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Article

Fluorinated Precursor Compounds in Sediments as a Source of Perfluorinated Alkyl Acids (PFAA) to Biota

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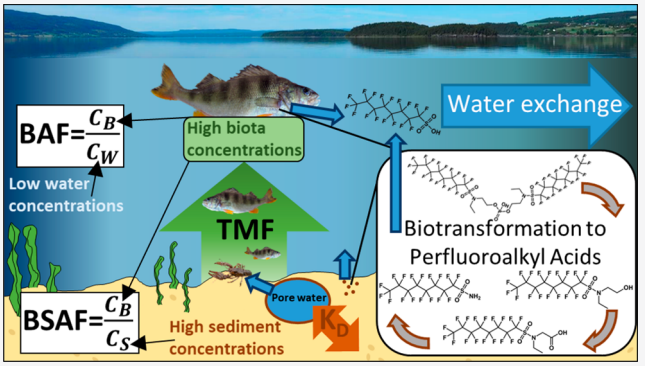
ABSTRACT: The environmental behavior of perfluorinated alkyl acids (PFAA) and their precursors was investigated in lake Tyrifjorden, downstream a factory producing paper products coated with per- and polyfluorinated alkyl substances (PFAS). Low water concentrations (max 0.18 ng L^{-1} linear perfluorooctanesulfonic acid, L-PFOS) compared to biota (mean 149 $\mu g\ kg^{-1}$ L-PFOS in perch livers) resulted in high bioaccumulation factors (L-PFOS $BAF_{Perch\ liver}$: 8.05×10^5−5.14×10^6). Sediment concentrations were high, particularly for the PFOS precursor SAmPAP diester (max 1 872 $\mu g\ kg^{-1}$). Biota-sediment accumulation factors (L-PFOS $BSAF_{Perch\ liver}$: 22−559) were comparable to elsewhere, and concentrations of PFAA precursors and long chained PFAA in biota were positively correlated to the ratio of carbon isotopes ($^{13}C/^{12}C$), indicating positive correlations to dietary intake of benthic organisms. The sum fluorine from targeted analyses accounted for 54% of the extractable organic fluorine in sediment, and 9−108% in biota. This, and high trophic magnification factors (TMF, 3.7−9.3 for L-PFOS), suggests that hydrophobic precursors in sediments undergo transformation and are a main source of PFAA accumulation in top predator fish. Due to the combination of water exchange and dilution, transformation of larger hydrophobic precursors in sediments can be a source to PFAA, some of which are normally associated with uptake from water.



KEYWORDS: *PFAS, PFOS, SAmPAP diester, extractable organic fluorine (EOF), sediment−pore water partitioning coefficients (K_D), trophic magnification, bioaccumulation factors (BAF)*

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) refer to a class of anthropogenic chemicals that have been produced since the late 1940s and used for a variety of industrial processes and consumer products including firefighting foams, in oil production and mining, pesticides, cosmetics, household products, textiles, as well as food contact materials.[1] Due to the potential for adverse health effects,[2,3] sources, transport pathways, and environmental fate of well-known PFAS such as perfluorinated alkyl acids (PFAA) have received increasing attention from the scientific community.[1,4] PFAA are very persistent at environmentally relevant conditions.[5] Highly elevated concentrations have been reported at contaminated source areas including firefighting training facilities.[6−8] Lower, but detectable levels of PFAA have been reported in areas far from point sources,[9−11] and long-range atmospheric transport and subsequent degradation of precursor compounds is suggested to be one important mechanism for their global distribution.[12−14] The partitioning of PFAA and their precursors between air, water, sediment/soil, and biota phases provides information related to the environmental fate of these compounds. Differences in structure, including molecule size and functional hydrophilic group result in differing physiochemical properties among compounds and thus different partitioning between environmental media. In the environment, PFAS exist as anions, zwitterions, cations or neutral compounds.[15] Generally, ions are more hydrophilic compared to neutral compounds of comparable size, and larger PFAS are generally more hydrophobic and have higher affinities for sediments compared to smaller sized homologues.[16−21] However, soil and sediment properties add to the complexity of sorption processes and make it difficult to predict soil/sediment−water partitioning coefficients (K_D). Soils and sediments are comprised of organic and inorganic matter and positive correlations have most often been reported between organic matter and sorption of anionic PFAS.[17,19]

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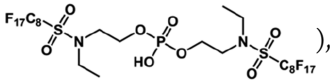
Two groups of PFAA have received the most attention from the scientific community: perfluoroalkyl carboxylic acids (PFCA) and sulfonic acids (PFSA).[22] These PFAA have small pK_a values and are therefore present as anions at environmentally relevant pHs.[22] Long chained PFAA (number of carbon atoms [C] ≥ eight for PFCA, and C ≥ six for PFSA) have higher potentials for bioaccumulation than shorter homologues and have been globally detected in organisms.[23,24] In addition, uptake and metabolization of precursor compounds has been suggested to be a source of PFAA to organisms.[25,26] Historically, large amounts of perfluorooctane sulfonyl fluoride (POSF) has been used as the starting material for the production of the eight-carbon PFSA, perfluorooctanesulfonic acid (PFOS; $F_{17}C_8-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-OH$) and PFOS precursor compounds including *N*-alkyl substituted perfluorooctane sulphonamides with eight perfluorinated C ($F_{17}C_8-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-N(R)-R$, for simplicity termed preFOS throughout this work), and potential parent compounds: mono-, di-, and trisubstituted phosphate esters of *N*-ethyl perfluorooctane sulfonamido ethanol (SAmPAPs).[27−30] PreFOS and SAmPAPs were used in food contact paper and packaging from the 1970s.[28,29] Commercial SAmPAP formulations were dominated by the disubstituted SAmPAP (SAmPAP diester; ), and the presence of this compound has been investigated in a few previous studies.[29,31,32] PreFOS have a sulfonyl group, the same perfluorinated moiety as PFOS, and have the potential to be degraded to PFOS if the amine group is replaced with a hydroxy group. PFOS was reported to have higher trophic magnification factors (TMF) compared to other long chained PFAA in several studies,[33−35] and transformation of the large amount of preFOS[36] to PFOS has been suggested to be the main mechanism behind this.[33] Some preFOS are neutral at environmentally relevant pH, which combined with their larger size, makes them less water-soluble compared to the anionic PFOS,[37,38] and thus more prone to reside in environmental compartments other than water.

The objective of the present work was to investigate the fate and transport of PFAS, including contribution from transformation of precursor compounds, in both the abiotic and biotic environment close to a point source: lake Tyrifjorden (Norway), downstream of a shutdown factory which produced PFAS coated paper products. A combination of targeted chemical analysis of a limited number of compounds and determination of extractable organic fluorine (EOF) was applied to capture more of the vast number of PFAS. Stable nitrogen and carbon isotope ratios (δ^{15}N and δ^{13}C) were used to assess biota trophic levels and carbon sources in order to investigate transfer and transformation of PFAS through the food chain. Based on concentrations in (abiotic and biotic) field samples, sediment−water partitioning coefficients (K_D), bioaccumulation factors (BAF), biota-sediment accumulation factors (BSAF), and trophic magnification factors (TMF) were calculated for PFSA, PFCA, fluorotelomer sulfonic acids (FTS), and preFOS. This study is the first of its kind to report the fate and transport of a PFAS mixture originating from the paper industry, and where this resulted in a difference in environmental behavior to previously reported studies.

MATERIALS AND METHODS

Case Study Site and Sampled Media. Lake Tyrifjorden (60.03° N, 10.17° E) is a large (138 km^2) and deep (max 288 m) freshwater lake in Norway (more details in the Supporting Informstion (SI)). High levels of PFOS were found in perch livers (*Perca fluviatilis*) sampled in the middle of the lake in 2015 (mean 183 μg kg^{-1}, close to area L3 see SI Figure S1).[39] A shutdown factory which produced disposable paper products (bowls, plates, cups, etc.) from 1964 to 2013, was later identified as the major PFAS source.[40,41] In the present study, lake and river water, pore water, sediments, and aquatic organisms with different diets and trophic levels were sampled. Sampling was performed during spring and summer 2018, with additional sampling in summer 2019, from six sampling areas in the lake itself and from one area in the river directly downstream the factory (factory area). Sampling areas in the lake were chosen with an increasing distance from the river mouth, and thus with an expected decreasing impact of contamination from the river. Lake sampling areas were named L1−L6 and are shown in SI Figure S1.

Sampling. Sampling is described in brief below. Detailed descriptions and quality assurance procedures are provided in the SI.

Abiotic Samples. River and lake water were sampled in triplicate from five areas in the lake (L1, L3, L4, L5, and L6) and from the factory area, shown in SI Table S1. Sediments were sampled from 94 locations in the lake, two locations upstream and nine locations in the river downstream of the factory (shown in SI Figure S3). Sediments for pore water analysis were sampled in triplicate from sampling areas L1, L3, L4, L5, L6, and in the river upstream of the river mouth, shown in SI Figure S4. Lake water, sediment, and pore water were sampled in September 2018. One additional water sample and five sediment samples (from the lake and factory area) were taken in June 2019 and analyzed for SAmPAP diester (which was not analyzed in most samples in 2018, see the SI).

Biota. Fish (perch (*Perca fluviatilis*), pike (*Esox lucius*), whitefish (*Coregonus lavaretus*), roach (*Rutilus rutilus*), trout (*Salmo trutta*), bream (*Abramis brama*), arctic char (*Salvelinus alpinus*)) and crayfish (*Astacus astacus*) were collected in 2018 using nets and traps. Sampled biota varied between areas as shown in SI Table S2. In alignment with the abiotic samples, supplementary analyses were carried out in 2019 to investigate levels of SAmPAP diester in biota from the factory area (2 perch), L1 (2 perch, 2 crayfish), and L3 (2 perch, 2 crayfish), see the SI.

Laboratory Methods. Laboratory methods are described briefly below. Quality assurance, method limit of detections (LOD) and limit of quantifications (LOQ), treatment of sediments for pore water analysis, analysis of total organic carbon (TOC), sediment grain size, and analysis of extractable organic fluorine (EOF) are described in the SI.

The ratio between the stable nitrogen ^{15}N and ^{14}N (δ^{15}N), and carbon ^{13}C and ^{12}C (δ^{13}C) isotopes in muscle tissue were determined for the assessment of trophic level and carbon sources. The δ^{15}N of a consumer is enriched relative to its diet, thus the δ^{15}N can be used to estimate the trophic level of an organism. Trophic fractionation of 3.4 ‰ in lake ecosystems has been reported,[42] thus relative trophic levels were calculated by dividing δ^{15}N by 3.4. δ^{13}C has been used to link increased PFOS concentrations to marine mammals feeding on inshore, benthos linked food webs compared to marine mammals

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Table 1. Mean, Median, And Maximum Concentrations ($\mu g\ kg^{-1}$ d.w.) for PFAS Compounds in the Lake (Areas L1, L2, L3, L4, L5, L6; $n = 94$) and River (Factory Area; $n = 9$) Sediments Collected in 2018 (Only Compounds Detected in at Least One Sample Are Included)[a]

			lake			factory area		
PFAS group	acronym	abbreviation	mean	median	max	mean	median	max
PFCA	perfluorohexanoic acid	PFHxA	0.5 ± 0.1	0.3	4.0	1.0 ± 0.5	0.3	5.0
	perfluoroheptanoic acid	PFHpA	0.3 ± 0.0	0.3	0.3	1.3 ± 0.8	0.3	7.8
	perfluorooctanoic acid	PFOA	0.3 ± 0.0	0.3	0.3	9.3 ± 8.1	0.3	81.6
	perfluorononanoic acid	PFNA	0.2 ± 0.0	0.2	1.4	6.9 ± 6.6	0.2	65.9
	perfluorodecanoic acid	PFDA	1.1 ± 0.2	0.5	5.7	69.4 ± 66.2	0.2	665
	perfluoroundecanoic acid	PFUnDA	0.8 ± 0.1	0.2	4.4	19.9 ± 18.5	0.2	186
	perfluorododecanoic acid	PFDoDA	1.4 ± 0.2	0.6	7.6	21.0 ± 18.3	0.2	184
	perfluorotridecanoic acid	PFTrDA	0.4 ± 0.0	0.2	2.5	3.2 ± 2.4	0.2	24.6
	perfluorotetradecanoic acid	PFTeDA	0.8 ± 0.1	0.2	4.8	23.3 ± 20.1	0.2	203
	perfluoropentadecanoic acid	PFPeDA	0.2 ± 0.0	0.2	0.2	1.5 ± 1.1	0.2	11.1
	perfluorohexadecanoic acid	PFHxDA	0.2 ± 0.0	0.2	0.2	2.8 ± 2.3	0.2	23.7
		∑PFCA	**6.2 ± 0.6**	**3.6**	**25.2**	**160 ± 145**	**3.1**	**1 458**
PFSA	perfluorobutanesulfonic acid	PFBS	0.1 ± 0.0	0.1	0.2	0.1 ± 0.0	0.1	0.1
	perfluorohexanesulfonic acid	PFHxS	0.0 ± 0.0	0.1	0.1	0.3 ± 0.2	0.1	1.5
	perfluoroheptanesulfonic acid	PFHpS	0.0 ± 0.0	0.1	0.1	2.2 ± 2.1	0.1	21.3
	perfluorooctanesulfonic acid[b]	L-PFOS	3.8 ± 0.6	1.2	24.2	179 ± 178	0.4	1 780
	branched PFOS	Br-PFOS	0.2 ± 0.0	0.1	1.1	68.0 ± 67.7	0.1	677
	perfluorodecanesulfonic acid	PFDS	0.0 ± 0.0	0.1	0.1	0.7 ± 0.6	0.1	6.0
	perfluorododecansulfonic acid	PFDoS	0.1 ± 0.0	0.1	0.1	0.2 ± 0.2	0.1	1.9
		∑PFSA	**4.4 ± 0.6**	**1.6**	**25.4**	**250 ± 248**	**1.3**	**2 486**
preFOS	perfluorooctanesulfonamide	FOSA	1.4 ± 0.3	0.5	14.6	13.6 ± 11.0	0.2	112
	methylperfluorooctanesulfonamide	MeFOSA	0.2 ± 0.0	0.2	0.4	0.2 ± 0.0	0.2	0.2
	ethylperfluorooctanesulfonamide	EtFOSA	0.3 ± 0.0	0.2	1.1	6.8 ± 4.9	0.2	49.4
	ethylperfluorooctanesulfonamido ethanol	EtFOSE	7.4 ± 1.6	1.0	72.2	313 ± 243	4.5	2 455
	perfluorooctanesulfonamido acetic acid	FOSAA	0.9 ± 0.1	0.2	8.6	2.7 ± 1.9	0.2	19.2
	methylperfluorooctansulfonamido acetic acid	MeFOSAA	0.2 ± 0.0	0.2	0.4	0.2 ± 0.0	0.2	0.2
	ethylperfluorooctanesulfonamido acetic acid	EtFOSAA	9.4 ± 2.2	0.9	126	258 ± 187	3.9	1 831
		∑preFOS	**19.7 ± 3.7**	**3.2**	**178**	**594 ± 445**	**17.2**	**4 467**
FTS	6:2 fluorotelomer sulfonic acid	6:2 FTS	0.2 ± 0.0	0.2	0.2	0.9 ± 0.6	0.2	6.6
	8:2 fluorotelomer sulfonic acid	8:2 FTS	2.1 ± 0.3	0.6	15.8	253 ± 212	7.5	2 150
	10:2 fluorotelomer sulfonic acid	10:2 FTS	25.2 ± 4.6	2.3	221	472 ± 269	39.7	2 120
	12:2 fluorotelomer sulfonic acid	12:2 FTS	17.2 ± 3.5	2.8	254	370 ± 182	110	1 723
	14:2 fluorotelomer sulfonic acid	14:2 FTS	1.0 ± 0.2	0.2	18.3	106 ± 68.2	18.9	688
		∑FTS	**45.6 ± 8.4**	**6.4**	**509**	**1 201 ± 657**	**176**	**5 540**
∑PFAS 29			**75.9 ± 11.0**	**18.9**	**606**	**317 ± 157**	**43.7**	**1 3951**

[a]Mean concentrations are shown with the standard error of the mean. Concentrations below the LOQ were treated as half the LOQ. [b]Linear Perfluorooctanesulfonic acid (PFOS).

feeding on offshore, pelagic food webs,[43] and a similar approach was used in the present study. The $\delta^{13}C$ is enriched in benthic-littoral food webs compared to pelagic food webs[44] thus, increased (i.e., less negative) $\delta^{13}C$ in organisms can be interpreted as indications of that biota have increased proportions of benthic organisms in their diet (i.e., increased dietary proportions of organisms from food webs with sediment living organisms at the base). A small trophic fractionation of carbon (i.e., organisms have less negative $\delta^{13}C$ compared with their diet) with an average fractionation of 0.39‰ has been reported.[42] Thus, trophic level adjusted $\delta^{13}C$ were calculated by subtracting relative trophic level multiplied by 0.39 from $\delta^{13}C$. Details about trophic level and carbon sources are described in the SI.

Water samples were extracted using solid-phase extraction (SPE). Sediment and biota samples were extracted using acetonitrile and ultrasonication. PFAS were analyzed using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF-MS, see all PFAS and acronyms in SI Tables S3 and S4). Initially, 44 PFAS were quantified using authentic and internal standards, while 19 PFAS were screened for using exact mass and retention time from authentic standards. In addition, peaks for branched PFOS (Br-PFOS) were identified using a standard mixture of Br-PFOS isomers and quantified against the standard for L-PFOS. An additional 28 PFAS were screened for using exact mass and estimated retention time. Three peaks were observed at expected retention times, and they were quantified using the standard for a similar compound. Following this, the detected compounds indicated the presence and thus use of an EtFOSE based PFAS product, which according to the literature may indicate that SAmPAPs were the parent compounds.[45,46]

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Therefore, SAmPAP diester was screened for in one sample taken in 2018 (the sediment sample used for analyses of EOF), however, the analytical range for most 2018 samples (m/z: 150−1100) did not include SAmPAP diester (m/z: 1203). Therefore, biota samples stored from 2018 sampling, and water and sediment samples from 2019 were reanalysed for SAmPAP diester in 2019. Details of the analytical methods and PFAS acronyms are given in the SI.

Statistics and Data Treatment. Means in the present work are arithmetic means, with standard error of the mean (SEM) where appropriate. Relationships between K_D values, fraction of organic carbon (f_{OC}), and particle size distribution were evaluated using stepwise regression. Relationships between relative trophic level or trophic level adjusted $\delta^{13}C$, and PFAS concentrations in biota were evaluated using Spearman rank correlation coefficient (Spearmans rho). Unpaired Wilcoxon Test was used to test differences in trophic level adjusted $\delta^{13}C$ or relative trophic level between pike and perch.

Trophic magnification factors (TMF) were calculated using linear regression of relative trophic level against log-transformed PFAS concentrations, as previously reported in several studies.[10,33,34] Methods for calculating sediment-water partitioning coefficients (K_D values), bioaccumulation factors (BAF), biota-sediment accumulation factors (BSAF), biota trophic level and carbon sources, and fluorine mass balance are shown in the SI along with details for statistical analysis.

RESULTS AND DISCUSSION

PFAS Concentrations in Water. In lake water, PFOS was the only compound detected above the LOQ. Linear (L) PFOS concentrations of 0.15 and 0.18 ng L^{-1} and branched (Br) PFOS concentrations of 0.07 and 0.10 ng L^{-1} were detected (areas L4 and L6, respectively). Samples from areas L1, L3, and L5 were unfortunately lost; however, it is probable that concentrations at these sites would also be low because they all receive the majority of water (and thus PFAS) from the river. The PFOS concentration in river water from the factory area was <LOQ in 2018, while concentrations of 1.5 and 1.9 ng L^{-1} for L and Br-PFOS, respectively, were detected in the supplementary sample of river water from the factory area sampled in 2019. The reason for this difference could be the larger water volumes and river current and in 2019, which may have remobilized contaminants from banks and riverbeds (the river water volume was on average 21 m^3 s^{-1} in August 2018 and 105 m^3 s^{-1} in June 2019, (measuring station Kistefoss, The Norwegian Water Resources and Energy Directorate, personal communications). Increased and different mobilization is also possibly the reason for the difference in Br-PFOS relative to L-PFOS, in the 2019 sample compared to lake water samples from 2018. However, additional samples are needed to confirm this. Concentrations of all PFAS above the LOQ in water samples are listed in SI Table S5. SAmPAP diester was analyzed in the 2019 sample but was not detected. River and lake water concentrations reported in the present study are low and more comparable to pristine lakes than lakes close to PFAS point sources or urban areas (see SI Tables S5 and S6 for a comparison),[9,33,47−49] although it must be kept in mind that such water bodies are highly variable in nature as well as PFAS source contribution.

PFAS Concentrations in Sediment. A large suite of different compounds (29 PFAS and Br-PFOS) was detected in sediments sampled in 2018. PFAS concentrations (dry weight (d.w.)) in river sediments from the factory area varied greatly between samples, however maximum concentrations were high (e.g., max 2455 μg kg^{-1} of ethylperfluorooctanesulfonamido ethanol [EtFOSE]). Except for SAmPAP diester, which was only analyzed for in one sample in 2018, the highest concentration in lake sediments analyzed in 2018 was found for 12:2 FTS at 253.7 μg kg^{-1}. The one sample analyzed for SAmPAP diester in 2018 showed a SAmPAP diester concentration of 850 μg kg^{-1}. The dominant PFAS in sediments were the C9−C14 PFCA, PFOS, four preFOS compounds, and C10−C16 FTS. Mean, median, and maximum concentrations are shown in Table 1. PFAS were relatively evenly distributed in the lake sediments; however, concentrations were highest closest to the river (L1, L2, and L3, see SI Figures S3 and S5−S8) pointing to the fact that the factory is assumed to be the main contamination source.

Supplementary sediment sampling was conducted in 2019 from the factory area (one sample), and the lake (four samples). Results are shown in SI Table S7. Concentrations in the sample from the factory area were low and mostly below the LOQ. The reason for this was likely related to the high water levels and strong current at the time of sampling, which rendered only coarse sediments below a bridge available for sampling. Concentrations in lake sediment samples from 2019 were comparable to samples analyzed in 2018, see SI Table S7 compared to Table 1. SAmPAP diester dominated (70−93% of the total sum detected PFAS in lake sediments; however, concentrations varied significantly (2.1−1 872 μg kg^{-1}). This indicates that a PFAS product dominated by SAmPAP diester was used at the factory, in agreement with the previously reported use of this compound in paper products.[45,46,50] It is known that commercial SAmPAP formulations were dominated by diester,[29] and for this reason this compound was prioritized for analysis. However, the presence of SAmPAP mono- and triester in sediments are expected as well, as has previously been reported.[32] Interestingly, another group of compounds reported in paper products, fluorotelomer alcohol (FTOH) mono- and disubstituted phosphates (diPAP),[50] were analyzed in 2018, but not detected, indicating that these compounds were not used at the factory (SI Table S3).

The sediment concentrations in lake Tyrifjorden were significantly higher than concentrations reported for pristine lakes. For example, sediment concentrations of 0.001 to 0.44 μg kg^{-1} and 0.19 to 2.7 μg kg^{-1} for PFOS and $\sum$PFAS 19 respectively, were reported in four Canadian arctic lakes not affected by known point sources.[9] Furthermore, mean concentrations in river sediments directly downstream to the factory reported herein were higher than concentrations in Canadian lake sediments downstream of an airport (28−49 μg kg^{-1} for PFOS and 57−64 μg kg^{-1} for $\sum$PFAS 19).[9] Sediment PFOS concentrations (which dominated) in rivers, lakes, and canals in The Netherlands (0.5−8.7 μg kg^{-1}) were comparable to lake sediment concentrations in the present study.[47] SAmPAP diester concentrations reported here (up to 1 872 μg kg^{-1} in lake sediments) are very high compared to previous reported concentrations: SAmPAP diester and preFOS have previously been reported in freshwater sediments in Taihu Lake, China (max 4.3 μg kg^{-1}),[32] and in marine sediments from an urban area in Canada (max 0.2 μg kg^{-1}).[31] Thus, sediment PFAS concentrations reported here are higher than concentrations in pristine lakes and generally comparable to water bodies close to point sources and/or urban areas.

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Relatively high PFAS concentrations were detected in sediment pore water (SI Table S8). The highest concentration was for PFOA (1246 ng L^{-1}, area L1). Overall, the C5−C10 PFCA and PFOS were most abundant, whereas preFOS and FTS were only detected above the LOQ in a few samples. The PFAS in sediment pore water are those that are readily bioavailable and represent the risk of the PFAS to biota and surrounding environment.[51] The use of passive samplers[52] in sediments can be a useful approach to assess pore water concentrations in future studies. The lower levels of preFOS and FTS compared to the above-mentioned PFAA are likely due to lower solubility of these larger compounds. This is demonstrated by no concentrations of EtFOSE above the LOQ in porewater, a neutral, large compound (compared to, e.g., PFOS). The importance of the high sediment and pore water concentrations will be discussed below in the context of sediment−water partitioning and uptake by biota.

Sediment−Water Partitioning Coefficients (K_D). Sediment-pore water partitioning coefficients (K_D, L kg^{-1}) are shown in Figure 1 for different PFAS across the whole data set. K_D values for all individual samples are listed in SI Table S10. Generally, K_D values increased with increasing number of C atoms, and preFOS and FTS had higher K_D values than PFAA (e.g., median log K_D: PFHxA 0.9, PFOA 1.1, PFDA 1.6, PFOS 1.1, FOSA 3.2, 10:2 FTS 3.6).

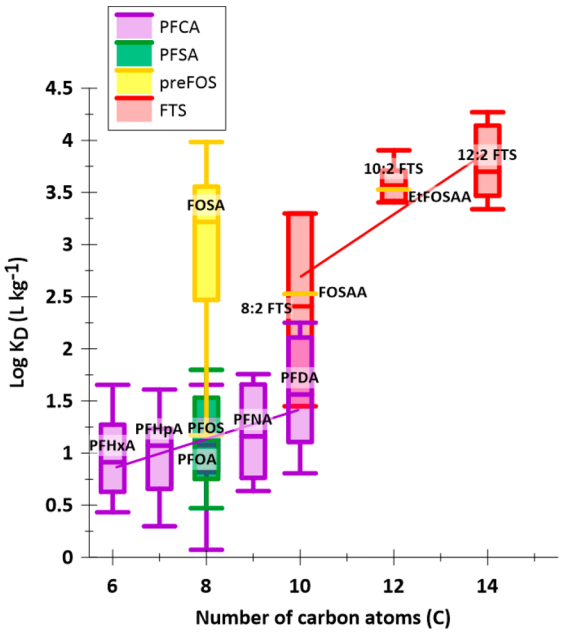

Figure 1. Partitioning coefficients (sediment−pore water, median log K_D values) for different PFAS as a function of number of carbons. Boxes show upper and lower quartiles and whiskers show maximum and minimum values. The purple and red regressions are the relationships between partitioning coefficients and carbon chain length for PFCA log K_D = 0.14C+0.01; R^2:0.17; $p < 0.01$) and FTS (log K_D = 0.30C−0.32; R^2:0.48; $p < 0.01$), respectively. Only compounds for which at least one concentration above the LOQ was detected in both sediments and pore water for at least one replicate are shown. For PFSA, only PFOS showed concentrations above the LOQ in both pore water and sediments in the same sample, and a potential relationship between K_D values and chain length could not be evaluated. Concentrations below the LOQ were treated as half the LOQ. Note that some compounds overlap (PFOS and PFOA, 8:2 FTS and FOSAA, 10:2 FTS and EtFOSAA) and are plotted on top of each other.

The positive association between K_D values and chain length for PFCA and FTS was comparable to values reported elsewhere (see Discussion in the SI).[49] PreFOS have higher K_D values compared to PFOS and PFCA (see Figure 1 and SI Table S10) which is in agreement with previously reported partitioning behavior for EtFOSAA and FOSA compared to PFCA.[53] PreFOS K_D values have also been reported to increase with *N*-alkyl substitution.[31] Indeed, in the present study K_D values follow this trend (FOSAA versus EtFOSAA), and neutral preFOS (i.e., FOSA, EtFOSE) had higher or comparable K_D values than larger acids (EtFOSAA, FOSAA), as expected based on the lower water solubility of neutral compounds. However, these results are based on a few data points (see SI Table S10) and should be treated with care.

As for preFOS, K_D values for long chained FTS were high compared to the shorter PFAA. Based on the K_D values reported herein, long chained PFAA, preFOS, and C > 10 FTS are expected to preferentially partition to the sediment phase, rather than remaining in the water column. This is in agreement with a previous study in which FTS (especially 8:2 FTS) was predominantly found in sediments as compared to other environmental media.[9]

In addition to compound specific properties, K_D values are affected by environmental factors such as sediment characteristics, particularly TOC content.[19] There was no correlation between K_D and sand, silt, or clay content in these sediments or pore waters (Discussion in the SI). A significant relationship between K_D and TOC was found for PFOS ($p = 0.01$, $n = 11$), but no other PFAS in the present study. For a detailed discussion related to this, see the SI.

PFAS Concentrations in Biota. *Fish Liver.* Concentrations in biota varied between tissues and species as summarized in Figure 2. A total of 23 PFAS (+ Br-PFOS) were detected in biota. The dominant PFAS in fish liver were the C10−C13 PFCA and PFOS which were detected in all analyzed samples. The highest concentrations in lake biota were in perch liver ($n = 20$), for example, mean concentrations of PFDoDA: 33.2 $\mu g\ kg^{-1}$; PFTrDA: 22.0 $\mu g\ kg^{-1}$; L-PFOS: 149 $\mu g\ kg^{-1}$; FOSA: 1.3 $\mu g\ kg^{-1}$; and 10:2 FTS: 1.4 $\mu g\ kg^{-1}$. The mean ∑PFAS 23 in perch liver from the lake was 280 $\mu g\ kg^{-1}$, whereas it was 668 $\mu g\ kg^{-1}$ in perch liver from the factory area. PFAS profiles in perch and pike from the factory area were comparable, but PFOS, preFOS, and FTS concentrations were higher, compared to the same biota in the lake, for example, perch liver concentrations of PFDoDA: 42.0 $\mu g\ kg^{-1}$; PFTrDA: 20.0 $\mu g\ kg^{-1}$; L-PFOS 371.5 $\mu g\ kg^{-1}$; FOSA: 44.4 $\mu g\ kg^{-1}$; and 10:2 FTS: 31.3 $\mu g\ kg^{-1}$ (full list for all species is shown in SI Tables S12 and S14). SAmPAP diester was not detected in biota during the supplementary analysis in 2019 (not analyzed for in 2018). In Lake Halmsjön which is significantly impacted with PFAS pollution from firefighting activities at Stockholm airport, ∑PFAS 11 concentrations of 3900 $\mu g\ kg^{-1}$ in perch liver consisting almost entirely PFOS were reported, in contrast to the variety of compounds reported in the present study.[49] It is clear that the PFAS pollution source in the present study directly affects the concentration profile in biota liver and that the PFAS profile is different to biota profiles impacted by previously reported AFFF point sources.

Fish and Crayfish Muscle. PFAS profiles in fish and crayfish muscle were similar to profiles in liver although concentrations

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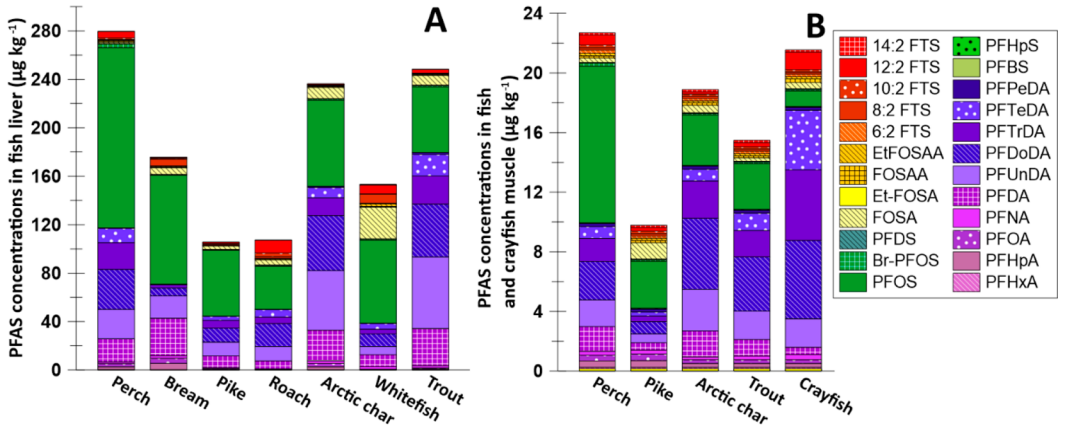

Figure 2. Mean concentrations of detected PFAS ($\mu g\ kg^{-1}$ w.w.) in fish liver (A) and fish and crayfish muscle (B) from lake Tyrifjorden (biota from factory area is not included). Only compounds detected above the LOQ in at least one sample replicate are included. Values below the LOQ were treated as half the LOQ.

were lower (Figure 2B). PFOS was the only compound detected above the LOQ in all analyzed muscle samples, and as for liver, the highest concentrations in lake biota were in perch: 10.5 $\mu g\ kg^{-1}$, $n = 35$. Concentrations in fish muscle from the factory area were higher than concentrations in the lake: perch muscle PFOS concentrations: 25.2 $\mu g\ kg^{-1}$, $n = 5$ (full list for all species is shown in SI Tables S13 and S14).

PFOS in perch muscle has been reported to decrease with increasing latitude in a study of pristine Swedish lakes.[54] In the two lakes located at comparable latitudes to lake Tyrifjorden, lakes Långtjärn (60°01′N 15°53′E) and Kroktjärn (60°07′N 13°58′E), the ∑PFAS 11 concentrations in perch muscle were approximately 0.6 and 1 $\mu g\ kg^{-1}$.[54] It is clear that lake Tyrifjorden is more heavily contaminated than these Swedish lakes which are not considered to be impacted by a specific PFAS source.

In Lake Halmsjön (PFAS pollution from firefighting activities), ∑PFAS 11 concentrations of 330 $\mu g\ kg^{-1}$ in perch muscle were reported and concentrations consisted almost entirely of PFOS.[49] In the Taihu Lake in China (where reported PFAS levels in lake water are high compared to the present study, that is, 13.7 vs 0.18 ng L^{-1}), which is contaminated by wastewater treatment plants (WWTP) and industry, mean PFOS concentrations in fish muscle were between 11.4 and 94.9 $\mu g\ kg^{-1}$, depending on species.[33] Concentrations in lake Tyrifjorden are therefore most similar to those reported from an area with a direct PFAS pollution source.

Pathway from Abiotic to Biota Media and Trophic Transfer. *Bioaccumulation Factors (BAF) and Biota-Sediment Accumulation Factors (BSAF).* BAF for L-PFOS in perch and pike (liver and muscle, the species sampled in the greatest numbers) at stations factory area and L6 are shown in Table 2. These values were calculated for stations where water concentrations were available. Details related to assumptions behind the calculated BAF as well as values for all species and stations can be found in the Methods Section of the SI and Tables S15 and S16). Owing to higher liver concentrations, BAF for liver were higher than for muscle. The highest and lowest BAF_{Liver} for L-PFOS were in perch liver: 5 143 227 (area L5), and in roach liver: 45 283 (area L6), respectively. The highest L-PFOS BAF_{muscle} was 505 582 for perch (area L1) and the lowest was 3114 for crayfish (area L6). The BAF for L-PFOS reported here are higher than reported in previous studies for the same species (Table 2): L-PFOS BAF for perch liver and muscle of 39 000 and 3400, respectively, were calculated for samples taken nearby Stockholm Arlanda airport (AFFF PFAS source),[49] and L-PFOS BAF for whole perch and pike of up to 6300 and 1550 respectively, were reported in samples from Schiphol Amsterdam Airport, again with an AFFF PFAS source.[55] Whole fish concentrations are generally expected to be higher than muscle concentrations,[56] thus the BAF for whole fish is expected to be higher than for muscle. A comparison of the results presented here to previously reported BAF (Table 2), shows that the BAF herein are among the highest ever reported. This may be because the biota are not in equilibrium with the water phase, and that continuous dietary uptake results in relatively high biota concentrations and hence BAF.

The ratios of concentrations in biota ($\mu g\ kg^{-1}$ w.w.) to sediment ($\mu g\ kg^{-1}$ d.w.), that is, the BSAF for PFAS in liver and muscle are shown in SI Tables S17−S22. The highest BSAF were for L-PFOS in perch liver: 559, 113, 90, and 22 sampled at different areas in the lake (sampling areas L6, L5, L1, and L3 respectively), and PFOS in pike and whitefish liver, 268 and 126 respectively, sampled furthest from the river mouth (sampling area L6). A detailed discussion about BSAF can be found in the SI, however BSAF in the present study vary between areas but are comparable to previously reported BSAF in freshwater environments.[55,57]

The very high BAF in this study compared to previous studies, combined with the BSAF in this study which are comparable to other studies, strengthens the conclusion that uptake routes other than surrounding water and uptake via gills are important in the present study. This suggests that sediments/pore water are an important source of PFAS to the food web.

Correlations with the Benthic Food Web and Uptake from Sediments. Due to the combination of high PFAS concentrations in biota compared to lake water (high BAF) and high concentrations of certain PFAS in lake sediments and pore water (BSAF comparable to elsewhere), correlations between PFAS concentrations and trophic level adjusted muscle $\delta^{13}C$ (as an indicator of dietary sources) were tested. Due to differences in expected contaminant loads between areas, relationships were tested within each area. Significant ($p \leq 0.05$) positive relationships (indicating increased proportions of benthic organisms in the diet, see Materials and

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Table 2. Bioaccumulation Factors (BAF, Water:Biota Tissue) for PFOS in Perch and Pike Sampled at Stations Factory Area and Area L6 in the Present Study Compared to Literature Values[a]

species							
common name	scientific name	marine or freshwater	BAF (L kg^{-1})	water concentration (ng L^{-1})	PFAS source	study type	study
Liver							
perch	*Perca fluviatilis*	freshwater	804 900–>3 714 600	<0.10–0.18	paper industry	field	present study
pike	*Esox lucius*	freshwater	386 000–>484 900	<0.10–0.18	paper industry	field	present study
perch	*Perca fluviatilis*	freshwater	39 000	98	AFFF	field	Ahrens et al. (2015)[49]
common shiner	*Notropus cornutus*	freshwater	6250–124 700	320	AFFF	field	Moody et al. (2002)[58]
mullet	*Mugilidae*	marine	12 400	13	industry/WWTP	field	Yoo et al. (2009)[59]
bluegil	*Lepomismacrochirus*	freshwater	41 600[b]	7	industry/WWTP	field	Taniyasu et al. (2003)[60]
silver perch	*Bidyanus bidyanus*	freshwater	26 000	10	reclaimed water	field	Terechovs et al. (2019)[61]
crucian carp	*Carassius carassius*	freshwater	1500[c]	13–18	industry/WWTP	field	Shi et al. (2018)[62]
chub	*Leuciscus cephalus*	freshwater	4600	27	WWTP	field	Becker et al. (2010)[63]
Muscle							
perch	*Perca fluviatilis*	freshwater	59 200–>251 900	<0.10–0.18	paper industry	field	present study
pike	*Esox lucius*	freshwater	18 700–>57 200	<0.10–0.18	paper industry	field	present study
perch	*Perca fluviatilis*	freshwater	3400	98	AFFF	field	Ahrens et al. (2015)[49]
	Cyprinus carpio	freshwater	10 000	0.03	background	field	Meng et al. (2019)[64]
	Carassius auratus	freshwater	4000	0.03	background	field	Meng et al. (2019)[64]
	Erythroculter dabryi	freshwater	26 670	0.03	background	field	Meng et al. (2019)[64]
	Hypophthalmichthys molitrix	freshwater	8330	0.03	background	field	Meng et al. (2019)[64]
	Siniperca chuatsi	freshwater	65 000	0.03	background	field	Meng et al. (2019)[64]
minnow	*Hemiculter lcucisculus*	freshwater	6092	5.68	industry/WWTP	field	Fang et al. (2014)[33]
silver carp	*Hypophtha lmichthys molitrix*	freshwater	1761	5.68	industry/WWTP	field	Fang et al. (2014)[33]
whitebait	*Reganisalanx brachyrostralis*	freshwater	2835	5.68	industry/WWTP	field	Fang et al. (2014)[33]
crucian	*Carassius cuvieri*	freshwater	15 599	5.68	industry/WWTP	field	Fang et al. (2014)[33]
lake saury	*Coilia mystus*	freshwater	9190	5.68	Industry/WWTP	field	Fang et al. (2014)[33]
carp	*Cyprinus carpio*	freshwater	7623	5.68	Industry/WWTP	field	Fang et al. (2014)[33]
mongolian culter	*Culter mongolicus*	freshwater	15 088	5.68	industry/WWTP	field	Fang et al. (2014)[33]
mud fish	*Oriental weatherfish*	freshwater	10 810	5.68	industry/WWTP	field	Fang et al. (2014)[33]
chinese bitterling	*Rhodeus sinensis Gunther*	freshwater	6444	5.68	industry/WWTP	field	Fang et al. (2014)[33]
gobies	*Ctenogobius giurinus*	freshwater	6144	5.68	Industry/WWTP	field	Fang et al. (2014)[33]
crucian carp	*Carassius auratus*	freshwater	120 000	0.48	industry	field	Wang et al. (2012)[65]
silver perch	*Bidyanus bidyanus*	freshwater	6000	10	reclaimed water	field	Terechovs et al. (2019)[61]
crucian carp	*Carassius carassius*	freshwater	900[c]	13–18	industry/WWTP	field	Shi et al. (2018)[62]
nile tilapia	*Oreochromis niloticus*	freshwater	398	0.073–5.6	Industry/WWTP	field	Ahrens et al. (2016)[66]
	Labeobarbus megastoma	freshwater	5012	0.073–5.6	industry/WWTP	field	Ahrens et al. (2016)[66]
	Labeo- barbus gorguari	freshwater	3981	0.073–5.6	industry/WWTP	field	Ahrens et al. (2016)[66]
	Labeobarbus intermedius	freshwater	794	0.073–5.6	industry/WWTP	field	Ahrens et al. (2016)[66]
eel	*Anguilla anguilla*	freshwater	234–1148	20–490	AFFF	field	Kwadijk et al. (2014)[55]
Whole Fish							
pike	*Esox lucius*	freshwater	1549	340–490	AFFF	field	Kwadijk et al. (2014)[55]
perch	*Perca fluviatilis*	freshwater	2344–6310	20–490	AFFF	field	Kwadijk et al. (2014)[55]
perch	*Perca fluviatilis*	freshwater	6400	98	AFFF	field	Ahrens et al. (2015)[49]
lake trout	*Salvelinus namaycush*	freshwater	12 589	0.2–5.9	background/unknown		Furdui et al. (2007)[67]
	Pseudohemiculter dispar	freshwater	25 670	0.03	background	field	Meng et al. (2019)[64]
sculpin	*Cottus cognatus*	freshwater	234 000	2.20	unknown	field	Houde et al. (2008)[68]
lake trout	*Salvelinus namaycush*	freshwater	34 000	2.20	unknown	field	Houde et al. (2008)[68]
herring	*Clupea harengus membras*	marine	22 000	0.25	background	field	Gebbink et al. (2016)[69]

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Table 2. continued

species							
common name	scientific name	marine or freshwater	BAF (L kg^{-1})	water concentration (ng L^{-1})	PFAS source	study type	study
Whole Fish							
sprat	*Sprattus sprattus*	marine	23 200	0.25	background	field	Gebbink et al. (2016)[69]

[a]Only studies reporting specific species and tissue (liver, muscle, or whole organism) were included. [b]The highest BAF reported in the study. No other species-specific values were reported [c]Value from figure (approximate)

methods and SI) were found (for at least one area) between trophic level adjusted $\delta^{13}C$ and PFAS concentrations in muscle and/or liver for C11−C14 PFCA (PFUnDA, PFDoDA, PFTrDA, PFTeDA), the C10 PFSA (PFDS), two preFOS compounds (FOSA and FOSAA), and the 12−14C FTS (10:2 FTS and 12:2 FTS) (SI Table S25). In areas where the greatest diversity of species was sampled (and the greatest variability in $\delta^{13}C$ was found: muscle samples from areas L3 and L6) significant positive correlations were shown for C11−C14 PFCA, preFOS (FOSAA), and 12:2 FTS. The compounds for which positive correlations with trophic level adjusted $\delta^{13}C$, and thus the benthic food web, were shown are relatively consistent with those compounds that have high K_D values. This suggests that uptake of these compounds is associated with the benthic food web, and thus the sediments are an important PFAS source. Indeed, based on PFAS profiles in Canadian lake food webs, sediments (via the benthic food web) are suggested to be the major source to PFAS in arctic char.[9] Higher PFOS concentrations in river goby (*Gobio gobio*) compared to chub (*Leuciscus cephalus*) have previously been suggested to be due to higher intake of benthic invertebrates living in PFOS contaminated sediments.[63] Similarly, sediments, not water, were suggested to be the major PFAS source to the aquatic food web in Lake Ontario.[34]

Biomagnification. High concentrations in top predator fish feeding on the benthic food web were previously suggested to be due to biomagnification.[34] A similar mechanism could possibly explain the high levels observed in top predatory fish in the present study. Individual relative trophic levels are shown in SI Table S24. In the present study, liver and muscle samples were analyzed in fish and muscle samples were analyzed in crayfish. In order to include both invertebrates (crayfish) and several species of fish in the TMF calculations, TMF are only reported for muscle samples (TMF_{muscle}) from area L3 and L6 (areas were the greatest diversity of species were sampled). The TMF_{Muscle} for L-PFOS was 3.7 and 9.3 at areas L3 and L6, respectively ($p < 0.05$). TMF_{muscle} for PFCA at areas L3 and L6 were below 1 or nonsignificant, except for PFDA at area L6 which had a TMF_{muscle} of 1.8 ($p = 0.01$). TMF_{muscle} for preFOS and FTS were below 1 or nonsignificant ($p > 0.05$). In two freshwater food web studies similar to the present, in Taihu Lake (where PFOS and PFCA were the dominate compounds), TMF for PFOS were reported to be 2.9 and 3.86.[33,70] TMF for PFOS reported in studies of river and estuarine food webs were between 0.94 and 1.5.[71−73] Thus, the TMF for PFOS reported for lake Tyrifjorden were relatively high compared to previous reported values in comparable studies. The low TMF_{muscle} for PFCA are due to relatively high concentrations of these compounds in crayfish which are at a lower trophic level than the investigated fish. High levels in crayfish are likely due to uptake of these compounds (or their precursors) from sediments (pore water and/or benthic organisms) as discussed above.

Franklin[74] reviewed TMF in studies with varying organisms and tissues and argue that the use of different tissues for the different trophic levels (e.g., whole body homogenate versus liver) introduces uncertainties when calculating TMF.[74] Whole body homogenates is recommended, but not always practical.[74] In this study, it was challenging to prepare whole body homogenates (e.g., the scull of large fish and exoskeleton of crayfish). For this reason, muscle samples were used to calculate TMF in the present study. Furthermore, plankton could not be sampled in great enough numbers at the site as has been done in previous studies (e.g., refs 33, 70, 75, and 76). Thus, the results reported here should be interpreted with these factors in mind. One explanation for the high PFOS TMF and relatively large variation between areas in the present study could be related to the role of precursor compounds. Transformation of precursors has been suggested to be one reason for high PFOS TMF[33] and the large variation in TMF values between studies.[74] Therefore, the relatively high TMF for PFOS reported here indicate possible transformation of precursor compounds (released from the factory), and strongly suggest that not all of these compounds were detected by the targeted analysis. However, mechanisms behind the contribution from precursor compounds to TMF values for PFAA are complex and not well understood, and laboratory studies that evaluate biomagnification potential of PFAS are needed.[74]

Precursor Compounds and Biotransformation. EOF was used to investigate to what extent the targeted PFAS analyses could explain the total organic fluorine in sample extracts (assuming that PFAS constitutes a large fraction of the EOF and that inorganic fluoride is not extracted, see the SI).[77−79] Of seven sediment samples analyzed for EOF, only one was above the LOQ (39−133.0 μg F kg^{-1}): a sediment sample from area L1 with 964 μg F kg^{-1}. In fish liver, EOF concentrations varied between 86 μg kg^{-1} (perch from area L6) and 1 348 μg kg^{-1} (perch from area L3). EOF concentrations and the sum of organic fluorine from targeted PFAS analysis (compounds in concentrations above LOQ only) are shown in Figure 3. The sum fluorine from the targeted analysis ($\sum F_{targ}$) as a percent of EOF are shown in SI Figure S10 and Table S28.

$\sum F_{targ}$ accounts for approximately 54% of the EOF in the sediment sample. Previous studies have reported that identified PFAS accounted for between 2 and 44% of the anionic fraction of the extractable organic fluorine in sediments,[80] and less than 8% in water.[77] In the samples in this study, approximately 48% of the EOF in the sediment sample is due to SAmPAP diester. SAmPAP diester has been reported to strongly sorb to sediments,[31] and this can decrease bioavailability[81] and thus dietary absorption efficiency in biota (0.04−2.25% in perch).[82] Nevertheless, given the high sediment concentrations reported here (max: 1872 μg kg^{-1}), uptake of small amounts is likely even though concentrations were below the LOQ in biota (which can occur if degradation rates are much higher than

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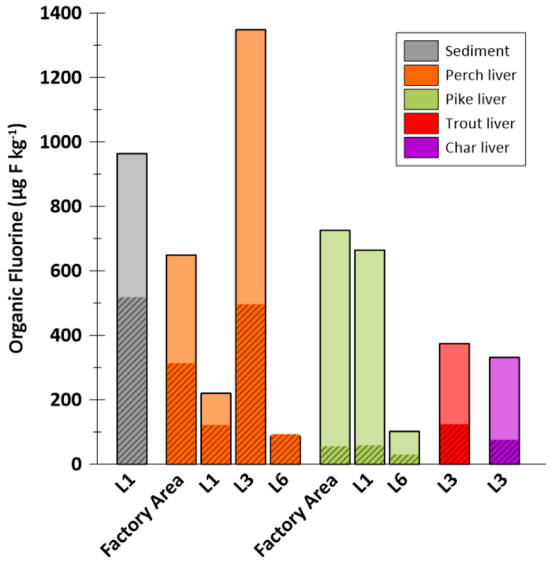

Figure 3. Sum of extractable organic fluorine (EOF, solid bars with black outline, i.e., the complete bar) as well as sum fluorine from detected compounds from targeted analysis (hatched bars) in sediment (d.w.) and in fish livers (w.w.) from areas factory area, L1, L3, and L6 (n = 1).

uptake rates). Perch has previously been reported to biotransform SAmPAP diester to preFOS compounds (EtFOSAA, FOSAA, and FOSA), and PFOS.[82] Contradictory results have previously been reported related to the role of microbial processes on the production of preFOS and PFOS from SAmPAP diester in sediment. Negligible degradation was reported in marine sediments;[81] however, significant degradation was reported in freshwater sediments[32] possibly indicating a difference between the microbial processes in marine and freshwater sediments.[32] In agreement with this, the two 2019 samples with the highest SAmPAP diester concentrations also had high concentrations of the known degradation product, EtFOSAA (SI Table S7). The same applies for the sediment sample analyzed for SAmPAP diester in 2018 (850 μg kg^{-1} and 56.4 μg kg^{-1} SAmPAP diester and EtFOSAA, respectively). Thus, the high SAmPAP diester concentrations in sediments in the present study suggest that there may be significant production of preFOS and PFOS via a similar dissimilatory mechanism.

Intermediates, from bacterial degradation in sediments or biotransformation in higher organisms, and isomers, not targeted by the chemical analysis, as well as SAmPAP mono- and triester might explain some of the unknown EOF. The $\sum F_{targ}$ as a percent of EOF in fish livers varied between species and increased with distance from the factory (highest percentages in area L6), meaning that more of the PFAS present are captured by the target analysis further from the source. The increasing fraction of known PFAS with distance from the factory likely reflects a more complete degradation to terminal end products such as PFSA and PFCA that were targeted as this process progresses with increasing time and in this case, therefore, with distance from the source. The highest percentages of EOF explained by $\sum F_{targ}$ in biota were in perch (37−108%), while the lowest were in pike liver (9−30%). Pike and perch did not differ in trophic level adjusted δ^{13}C and relative trophic levels (p: 0.19−0.90), thus differences in dietary PFAS exposure do not appear to explain the observations. Differences in biotransformation potential is a possible explanation.

In the present study, preFOS compounds have high K_D (e.g., FOSA log K_D: 3.2), are found in high concentrations in sediments (FOSA, EtFOSE, FOSAA, EtFOSAA) and some (FOSA, FOSAA) are positively correlated with δ^{13}C in biota (i.e., increased proportions of benthic organisms in their diet). The relatively low K_D value for PFOS (log K_D: 1.1) and the low water concentrations indicate that PFOS produced from precursors in sediments over time will be dissolved in water, diluted due to the large body of water and removed due to water exchange. The detected concentrations of preFOS and SAmPAP diester in lake Tyrifjorden sediments indicate they are a large potential source for continuous input of PFOS to lake water and the food web. Biotransformation (in sediments) and water exchange and dilution are possible explanations for the relatively low PFOS concentrations reported in lake water compared to sediments. C9−C14 PFCA and long chained FTS dominated sediment concentration profiles, and concentrations in biota were positively correlated to δ^{13}C (C12−C14 PFCA and C12−C14 FTS). High K_D values were calculated for long chained FTS, while lower K_D values were calculated for PFCA. The shorter chain FTS, 6:2 FTS, has previously been reported to degrade to PFCA with a carbon chain length $\leq$ six.[83] Assuming that the longer FTS, which dominate here, follow the same degradation pattern, they will be transformed to PFCA with chain length shorter, or similar to, the perfluorinated alkyl chain in FTS (C $\leq$ 14). Thus, in addition to direct exposure to PFCA released from the factory, long chained FTS found in sediments are possibly precursors responsible for the high PFCA concentrations reported for crayfish and fish in the present study (due to biotransformation in crayfish/fish or in organisms which make up their diet). Indeed, transformation of 8:2 and 10:2 FTS (and unknown precursors) has previously been suggested to be a significant contribution to PFCA in an urban river in France,[73] and unknown PFCA precursors have been suggested to be a major exposure pathway to PFCA for fish from the Baltic sea.[69] Indications of significant contributions from PFAA precursors in sediments to PFAA concentrations in biota reported in the present study, and the proposed mechanisms (uptake into benthic organisms and biotransformation as they are transported through the food chain) warrant future laboratory exposure studies, as well as investigations of similar case sites expected to be dominated by PFAA precursor compounds.

Environmental Implications. The low water concentrations in lake Tyrifjorden reflect water exchange and dilution of dissolved compounds. Half-lives of 12 days have been reported for PFOS in blood of rainbow trout (*Oncorhyncus mykiss*) exposed to clean water.[84] It is likely that PFOS, and PFCA of similar chain length or shorter (that are more water-soluble than preFOS and the long FTS compounds), dissolved in lake water or taken up by fish, may be relatively quickly removed from the lake system. It follows therefore that the high biota concentrations reported here are indicative of continuous input to the system, which cannot be explained by active industrial sources in the area. Input from sediments/pore water is a likely explanation.

The overwhelming number of PFAS makes it practically impossible to analyze and track the behavior of each individual compound. However, as illustrated in this study, the complex behavior of PFAA and their precursors can be elucidated to some degree using a combination of targeted analysis of a

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limited number of compounds and nontargeted approaches such as EOF, in combination with the analysis of biota trophic levels and carbon sources. The results illustrate the importance of investigating other matrixes in addition to water, especially in cases where sources are unknown or the PFAS mixture released is not well characterized. PFAA exposure and future exposure potential to biota in the lake would be greatly underestimated if only PFAA concentrations (without precursors) in water and sediments were considered. Due to transformation of larger, less water-soluble, precursor compounds, sediments can be a source to PFAA, some of which are normally associated with uptake from water.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c04587.

Detailed site description; details for sampling and sample preparations; laboratory methods, including details for extraction methods and analytical methods (targeted PFAS and extractable organic fluorine); quality assurance procedures; details of statistical methods and data analyses; methods for calculating sediment−water partitioning coefficients (K_D values), bioaccumulation factors (BAF), biota-sediment accumulation factors (BSAF), biota trophic level and carbon sources, and fluorine mass balance; supplementary results and discussion (related to relationships between PFAS carbon chain length and K_D values, and accumulation factors); supplementary tables and supplementary figures (PDF)

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Notes

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