF literature data for food webs of lakes, rivers, and estuaries (Fang et al., 2014; Li et al., 2022; Loi et al., 2011; Martin et al., 2004; Miranda et al., 2021; Munoz et al., 2017b; Penland et al., 2020; Simonnet-Laprade et al., 2019; Xu et al., 2014). The geometric mean of TMF values from this and other listed studies is also included (Geomean derived from a single TMF datum are indicated in parentheses).

	Present study	Fang et al.	Li et al.	Loi et al.	Martin et al.	Miranda et al.	Munoz et al.	Penland et al.	Simonnet-Laprade et al.	Xu et al.	Geomean
Ecosystem	**River**	**Lake**	**Estuary**	**Wetlands**	**Lake**	**Estuary**	**Estuary**	**River**	**River**	**Lake**	
Site	**St. Lawrence**	**Taihu Lake**	**Xiaoqing River**	**Mai Po Marshes**	**Lake Ontario**	**Subaé**	**Gironde**	**Yadkin-Pee Dee**	**5 rivers in France**	**Taihu Lake**	
Samples	110	260	50	49	>30	44	67; 80	130	15–26	113	
TL range	2.7	3.2	2.8	4.8	1.6	2.5	2.7	3.9	1.8–3.6	3.5	
PFBA	–	–	0.36	–	–	–	–	–	–	–	(0.36)
PFHpA	–	–	–	–	–	–	–	0.75	–	–	(0.75)
PFOA	0.40 [0.31; 0.51]	2.13	–	–	0.37; 0.58	–	6.0; 1.0	0.81	0.39; 0.50	–	0.82
PFNA	1.43 [1.35; 1.52]	2.19	–	–	~1	1.34	3.1; 0.88	–	0.61; 3.1; 4.5; 9.9	2.1	2.0
PFDA	1.63 [1.61; 1.66]	2.43; 2.53	–	1.5	~1; 3.67	–	1.7; 0.96	0.83	2.6; 3.2; 3.3; 5.7; 10.9	3.7	2.4
PFUnDA	1.50 [1.47; 1.52]	2.25	–	1.74	4.71	0.41	1.8; 0.93	–	2.4; 2.5; 2.6; 3.4; 4.2	3.1	2.1
PFDoDA	1.48 [1.44; 1.52]	2.68; 3.19	–	1.38	~1	0.94	1.1; 1.3	–	1.4; 1.8; 2.1; 2.1; 2.7	2.4	1.7
PFTrDA	1.20 [1.16; 1.24]	–	–	–	~1; 2.45	0.39	0.66; 0.96	–	0.9; 1.8; 1.9; 2.5; 14.9	–	1.5
PFTeDA	1.57 [1.49; 1.64]	–	–	–	0.43; ~1	–	0.33; 1.2	–	1.4; 1.9; 2.1; 2.8	–	1.2
PFBS	–	–	–	–	–	–	–	1.08	–	–	(1.1)
PFHxS	1.05 [0.76; 1.43]	–	–	–	–	–	4.3; 1.5	–	0.36; 0.76; 1.5; 3.7	–	1.4
PFHpS	3.68 [3.04; 4.47]	–	–	–	–	–	–	–	0.65; 1.20; 8.3	–	2.2
PFOS	1.60 [1.58; 1.63]	3.46; 3.74	1.62	1.3	1.86; 5.88	1.53	2.5; 0.94	0.93	2.4; 2.6; 2.6; 3.1; 4.1	2.9	2.3
PFDS	1.03 [1.00; 1.06]	–	–	–	–	–	–	–	0.73; 2.1; 2.1; 3.0	–	1.6
FBSA	1.35 [1.03; 1.78]	–	–	–	–	–	–	–	–	–	(1.4)
FOSA	4.62 [3.14; 6.78]	–	–	–	0.51	0.64	2.3; 1.2	–	0.56; 0.69; 1.1; 1.3; 5.9	–	1.3
MeFOSAA	–	–	–	–	–	–	0.18	–	0.54; 1.2; 2.3	–	0.72
EtFOSAA	0.46 [0.34; 0.63]	–	–	–	–	–	–	–	0.43; 0.64	–	0.50
PFECHS	1.98 [1.52; 2.57]	–	–	–	–	–	–	–	–	–	(2.0)
6:2 FTSA	–	–	–	–	–	–	–	–	0.14; 0.55	–	0.28
6:2 diPAP	0.09 [0.046; 0.17]	–	–	–	–	–	–	–	–	–	(0.09)

2019).

Several PFAS qualified both as very bioaccumulative (BAF >5000) and biomagnifying (TMF >1), including long-chain (C10–C13) PFCAs, PFOS, PFDS, and FOSA. Newly monitored PFAS such as FBSA and PFECHS were biomagnified but moderately bioaccumulative (mean BAFs of ~600 and 1400 L/kg, respectively), while PFOA and EtFOSAA were biodiluted (TMFs <0.5). Other factors not investigated here could explain the PFAS variations in this food web, as discussed below. Although the observations on trophic magnification were generally unaffected when considering PFAS data normalized to total proteins, interspecific PFAS variations could be tested against more specific macromolecules, including serum albumin, liver fatty acid binding proteins, and phospholipids (Babut et al., 2020; De Silva et al., 2021). Sources of intraspecific PFAS variations in fish (e.g., morphometrics and allometry) would also require a much larger *n* per species than investigated here. Future studies could also investigate the accumulation patterns of PFAS at different life stages of invertebrates (e.g., larval, molting, adult), with the aim to calibrate toxicokinetic models (Bertin et al., 2014).

Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be available on the Canada Open Data portal

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.119739.

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