

# Perfluorinated and Polyfluorinated Compounds in Lake Food Webs from the Canadian High Arctic

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## S Supporting Information

**ABSTRACT:** Per- and polyfluorinated alkyl substances (PFASs) enter Arctic lakes through long-range atmospheric transport and local contamination, but their behavior in aquatic food webs at high latitudes is poorly understood. This study compared the concentrations of perfluorocarboxylates, perfluorosulfonates, and fluorotelomer sulfonates (FTS) in biotic and abiotic samples from six high Arctic lakes near Resolute Bay, Nunavut, Canada. Two of these lakes are known to be locally contaminated by a small airport and Arctic char (*Salvelinus alpinus*) from these lakes had over 100 times higher total [PFAS] when compared to fish from neighboring lakes. Perfluorononanoate (PFOA) and perfluorooctanesulfonate (PFOS) dominated in char, benthic chironomids (their main prey), and sediments, while pelagic zooplankton and water were dominated by lower chain acids and perfluorodecanesulfonate (PFDS). This study also provides the first measures of perfluoroethylcyclohexanesulfonate (PFECHS) and FTS compounds in water, sediment, juvenile char, and benthic invertebrates from lakes in the high Arctic. Negative relationships between [PFAS] and  $\delta^{15}\text{N}$  values (indicative of trophic position) within these food webs indicated no biomagnification. Overall, these results suggest that habitat use and local sources of contamination, but not trophic level, are important determinants of [PFAS] in biota from freshwater food webs in the Canadian Arctic.



## 1. INTRODUCTION

Per- and polyfluorinated alkyl substances (PFASs<sup>5</sup>) are entirely anthropogenic compounds, originally created for industrial purposes in the 1950s, and are widely used in textile, upholstery, nonstick product manufacturing, aqueous film forming foams (AFFF), and hydraulic fluids.<sup>49</sup> As a group, PFASs are defined by fluorocarbon chains (4–18 carbons) and are highly persistent once released into the environment.<sup>5,28,49</sup> These chemicals can be further classified based on compound structure and functional groups, and include perfluorosulfonates (PFSAs), perfluorocarboxylates (PFCAs), and fluorotelomer sulfonates (FTSs). Several PFSAs, such as perfluorooctanesulfonate (PFOS), and PFCAs, such as perfluorooctanoate (PFOA), have been detected in various biota and human blood samples from around the world, including the high Arctic.<sup>6,19</sup> Detectable levels of PFASs have been reported in Arctic char (*Salvelinus alpinus*), one of the only circumpolar freshwater fish, from the Central and Eastern Canadian Arctic<sup>14,44</sup> and the Faroe Islands<sup>23</sup> and in the recent assessment of persistent organic pollutants in the Canadian Arctic.<sup>33,36</sup>

PFASs enter Arctic systems directly through runoff from local sources (e.g., airports<sup>37,42</sup>) or indirectly through long-range oceanographic or atmospheric transport.<sup>2,3</sup> Perfluoro-

ethylcyclohexanesulfonate (PFECHS<sup>21</sup>), a PFAS recently recognized as potentially bioaccumulative, is used in aircraft fluid for antierosion purposes and has recently been found in lake trout (*Salvelinus namaycush*) from the Great Lakes,<sup>8</sup> various aquatic biota downstream of an Ontario airport,<sup>9</sup> and northern pike (*Esox lucius*) from the St. Lawrence River.<sup>20</sup>

Although many PFASs are being phased out of use in North America, there is concern about the continued approval for their use by other governing bodies<sup>34</sup> and the existing stock of highly stable PFASs in the environment, as these chemicals are not likely to fully break down.<sup>28</sup> Further, the use of fluorotelomer substances is increasing; FTS are not as environmentally stable as the PFSAs they are replacing in industry, but they can degrade to the persistent PFCAs, rendering them of environmental concern.<sup>28</sup>

To date, only two studies have looked at PFAS bioaccumulation in Arctic char.<sup>14,44</sup> Both concluded that PFAS concentrations in char are highly variable between

Received: October 4, 2014

Revised: December 31, 2014

Accepted: January 20, 2015

Published: January 20, 2015

lakes and found no evidence of biomagnification; for example, Gantner et al.<sup>14</sup> report total PFAS concentrations in char ranging from 28 to 64 pg/g (wet wt.) between two lakes in the eastern high Arctic and no relationship between PFAS concentration in char and  $\delta^{15}\text{N}$  values (representative of trophic level). Studies on PFASs in the Arctic have focused mainly on the marine environment and, as such, less is known about the concentrations in various freshwater biota, especially lower-trophic-level invertebrates.<sup>6,36</sup> High Arctic lakes have highly simplistic food webs; Arctic char, the only fish species in these lakes, are the top predator and preferentially feed on benthic chironomids (Order Diptera) rather than pelagic copepods (i.e., zooplankton), the two dominant invertebrates groups.<sup>7,13,27</sup> Previous studies have used stable isotope analysis (SIA) to characterize food webs; nitrogen isotopes ( $\delta^{15}\text{N}$ ) are indicative of an animal's trophic position, while carbon isotope values provide a measure of littoral versus pelagic feeding in lakes.<sup>38</sup>

To better understand the fate and accumulation of PFASs in aquatic food webs in the Canadian Arctic, this study used SIA to characterize food webs; PFAS concentrations were compared between the char, invertebrates, water, and sediments of six lakes and biomagnification was assessed in each food web. Two of the systems, Meretta and Resolute Lakes, are downstream of the local airport (see Supporting Information (SI) Figure SI-1) and were likely affected by PFAS inputs when wastewater from the airport and military base was discharged with little treatment into the Meretta catchment from 1949 to 1998.<sup>10,41,42</sup> The lakes around Resolute Bay therefore offered a unique opportunity to compare locally contaminated systems with those contaminated solely via atmospheric deposition within the same geographic area. This study also compared PFAS compound profiles between biotic groups to better understand how energy sources can affect PFAS accumulation in organisms and help explain the variability in biotic PFAS concentrations previously reported among high Arctic lakes.

## 2. MATERIALS AND METHODS

**2.1. Study Site and Sample Collection.** To assess the PFAS concentrations ([PFAS]), we sampled water, sediments, and biota from six lakes (Meretta, Resolute, Char, Small, North, and 9 Mile) located on Cornwallis Island (75°08'N 95°00'W; see SI Figure SI-1) and near the Inuit community of Resolute Bay in northern Nunavut, Canada. This community has a local airport, a known point source of PFAS contamination. Runoff from this airport flows into Meretta Lake and then Resolute Lake, located approximately 0.5 km downstream. A summary of the mean water chemistry parameters and physical features of these lakes can be found in the SI (Table SI-1) and in Lescord et al.<sup>27</sup>

Six lakes were sampled weekly from July to August in 2010 and 2011. Briefly, adult and juvenile char, chironomids, and zooplankton were collected between 1 and 5 times on each lake in both years using clean techniques similar to Gantner et al.<sup>13</sup> and Veillette et al.<sup>44</sup> Water samples (1 L) were collected weekly in 2010 and biweekly in 2011 using a Niskin water sampler from the surface (~2 m below ice cover) and approximate deep points of each lake.<sup>13</sup> Surface sediments (~0.5 cm) were also collected ( $n = 1/\text{year}$ ) from the deep point or littoral zones of each lake using a gravity corer. See the SI and Lescord et al.<sup>27</sup> for further details on field collection methods.

**2.2. Laboratory Analysis.** **2.2.1. Stable Isotope Analysis.** Dorsal muscle or whole-body homogenates of individual fish,

pooled whole-body invertebrates, sediments, and periphyton were freeze-dried, ground, and processed for stable isotope analyses as per Lescord et al.<sup>27</sup> Briefly, samples were analyzed using an Elemental Analyzer interfaced with a Finnigan Delta Plus Mass Spectrometer at the University of New Brunswick; values were calculated as a ratio to a known standard.<sup>38</sup> Duplicate samples ( $n = 11$ ) were <1–15% different from one another and certified reference materials ( $n = 162$ , 11 CRMs) were between 98–105% of expected values.

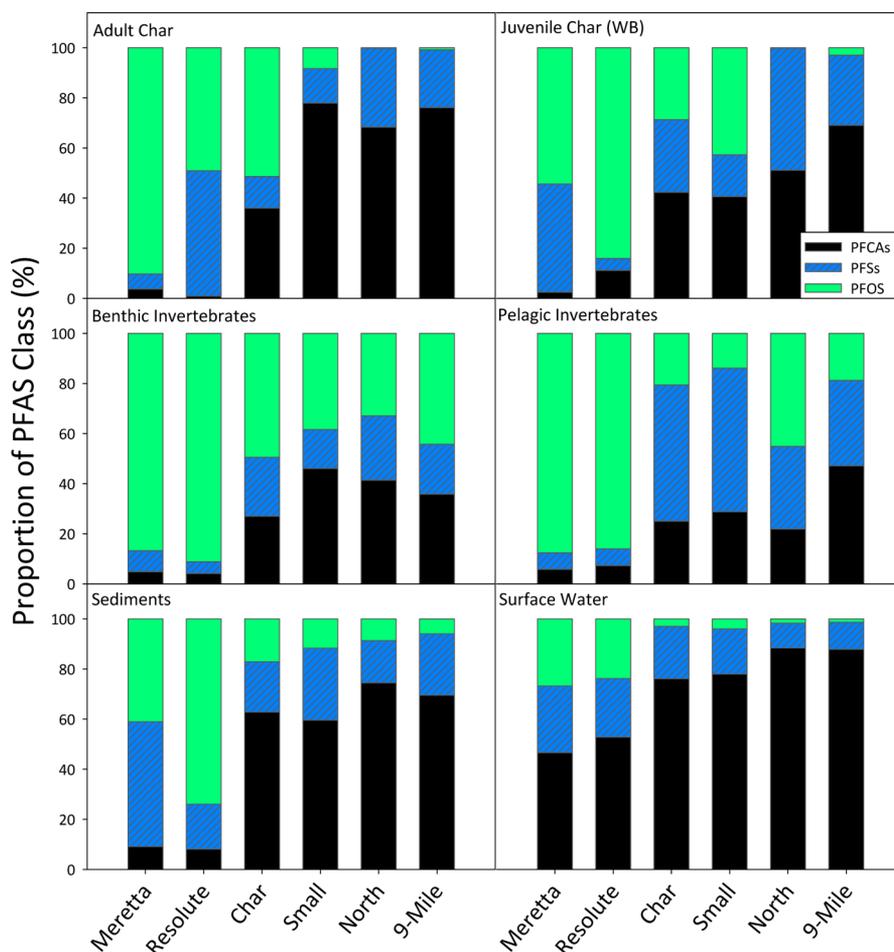
**2.2.2. PFAS Analysis.** Prior to PFAS extraction, all samples, blanks, and reference materials were spiked with a mix of isotopically labeled ( $^{13}\text{C}$  and  $^{18}\text{O}$ ) internal standards (IS; Wellington Laboratories 2009; see SI Table SI-2), which were used to quantify PFAS concentrations (see below). After every 10 samples, a native-spiked replicate (SR) and a method blank were extracted; the mean recovery of spiked samples was  $90 \pm 12\%$  ( $n = 33$ ) across compounds (see SI Table SI-4 for compound specific recoveries). Interlab certified reference materials (NIST 1947 Lake Superior Fish Tissue,<sup>39</sup>) were also run with biotic samples; percent recoveries from expected values averaged  $87 \pm 8\%$  ( $n = 18$ ; see SI Table SI-4). Sample concentrations were corrected for recovery and matrix effects through quantification using relative response calibration curves via the use of isotopically labeled standards. Procedural blanks were run approximately every 10 samples; the mean method blank concentrations across compounds were 0.02 ng/g, 0.07 ng/g and 0.004 ng/L in fish ( $n = 12$ ), invertebrates ( $n = 13$ ), and water ( $n = 4-5$ ), respectively. All samples were blank corrected using mean concentrations of each compound (see SI Table SI-6 and SI-7 for individual compound data).

**PFAS Extractions.** Pooled chironomids ( $n = 45$ ) and zooplankton ( $n = 46$ ), individual juvenile fish ( $n = 76$ ; 30 muscle, 46 whole-body homogenates), and muscle of adult char ( $n = 120$  muscle) were processed using an acetonitrile extraction and Supelco graphite carbon solid phase extraction (SPE) column clean up, as per De Silva et al.<sup>3</sup> and Reiner et al.<sup>39</sup> Extractions were performed on 0.25–0.30 g ( $\pm 0.001$  g, wet wt.) subsamples of char muscle and juvenile whole-body homogenates and 0.10–0.20 g ( $\pm 0.001$  g, wet wt.) of pooled invertebrate whole-body samples. Water samples ( $n = 30$ ) were extracted using Oasis WAX SPE columns as per Taniyasu et al.<sup>43</sup> Sediments ( $n = 23$ ) were extracted using a base digestion, liquid extraction and WAX cleanup as per Yeung et al.<sup>48</sup> Approximately 500 mL of water and 0.250–0.500 g of dry sediments were analyzed.

**PFAS Analysis.** For compound detection, 30  $\mu\text{L}$  of extract from each biotic sample was injected into an Agilent 1100© series HPLC paired with an AB SCIEX 4000 Q-Trap tandem mass spectrometer (MS/MS) operated in negative electrospray ionization multiple reaction monitoring (MRM).<sup>18</sup> In addition, 20  $\mu\text{L}$  injections of water, sediments, and some biotic samples were run on a Waters Acquity liquid chromatograph (LC).

**Data Integration and Handling.** All compound detection and integration was done using Analyst© 1.5.1. Samples and IS were compared using 6–14 point curve, with concentrations ranging from 0.42 pg/mL to 6.3 ng/mL across compounds. The mean accuracy of detected concentrations of each curve was between 87 and 137% and  $R^2$  was generally >0.99 (and never <0.96).

The method detection limits (MDLs) of each compound were determined as 3 times the standard deviation of the method blanks.<sup>8,18</sup> MDLs were calculated for fish, invertebrates, and water, and sediments separately, averaging 0.12 ng/g, 0.53



**Figure 1.** Mean proportions of the three PFAS classes measured in each biotic group and within the six lakes. Proportions were calculated as a percent of total sum of PFASs within a sample. Note: PFS = all PFSAs except PFOS.

ng/g, 0.016 ng/L, and 0.044 ng/g, respectively, across all compounds (see SI Tables SI-6 and SI-7). For statistical purposes, means were only calculated when more than 50% of samples (within a lake and by sample type) were above their respective MDL. When blank-correcting data resulted in numbers  $\leq 0$ , values were replaced with a random number less than half the instrument detection limits (IDLs). IDLs, defined as 3 times the signal-to-noise (S:N) ratio of the lowest standard of each curve, averaged 0.93 ng/L in sediments/water and 2.1 pg/g in biota across all compounds. IDLs for individual compounds can be found in SI Table SI-8. Any nondetectable blank sample was also replaced with a random number lower than half of the IDL of a corresponding compound before mean concentrations or MDLs were calculated.

**2.3. Statistical Analysis.** All statistical analyses were performed using SPSS 17.0 and Sigma Plot 11.0 and alpha ( $\alpha$ ) was set at 0.05 for all tests. All biotic concentrations are presented on a wet weight basis; due to high variability in percent moisture data, sediment PFAS data are presented as dry weight concentrations. Within a lake, samples were combined across years because no significant differences were seen between 2010 and 2011 for char, pooled benthic invertebrates, or pooled pelagic invertebrate samples in total PFCAs ( $p = 0.337$ ,  $0.337$ , and  $0.150$ , respectively) or total PFSAs ( $p = 0.748$ ,  $0.337$ , and  $0.715$ , respectively; Kruskal–Wallis H-Test).

Mean  $\sum$ PFAS and standard deviations ( $\pm$ SD) were then calculated within each lake for biotic and abiotic groups. Total

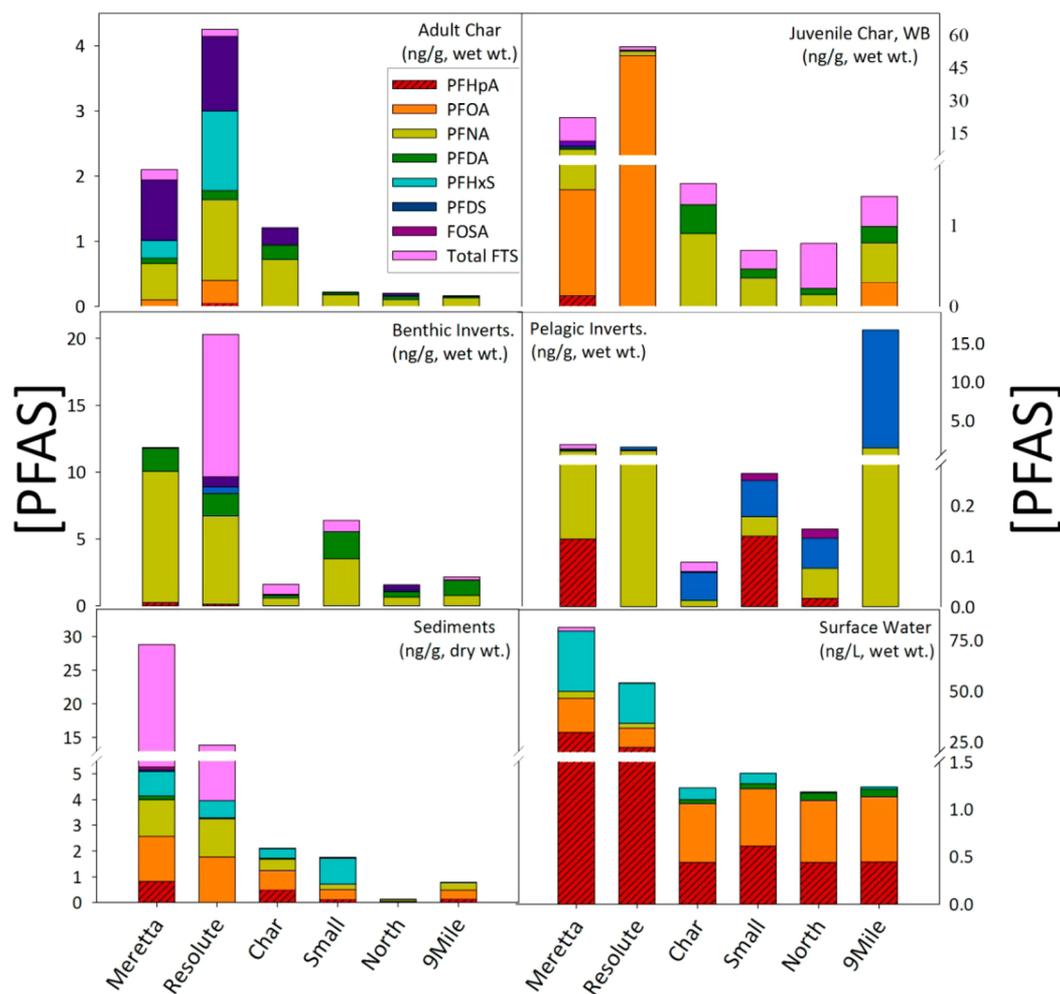
PFCA ( $\sum$ PFCA) calculations included nine compounds (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTTrA, and PFTA); total polyfluorinated sulfonate compounds ( $\sum$ PFS) calculations included 9 PFSA compounds (PFBS, PFHxS, PFHpS, PFDS, FOSA, PFECHS, 4:2 FTS 6:2 FTS, and 8:2 FTS; see SI for full names and other compound information). Because of its relatively high concentrations (especially in locally contaminated lakes), PFOS was kept separate from  $\sum$ PFCA and  $\sum$ PFS for all statistical analyses. All 19 analytes were included in total PFAS ( $\sum$ PFAS) calculations. It should be noted that, although whole body analysis was not possible for adult char, some juvenile char ( $n = 5$ – $14$  across lakes) were analyzed as whole body homogenates. These samples were statistically analyzed separately from muscle samples taken from other juvenile fish ( $n = 0$ – $9$  across lakes).

$\sum$ PFCA,  $\sum$ PFS, and PFOS concentrations were compared between the six lakes within each of the 4 biotic groups (adult and juvenile char, benthic and pelagic invertebrates) and two abiotic groups (water and sediments) using Kruskal–Wallis H-tests (Mann–Whitney-U tests used for post hoc analysis). Additionally, the proportion of each PFAS class ( $\sum$ PFCA,  $\sum$ PFS, and PFOS) was calculated as a percent of the total  $\sum$ PFAS (e.g.,  $(\sum \text{PFAS}_n / \sum \text{PFAS}) \times 100$ ). To better understand PFAS bioaccumulation across these aquatic food webs, linear regressions were run between log-transformed [ $\sum$ PFAS] and  $\delta^{15}\text{N}$  values for all char and chironomids. Isotope modeling reported by Lescord et al.<sup>27</sup> showed that char used in this study

Table 1. Various PFAS Concentrations within Biotic Groups<sup>a,b</sup>

sample type	lake (n)	∑PFAS	∑PFCA	∑PFS	PFOS	PFNA	PFUnA	PFECFS	6:2 FTS	
Benthic invertebrates	Meretta (8)	330 ± 297	15 ± 11	27 ± 22	287 ± 273	9.8 ± 7.5	0.70 ± 0.68	0.32 ± 0.73	ND	
	Resolute (10)	466 ± 558	11 ± 10	9.9 ± 9.5	445 ± 545	6.6 ± 6.1	0.94 ± 0.98	0.29 ± 0.50	ND	
	Char (6)	17 ± 18	1.8 ± 1.5	1.3 ± 1.0	14 ± 19	0.6 ± 0.70	0.21 ± 0.25	ND	ND	
	Small (4)	18 ± 15	9.6 ± 7.1	3.5 ± 3.3	5.3 ± 5.5	3.5 ± 2.6	2.42 ± 2.25	ND	0.43 ± 0.74	
	North (10)	12 ± 16	2.4 ± 1.7	2.4 ± 3.0	7.3 ± 15	0.63 ± 0.66	0.41 ± 0.41	ND	ND	
	9 Mile (6)	19 ± 24	5.6 ± 9.5	1.4 ± 0.9	11 ± 23	0.78 ± 1.4	2.27 ± 4.86	ND	ND	
	Pelagic invertebrates	Meretta (13)	55 ± 44	2.7 ± 2.6	3.5 ± 3.4	49 ± 40	0.88 ± 0.86	0.76 ± 1.89	ND	ND
		Resolute (9)	65 ± 72	2.6 ± 2.6	1.8 ± 1.3	60 ± 68	1.0 ± 1.2	ND	ND	ND
		Char (6)	1.4 ± 1.1	0.35 ± 0.30	0.88 ± 0.94	0.12 ± 0.14	0.01 ± 0.01	ND	ND	ND
		Small (7)	208 ± 547	0.7 ± 1.1	207 ± 546	0.22 ± 0.22	0.04 ± 0.02	ND	ND	ND
North (5)		2.4 ± 1.9	0.42 ± 0.28	0.90 ± 1.0	1.1 ± 0.7	0.06 ± 0.05	ND	ND	ND	
9 Mile (7)		34 ± 83	11 ± 23	21.4 ± 55.5	2.0 ± 4.6	1.4 ± 3.7	ND	ND	ND	
Juvenile char (whole body)		Meretta (5)	127 ± 108	8.8 ± 5.3	7.4 ± 7.7	181 ± 50	6.2 ± 4.8	0.32 ± 0.28	ND	0.97 ± 1.5
		Resolute (9)	280 ± 499	53 ± 157	3.0 ± 4.1	224 ± 491	2.0 ± 4.4	ND	ND	ND
		Char (5)	5.5 ± 4.9	2.7 ± 3.1	1.4 ± 1.1	1.5 ± 1.6	0.90 ± 0.91	0.30 ± 0.29	0.80 ± 0.86	ND
		Small (7)	1.7 ± 0.6	0.67 ± 0.28	0.26 ± 0.06	0.8 ± 0.5	0.35 ± 0.11	0.11 ± 0.04	ND	ND
	North (8)	1.1 ± 0.6	0.48 ± 0.20	0.65 ± 0.57	0.001 ± 0.001	0.14 ± 0.08	0.09 ± 0.04	ND	ND	
	9 Mile (14)	2.8 ± 4.9	1.7 ± 2.5	0.65 ± 0.86	0.4 ± 1.6	0.48 ± 0.36	0.24 ± 0.24	ND	ND	
	Juvenile char (muscle)	Meretta (5)	84 ± 23	4.4 ± 3.9	2.6 ± 1.1	77 ± 21	2.9 ± 2.3	0.50 ± 0.56	ND	ND
		Resolute (4)	29 ± 29	1.0 ± 1.1	0.4 ± 0.2	27 ± 22	0.81 ± 0.94	ND	ND	ND
		Char (9)	2.5 ± 2.5	0.54 ± 0.37	1.5 ± 2.8	0.54 ± 0.47	0.21 ± 0.16	0.08 ± 0.05	ND	ND
		Small (9)	1.0 ± 1.0	0.37 ± 0.32	0.60 ± 0.76	0.06 ± 0.04	0.18 ± 0.11	0.06 ± 0.04	ND	ND
North (5)		10 ± 19	0.40 ± 0.24	9.6 ± 18	<0.001 ± <0.001	0.17 ± 0.11	0.07 ± 0.04	1.55 ± 2.68	ND	
9 Mile (0)		NA	NA	NA	NA	NA	NA	NA	NA	
Adult char (muscle)		Meretta (21)	27 ± 6.8	1.1 ± 1.2	1.5 ± 0.4	24 ± 6.0	0.56 ± 0.24	ND	0.01 ± 0.01	ND
		Resolute (18)	122 ± 65	1.9 ± 1.6	3.0 ± 1.8	117 ± 64	1.3 ± 1.4	0.07 ± 0.06	ND	ND
		Char (13)	3.7 ± 2.4	1.3 ± 0.8	0.40 ± 0.25	2.0 ± 1.5	0.72 ± 0.38	0.14 ± 0.11	ND	ND
		Small (20)	0.36 ± 0.15	0.27 ± 0.11	0.05 ± 0.06	0.03 ± 0.04	0.17 ± 0.09	ND	ND	ND
	North (25)	0.32 ± 0.12	0.27 ± 0.12	0.09 ± 0.05	<0.001 ± 0.001	0.11 ± 0.06	0.04 ± 0.03	ND	ND	
	9 Mile (23)	0.28 ± 0.09	0.22 ± 0.09	0.07 ± 0.06	0.002 ± 0.009	0.13 ± 0.06	ND	ND	ND	

<sup>a</sup>All measures are in ng/g (wet wt.); ND = no detectable; NA = not applicable (not data available). <sup>b</sup>Total PFAS concentrations include all 19 compounds analyzed. Total PFCA calculations included PFHx<sub>4</sub>, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, and PFTA. Total PFSs calculations included PFBS, PFHxS, PFHpS, PFDS, PFECFS, FOSA 4:2 FTS, 6:2 FTS, and 8:2 FTS. PFOS concentrations are presented separately.



**Figure 2.** Partial compound profiles detected in different biotic and abiotic compartment of each lake. Data are presented as ng/g wet wt. concentrations for sample types except water (ng/L) and sediments (ng/g, dry wt.). Note: WB = whole body homogenates; Inverts. = Invertebrates. Note the differences in scale between sample types.

fed mainly on benthic invertebrates, and therefore only adult char, juvenile char (whole body and muscle samples) and benthic invertebrates were included in these regressions.<sup>4,32</sup>

### 3. RESULTS AND DISCUSSION

**3.1. PFAS Concentrations in Surface Water and Sediments.** Total mean PFAS concentrations ( $[\sum\text{PFAS}]$ ) in water varied greatly between locally contaminated and atmospherically supplied lakes, ranging from  $153 \pm 14$  ng/L in Meretta Lake to  $1.9 \pm 0.42$  ng/L in 9 Mile Lake (see SI Table SI-9).  $[\sum\text{PFAS}]$  in surface waters from atmospherically supplied lakes (ranging from  $2.4 \pm 0.40$  to  $1.9 \pm 0.43$  ng/L in Small and 9 Mile Lakes, respectively; see SI Table SI-9) were comparable to those reported in previous studies from the Canadian high Arctic (e.g.,  $0.027$ – $0.754$  ng/L).<sup>44</sup> In contrast, [PFOS] in Meretta ( $41 \pm 9.3$  ng/L) and Resolute ( $26 \pm 5.2$  ng/L; see SI Table SI-9) Lakes were higher than those reported in Lake Ontario ( $5.51 \pm 0.89$  ng/L).<sup>8</sup> Results suggest that [PFOS] in water were strongly influenced by the point source contamination by the local airport; in Meretta Lake, the system closest to the airport, PFOS ( $41 \pm 9.3$  ng/L) was 27% of total PFAS concentrations in water (see Figure 1). Further from the source, PFOS became less dominant, constituting <1% in North and 9 Mile Lakes, the lakes furthest from the airport.

These results are in agreement with de Solla et al.<sup>9</sup> who report 19 times higher PFOS concentrations in water downstream of the Hamilton (Ontario) airport (130 ng/L) when compared to reference sites.

Concentrations of PFECHS in water from Meretta Lake ( $4.3 \pm 1.4$  ng/L; data not shown) were also comparable to those recently reported in the Great Lakes ( $0.16$ – $5.6$  ng/L).<sup>8</sup> PFECHS is used as an abrasion inhibitor for hydraulic fuels in aircrafts, and it is likely that use or emissions at the airport has increased nearby aquatic concentrations.<sup>9</sup> This association is further supported by [PFECHS] being detectable in Meretta and Resolute Lake sediments ( $0.07$  and  $0.01$  ng/g, respectively; data not shown), but nondetectable (i.e., < 50% of samples above the MDL) in sediments from the remote lakes.

Water samples from all lakes were dominated by lower-chain PFCAs (e.g., [PFHxA] ranged from  $30 \pm 4.7$  to  $0.43 \pm 0.09$  ng/L in Meretta and 9 Mile Lakes, respectively) and PFASs (e.g., [PFBS] ranged from  $4.9 \pm 1.0$  to  $0.07 \pm 0.01$  ng/L in Meretta and 9 Mile Lakes, respectively; data not shown). Several studies have shown that more hydrophobic longer-chain PFASs (>7 carbons) have strong sorption to sediments and can displace shorter chain compounds to the surrounding water.<sup>15,45</sup> It is therefore not surprising that longer-chain PFASs were also more dominant and at higher concentrations in sediments when compared to water from the same contami-

nated lakes; 8:2 FTS, for example, was detectable in most lake sediments (ranging from 13 ng/g in Meretta Lake to 0.002 ng/g in North Lake), but it was only detectable in water samples from Meretta ( $0.20 \pm 0.26$  ng/L) and Resolute ( $0.01 \pm 0.01$  ng/L) Lakes (see SI Table SI-10). Furthermore, the dealkylation of 6:2 FTS, another FTS detected in Meretta Lake water, and degradation of longer chain PFASs yield higher concentrations of lower chain acids in water.<sup>43,47</sup> It is also possible that short chain PFCAs (e.g., perfluorobutanoic acid, PFBA<sup>15</sup>), which were not measured herein and are more water-soluble (and therefore less likely to sorb to sediment or partition to biota), are dominating in these remote lakes.<sup>43</sup> However, Meretta and Resolute Lake water was also dominated by FTS compounds (e.g.,  $1.4 \pm 1.7$  and  $0.20 \pm 0.21$  ng/L of 6:2 FTS) and PFECHS ( $0.18 \pm 0.12$  and  $0.05 \pm 0.07$  ng/L; see Table 1); compounds that were nondetectable in lake water from the remote lakes. Furthermore, PFBS and PFHxS were between 40 to >1000 times higher in Meretta and Resolute Lake water samples when compared to atmospherically supplied lakes. These differences in compound detection further indicate an alteration of PFAS contamination related to the local airport in these remote lakes.

Similar to water,  $[\sum\text{PFAS}]$  were highest in sediments from Meretta ( $57 \pm 10$  ng/g, dry wt.) and Resolute ( $64 \pm 6.6$  ng/g, dry wt.; SI Table SI-9) Lakes when compared to the four remote lakes (range from  $2.7 \pm 0.18$  to  $0.19 \pm 0.03$  ng/g, dry wt.). The highest concentrations detected in sediment samples were PFOS, FTSS, PFOA, and PFNA (see Figure 2). The four atmospherically supplied lakes were dominated by PFCAs, which contributed ~67% of all PFASs detected in sediments (see Figure 1). Conversely, Meretta and Resolute sediments were dominated by PFS (~34%) and PFOS (~57%), while PFCAs were less abundant (~9%; see Figure 1). PFOS concentrations were highest in Resolute Lake sediments ( $49 \pm 29$  ng/g), and were 100+ times higher than those of the remote lakes (e.g., Char Lake  $0.44 \pm 0.08$  ng/g, dry wt.; see SI Table SI-9). In fact, [PFOS] in Resolute and Meretta ( $28 \pm 43$  ng/g dry wt.) sediments were higher than historically contaminated river sediments downstream of the Toronto, Ontario airport ( $13$  ng/g, dry wt.).<sup>3</sup>

**3.2. PFAS Concentrations in Invertebrates.** Within each lake, benthic invertebrates had the highest  $[\sum\text{PFAS}]$  of any taxa, ranging from  $466 \pm 558$  ng/g in Resolute Lake to  $12 \pm 16$  ng/g in Char Lake, and were significantly different between lakes ( $p = 0.007$  for  $\sum\text{PFCAs}$ ,  $<0.001$  for  $\sum\text{PFSs}$ , and  $0.036$  for PFOS; Kruskal–Wallis, see SI Table SI-12 for post hoc testing). Martin et al.<sup>32</sup> also found the highest [PFASs] in the benthic macroinvertebrates (*Diporeia*) within the food web of Lake Ontario. Similar to sediments, PFOS predominated in benthic invertebrates across lakes (ranging from  $445 \pm 546$  ng/g in Resolute Lake to  $5.3 \pm 5.5$  ng/g in Small Lake), especially in Meretta and Resolute Lakes where PFOS was 87 and 91% of invertebrate PFAS burdens, respectively (see Figure 1). In fact, [PFOS] in both benthic and pelagic invertebrates from Meretta and Resolute were only two to three times lower than those measured in Lake Ontario invertebrates.<sup>32</sup> However, despite relatively high [PFASs] in these chironomids, [PFOS] in water (max =  $41 \pm 9.3$  ng/L, Meretta Lake) were far below a median lethal concentration (LC50; 4520 ng/L) for *Chironomus tentans*.<sup>29</sup>

Other PFASs detected in benthic invertebrates included longer-chain PFCAs such as PFNA (means ranging from 9.8–0.59 ng/g), PFDA (2.0–0.04 ng/g; see Figure 2), and PFUnA

(2.3–0.70 ng/g; see Table 1). 8:2 FTS was also detected in benthic invertebrates from most lakes ( $11 \pm 7.9$  to  $0.22 \pm 0.19$  ng/g in Resolute and North Lakes, respectively; see SI Table SI-10), except Meretta Lake; a surprising result given its proximity to the airport. Notable concentrations of the novel compound PFECHS were detected in benthic invertebrates from Meretta ( $0.32 \pm 0.73$  ng/g) and Resolute ( $0.29 \pm 0.50$  ng/g; see Table 1) Lakes, again supporting the link between a local source and increased [PFECHS] in downstream water and biota.<sup>9</sup> To the best of our knowledge, this is the first study to detect PFECHS and FTS compounds in Arctic biota and, given the increased production of FTS compounds, high variability in samples, and improving analytical capabilities, more studies are needed to assess PFAS burdens in these invertebrates across a broader range of Arctic sites.<sup>47</sup>

Despite more variable [PFAS], zooplankton had 3–7 times lower  $[\sum\text{PFAS}]$  within lakes when compared to benthic invertebrates. Zooplankton concentrations of  $\sum\text{PFCAs}$  and PFOS were significantly different between lakes ( $p = 0.005$  and  $<0.001$ ; Kruskal–Wallis), while  $[\sum\text{PFS}]$  were not different ( $p = 0.106$ ). Total PFASs were highest in Small Lake ( $208 \pm 547$  ng/g), largely due to 1 high FTS measure (6:2 FTS;  $1436$  ng/g); if removed, Small Lake ( $n = 7$ ) has a  $[\sum\text{PFAS}]$  of  $2.5 \pm 4.2$  ng/g, the second highest after Meretta Lake zooplankton ( $65 \pm 72$  ng/g; see Table 1). Char Lake zooplankton had the lowest  $[\sum\text{PFAS}]$  of  $1.4 \pm 1.1$  ng/g; see Table 1, a value comparable to zooplankton caught on Ellesmere Island ( $0.955$  ng/g).<sup>44</sup> 9 Mile Lake zooplankton ( $[\sum\text{PFAS}] = 34 \pm 83$ ) had higher [PFDS] ( $15 \pm 40$  ng/g) and [PFNA] ( $1.4 \pm 3.7$  ng/g; see Figure 2). Mean PFOS concentrations in zooplankton were also highest in Meretta and Resolute Lakes, and ranged from  $60 \pm 68$  ng/g in Resolute Lake to  $0.12 \pm 0.14$  ng/g in Char Lake. These values are 10+ times lower than those measured in zooplankton downstream of the Hamilton, ON airport ( $581$  ng/g).<sup>9</sup> Furthermore, [PFOS] in water (max =  $41 \pm 9.3$  ng/L in Meretta Lake) were far below the LC50 concentration ( $17.95$  mg/L) for crustaceans.<sup>22</sup>

Other than PFOS, pelagic invertebrates were dominated by PFDS ( $15$ – $0.06$  ng/g) and lower chain PFCAs such as PFHxA ( $1.5$ – $0.057$  ng/g), PFHpA ( $0.13$ – $0.02$  ng/g), and PFNA ( $1.4$ – $0.01$  ng/g; see Table 1, SI SI-10, and Figure 2). This is in disagreement with Veillette et al.<sup>44</sup> who report PFNA and PFUnA as the only detectable compounds in high Arctic zooplankton from lakes on Ellesmere Island. However, given that smaller-chain acids were more dominant in Meretta and Resolute water samples and that they are known to flux from sediments to water,<sup>15</sup> it is possible that pelagic invertebrates bioaccumulate more of these lower chain PFCAs from their surroundings. It should be noted that PFDS, one of the highest PFASs detected in zooplankton samples, was not detected in any water samples. PFDS is reported to have been manufactured for use in consumer products such as floor polishes<sup>46</sup> but it may have also been used in PFOS-based AFFF formulations. PFDS has been detected in biota from sites near airports contaminated by AFFFs.<sup>9,25</sup>

**3.3. PFAS Concentrations in Char.** In adult char,  $\sum\text{PFCAs}$ ,  $\sum\text{PFSs}$ , and PFOS were significantly different between all lakes ( $p < 0.001$  for all comparisons; Kruskal–Wallis). Total PFAS concentrations were high in Meretta ( $27 \pm 6.8$  ng/g) and Resolute ( $122 \pm 65$  ng/g; see Table 1) char, far exceeding measures from northern Québec ( $0.028$  and  $0.064$  ng/g).<sup>14</sup> Similar to water and invertebrates, the %PFOS of  $\sum\text{PFASs}$  was particularly different between fish from

contaminated (>90% PFOS) and remote lakes (51% in Char Lake, 8% in Small Lake, and <1% in North and 9 Mile Lake char; see Figure 1), again indicating a strong influence by the local Resolute airport. Char from remote lakes on Cornwallis Island had similar [PFOS] (ranging from  $2.0 \pm 1.5$  ng/g in Char Lake to  $<0.001 \pm 0.001$  ng/g in North Lake; see Table 1) to those measured in fish from high-mountain lakes ( $0.23$  and  $0.41$  ng/g wet wt. respectively)<sup>40</sup> and in char from northern Québec ( $\sim 0.015$  ng/g wet wt.).<sup>14</sup> [PFOS] concentrations in char from Meretta ( $24 \pm 6.0$  ng/g) and Resolute ( $117 \pm 64$  ng/g; see Table 1) Lakes were more similar to those measured in brook trout (*Salvelinus fontinalis*) around Kuujuarapik in Northern Québec ( $39$  ng/g, range  $29$ – $50$  ng/g).<sup>35</sup> However, despite the high [PFOS] in char and water from Meretta and Resolute Lakes, much higher aqueous concentrations ( $>5$  mg/L) did not impact the survival of a small ricefish (*Oryzias latipes*).<sup>22</sup>

In both the locally contaminated and atmospherically supplied lakes from this study, PFOS and PFNA were the dominant PFASs detected in char muscle tissue, with PFNA becoming more dominant further from the airport (see Table 1 and Figure 2). Veillette et al.<sup>44</sup> also report that PFNA, PFDA, and PFUnA were the dominant compounds in the aquatic biota from Lake A, a remote lake on northern Ellesmere Island in the Canadian Arctic. This is in agreement with a review by Butt et al.,<sup>6</sup> who found that PFOS, PFNA, and PFUnA were the highest PFASs reported in various wildlife across the Arctic. Fluorotelomer alcohols (FTOHs) were the most abundant polyfluorinated compounds in the Canadian Arctic atmosphere;<sup>1</sup> FTOHs are well-known atmospheric precursors to PFCAs (including PFNA), potentially explaining why the lakes that are influenced more by atmospheric deposition have increasing proportions of PFCAs in biota (Figure 1).<sup>6,11</sup>

In all lakes except Resolute, juvenile char (muscle) had similar or slightly higher [ $\Sigma$ PFAS] when compared to adult char from the same lake (e.g.,  $84 \pm 23$  vs  $27 \pm 6.8$  ng/g in juvenile and adult char from Meretta Lake; Table 1). Detectable PFAS compounds were similar in juvenile and adult char muscle, with PFNA again being a dominant PFAS detected. However, in addition to PFNA, more PFCAs were detectable (e.g., PFOA, PFTrA) in homogenates of whole body juvenile char when compared to juvenile char muscle samples and, in general, [PFCA] were between 2 and 5 times higher in homogenates within a lake (see Table 1 and SI SI-10). Interestingly, PFECHS was detectable in juvenile char whole body homogenates from Char Lake (mean  $0.80$  ng/g) and muscle from North Lake (mean  $1.6$  ng/g), but not in the contaminated lakes (see Table 1). It is likely that different PFAS compounds are accumulating in different tissues based on their relative hydrophobicity, chain length, and other compound properties.<sup>16,26</sup> Overall, the high variability and low samples sizes analyzed herein warrant further study to understand the differences in PFAS burdens between fish tissue types.

**3.4. PFAS Concentrations through Food Webs.** Significant and negative relationships between  $\Sigma$ PFAS (log-transformed) and  $\delta^{15}\text{N}$  were found in Meretta ( $p < 0.001$ ;  $m = -0.17$ ), Small ( $p < 0.001$ ;  $m = -0.33$ ), and 9 Mile ( $p < 0.001$ ;  $m = -0.26$ ) lakes, implying no biomagnification of PFASs with increasing trophic level of the biota (see SI Figure SI-2 to SI-5). Data from Resolute, Char, and North lakes were more variable and no relationships were found. To the best of our knowledge, only two other studies have examined whether PFASs

biomagnify in Arctic char food webs in the high Arctic: neither Gantner et al.<sup>13</sup> nor Veillette et al.<sup>44</sup> report any PFAS biomagnification. PFOS and other PFASs accumulate more in liver and blood samples and using muscle homogenates may underestimate PFAS biomagnification.<sup>24,26,31</sup> However, it is believed that more water-soluble PFASs (i.e., < 8 carbon chain) can be excreted from a fish's gills, lowering overall PFAS concentrations in tissues,<sup>30</sup> and this may partly explain the lack of PFAS biomagnification within these lakes. This selective excretion may also explain why, despite short chain PFCAs predominating in water, the moderate to longer-chain PFCAs (such as PFNA, PFDA, PFUnA) are more dominant in char. Although not well understood, PFSAs are more likely to biomagnify than PFCAs due to the higher biotic retention of functional groups of PFSAs.<sup>26,28,30</sup> However, when  $\Sigma$ PFS and  $\Sigma$ PFCA were considered separately, all food web relationships were negative (slopes ranging from  $-0.10$  to  $-0.36$  for PFCAs and  $-0.07$  to  $-0.19$  for PFSs; see SI Figures SI-3 and SI-4).

These negative or non-existent relationships are in contrast to past studies that report trophic magnification of several PFOS isomers,<sup>18</sup> PFCAs (C9–12), PFDA, PFUnA, and PFTrA in pelagically dominated food webs in Lake Ontario.<sup>32</sup> However, similar to this study, no biomagnification was observed in benthic-based food webs from the same lake.<sup>32</sup> Many previous PFAS biomagnification studies have focused on longer food chains, with more fish species (e.g., Lake Ontario food webs) as well as birds or marine mammals which lack the gill-excretion pathway and that are more likely to biomagnify different PFASs.<sup>26,31</sup>

In general, sediments are believed to be the major source of PFASs in benthic freshwater food webs.<sup>18,32</sup> In the current study, benthic invertebrates [ $\Sigma$ PFAS] were 10 times higher than pelagic invertebrates from the same lake. Furthermore, while zooplankton had many of the same lower-chain PFASs as water samples within lakes, benthic invertebrates had more similar profiles to the sediments in which they live (e.g., dominated by PFNA and PFDA; see Figure 2).

As with other contaminants, such as mercury<sup>14</sup> or PCBs,<sup>17,35</sup> dietary choice can affect the PFAS concentrations in predatory fish. Unlike many freshwater fish from southern latitudes, landlocked char are known to feed benthically, rather than pelagically; according to stable isotope analysis, benthic invertebrates comprised between 91 and >100% of the chars' diets across lakes.<sup>27</sup> This is evident in the similarities between the PFAS profiles of adult char and benthic chironomids; each group had similar proportions of  $\Sigma$ PFCA,  $\Sigma$ PFS, and PFOS and both were dominated by the PFOS, PFNA, PFDS, and FTS compounds (see Figures 1 and 2). These trends are similar to those reported in Houde et al.,<sup>18</sup> who found that benthically feeding lake trout from Lake Ontario had different PFOS isomer profiles than pelagic zooplankton, a minor component of their diet. Martin et al.<sup>32</sup> also suggest that food source can impact fish PFAS profiles in Lake Ontario, with distinct differences between sculpin (*Cottus cognatus*; benthic feeder), alewife (*Alosa pseudoharengus*; pelagic feeders), and lake trout (both benthic and pelagic feeders).

Higher  $\Sigma$ PFAS concentrations and variations in PFAS compound profiles found in biota from Meretta and Resolute Lakes, which were affected by the local point source of contamination, support the hypothesis that uptake from surrounding water can also impact fish PFAS concentrations and profiles.<sup>12</sup> For example, although FTS compounds were detectable in juvenile char (whole body or muscle) and benthic

invertebrates from most lakes, they were only detectable in adult char from Meretta and Resolute Lakes. This suggests that FTS may be bioaccumulated due to local inputs, but that it may also be cleared from fish gills, similar to shorter chain PFASs.<sup>31</sup>

Overall, [PFAS] and trends detected in this study were similar to previous work; PFNA and PFOS were the dominant PFAS detected in these high Arctic systems and higher [PFAS] in Meretta and Resolute Lakes indicate a strong influence of the local airport. This study also provides the first measures of FTS and PFECHS compounds in the Arctic; FTS were detected mainly in char and benthic invertebrates across lakes, while PFECHS was detected in water and sediments from the locally contaminated lakes. Despite high variability, benthically feeding char had more similar PFAS compound profiles to sediments and chironomids (their main food source) than to zooplankton and water samples. Negative relationships between PFASs and  $\delta^{15}\text{N}$  were found in 3 out of 6 lakes, and suggest no biomagnification of PFASs through these food webs. Overall, these results suggest that a taxon's horizontal but not vertical position in the food web affects its PFAS concentrations in the high Arctic.

## ■ ASSOCIATED CONTENT

### Supporting Information

Further details on field collections, laboratory methods, and data handling are provided in a supplementary file. This file also includes detailed QA/QC data and mean concentrations of individual compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Funding and logistical support for this study was provided by the Natural Sciences and Engineering Research Council of Canada through their Canada Research Chair and Discovery Programs, the Northern Contaminants Program of Aboriginal Affairs and Northern Development, Environment Canada, and the Polar Continental Shelf (PCSP) Program of Natural Resources Canada. We thank the staff of the PCSP Base in Resolute for their assistance. We thank Angella Mercer, Günter Köck, Paul Drevnick, Debbie Iqaluk, and Brandy Iqaluk for assistance with field work and laboratory analyses.

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