Fractionation and Bioaccumulation of Perfluorooctane Sulfonate (PFOS) Isomers in a Lake Ontario Food Web

MAGALI HOUDE,[†] GERTJE CZUB,[‡] JEFF M. SMALL,[†] SEAN BACKUS,[§] XIAOWA WANG,[†] MEHRAN ALAEE,[†] AND DEREK C.G. MUIR*,[†]

Aquatic Ecosystem Protection Research Division, Water Science and Technology Directorate, Environment Canada, Burlington, Ontario, Canada, Department of Applied Environmental Science (ITM), Stockholm University, Sweden, and Water Quality Monitoring Division, Water Science and Technology Directorate, Environment Canada, Burlington, Ontario, Canada

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The environmental ubiquity of perfluorooctane sulfonate (PFOS) is well-known. However, little is known about the environmental fate of individual PFOS isomers. In this study, we investigated the fractionation and the bioaccumulation of PFOS isomers in water, sediment, and biota collected from Lake Ontario. A total of six isomers, three perfluoro-monomethyl-substituted compounds, and three perfluoro-dimethyl isomers in addition to the linear PFOS (L-PFOS) were detected in water, sediment and biota. L-PFOS represented a much higher proportion of total PFOS (sum of linear and branched) in all organisms (>88%) compared to its proportion in technical PFOS (77%). The predominance of L-PFOS suggests a reduced uptake of branched isomers, a more rapid elimination of the branched isomers and/or a selective retention of the L-PFOS. The PFOS isomer profile found in biota was very similar to sediment, even for pelagic organisms such as zooplankton, suggesting greater partitioning of L-PFOS to biota and to sediment. The bioaccumulation factor (BAF) for L-PFOS between lake trout (whole fish) and water was estimated to be 3.4×10^4 L/kg compared with 2.9×10^3 L/kg for the monomethyl-substituted group (MM-PFOS). The remarkable difference between L-PFOS and branched isomer BAFs is due to an enrichment of branched isomers in water. The trophic magnification factor of L-PFOS (4.6 ± 1.0) was greater than MM-PFOS isomers (1.3 ± 0.17 to 2.6 ± 0.51), whereas dimethyl-PFOS showed no biomagnification. The results illustrate the important influence of molecular structure on the bioaccumulation of perfluoroalkyl sulfonates.

Introduction

Perfluorooctane sulfonate (PFOS) is one of the predominant anthropogenic perfluoroalkyl compounds (PFCs) being measured worldwide in the aquatic and the terrestrial environment, including humans (*1, 2*). The sources and pathways of PFCs to the environment are still not completely characterized. PFOS and other perfluorosulfonates have been released to the environment directly through uses such as aqueous fire-fighting foams, or indirectly through either abiotic (*3, 4*) and/or biotic (*5, 6*) degradation of precursor molecules such as the polyfluorinated sulfonamides ($CF_3(CF_2)_nSO_2NR_1R_2$). Despite the phase out of C_8 sulfonyl chemistry by the major manufacturer in 2001, sulfonamides are still present in the atmosphere and degradation of these contaminants is a continuing source of PFOS to the environment (*7, 8*).

Due to limited resolution of HPLC separations, earlier studies focused primarily on the detection of all PFOS isomers without further differentiation. However, electrochemical fluorination (ECF), the only manufacturing process for PFOS and its precursors, yields a mixture of linear and ≤30% branched isomers (*9*−*12*). The largest fraction of the branched isomers consists of perfluoromethyl-substituted compounds (20−30%) and less than 2% of perfluorodimethyl substituted isomers (*13*). Although PFOS is generally characterized to be persistent, toxic, and to have a tendency to accumulate in biological tissues (*14*), little is currently known about the environmental fate, toxicity, and bioaccumulation behavior (i.e., preferential uptake, accumulation, excretion, and metabolism) of the individual PFOS isomers.

PFOS and other PFCs have amphiphilic properties and do not sequester to the same degree into lipid-rich tissues as other halogenated organic contaminants such as polychlorinated biphenyls (PCBs). Preferential binding to proteins and consequently a preferential partitioning into protein-rich tissues such as blood and liver has been observed (*15, 16*). If sorption to renal peptides or serum albumin was related to the molecular structure of PFCs biological half-lives might be affected. The consequence would be a fractionation of the isomers along the food webs and thus an enhanced exposure of top predators to certain isomers. Indications for such a biological fractionation have been reported in rats orally exposed to perfluorooctanoate (PFOA). After cessation of dosing, the concentration ratio of linear to branched isomers increased in the serum (*17*). Additionally, specific sources of isomers may also play a role in the distribution of PFOS and other perfluoroalkyl acids (PFAs). An example is the nondetectable branched PFOA isomers in polar bear liver samples from the Hudson Bay in the Canadian Arctic while samples from East Greenland contained both linear and branched isomers (*18*). Linear isomers of PFOA also predominated in human blood serum (*19, 20*). These results could indicate the exposure to PFOA from a non-ECF source but could also indicate food web fractionation of PFA isomers, especially in the case of polar bears which are apex predators (*18*).

The aim of this study was to explore the transfer of PFOS isomers from sediment and water through the food web to a predatory fish, and thus to deepen the understanding of the biological fractionation of PFOS. The well studied Lake Ontario food web consisting of invertebrates (zooplankton, *Diporeia hoyi* and *Mysis relicta*), forage fish (rainbow smelt (*Osmerus mordax*), slimy sculpin (*Cottus cognatus*), and alewife (*Alosa pseudoharengus*)), and the predator fish lake trout (*Salvelinus namaycush*) was chosen for this study. The same food web has been investigated in a previous study by Martin et al. (*21*), who observed lower (total) PFOS concentrations in lake trout than in the benthic *Diporeia* and in slimy sculpin, which feeds predominantly on *Diporeia*. These

* Corresponding author phone: (905) 319-6921; fax: (905) 336-6430; e-mail: derek.muir@ec.gc.ca.
[†] Aquatic Ecosystem Protection Research Division, Environment Canada.
[‡] Stockholm University.
[§] Water Quality Monitoring Division, Environment Canada.

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trends deviated from patterns observed for other halogenated compounds such as PCBs, and hexabromocyclododecane which showed increasing lipid normalized concentrations with the trophic position in the same food web (*22, 23*). Martin et al. hypothesized that the sediment was the major source of the PFCs, and that the lower concentrations in lake trout were due to the low fraction of benthic fish in the lake trout's diet. In this study, samples from the Lake Ontario food web, including samples also used in the study from Martin et al. (*21*), have been analyzed for individual PFOS isomers.

Material and Methods

Sample Collection. Archived samples of biota, sediment, and water were used in this study (Supporting Information (SI) Table S1). Sampling locations are shown in SI Figure S1. The samples were taken in October 2002 at an offshore site near Niagara-on-the-Lake, Lake Ontario (43°3′N, 79°2′W; SI Figure S1). The organisms were processed as composites of whole individuals (sculpin: mean fish weight 9.7 g, three fish per composite, $n = 5$; smelt: mean fish weight 9.0 g, five fish per composite, $n = 6$; alewife: mean fish weight 26.9 g, two fish per composite, $n = 6$). Details about sample collection, preparation and storage can be found in ref *21*. From the same study, one pooled sample of *Diporeia* was available taken at the same time and location as the forage fish (*21*). In addition, a second pooled *Diporeia* sample was collected in September 2003 at the same location. The pooled *Mysis* sample available for this study was collected with a modified epibenthic sled at an offshore site near Coburg (central Lake Ontario, 43°7′N, 78°3′W; SI Figure S1) in September 2001. Each invertebrate sample was processed as bulk composite. Zooplankton samples were collected with a 100 μm net at 1 m sec^{-1} (0−103 m, Niagara basin, 43°25′N, 79°24′W; 0−187 m, central Lake Ontario, 43°43′N, 78°01′W; SI Figure S1) in July 2004 and 2006 from the research vessel CCGS Limnos. The lake trout samples were provided from the Great Lakes Fisheries Specimen Bank (GLFSB). All samples represent male adult lake trout (age of 3−5 years), collected with a gill net in September 2002 at Port Credit (Niagara Basin, 43°4′N, 79°6′ to 79°9′W, SI Figure S1). The samples represented individual whole fish homogenates. All fish and invertebrate samples were archived frozen (−20 °C) in glass containers lined with aluminum foil.

Water samples (10 m depth; 1 L bulk water unfiltered) were taken in July 2004, i.e. at the same locations and time frame as the zooplankton samples. Sediment samples originated from two sediment cores collected in central Lake Ontario (43°35′N, 78°01′W) in June 2002 from the CCGS Limnos by subsampling 10 cm diameter cores from a large box core (samples provided by N. Stock, University of Toronto; further details in ref *24*). From both cores, the uppermost two layers with a layer thickness of 1 cm each were analyzed, corresponding to the period 1995−2002, i.e., prior to the phase out of PFOS-related products (*24*). Additionally, two deep layers of core no. 2 (25 and 26 cm) were analyzed as sediment blanks and were used for recovery studies.

Extraction of PFOS Isomers. The samples were extracted using the methanol extraction method described by Tomy and co-workers (*25*). About 0.15 g of each biota composite and homogenate were extracted in a polypropylene centrifuge tube by blending 3 times with 2 mL of 100% methanol, followed by centrifugation for 10 min (3500 rpm). The combined extracts were concentrated under high-purity N_2 gas to a solvent volume of about 0.1 mL and then reconstituted to 1 mL with 50% MeOH:water, followed by vortexing for 15 s. The use of 50% MeOH:water precipitates lipids and improves peak resolution by high performance liquid chromatography (HPLC). After a final centrifugation for 15 min at 6900 rpm, the concentrates were filtered through 0.2 μm GHP membranes (Pall Corp., East Hills NY) into polypropylene vials for analysis. For the invertebrates, three replicates were extracted for each sample. The same extraction procedure was used for the sediment samples. For the bulk water, three replicates of 0.5 L were extracted for both sample locations. The samples were extracted on Oasis WAX SPE cartridges (150 mg 6 mL, conditioned with 4 mL 0.1% NH_4OH in methanol, followed by 4 mL 100% methanol and then 4 mL water). After a washing step with 2.5 mM sodium acetate, the samples were extracted with 0.1% NH_4OH in methanol. The extracts were concentrated under high-purity N_2 gas to a solvent volume of about 0.1 mL and then reconstituted to 1 mL with 50% MeOH:water, followed by filtration through 0.2 μm GHP membranes into polypropylene vials for analysis.

Analysis of PFOS Isomers by LC-MS/MS. Analysis of target analytes was performed using LC-MS/MS, consisting of a Agilent 1100 Series liquid chromatograph (modified to omit PTFE fittings) coupled with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems-MDS Sciex, Concord, ON, Canada). HPLC involved a 50 μL injection volume onto a pentafluorophenyl phase column (150 × 3 mm, 3 μm particle size; Thermo Electron, Runicorn, UK). The LC gradient was as follows: initial composition was 50% methanol and 50% water (both containing 10 mM ammonium acetate) and was maintained for 1 min, then increased to 60% methanol and maintained for 10 min, increased to 70% methanol for 3.5 min, to 75% methanol for 1 min, then to 85% for 1 min, and back to 50% methanol for another 5 min to allow the column to re-equilibrate to the starting conditions. The mass spectrometer was operated in negative electrospray ionization multiple reaction monitoring (MRM) mode with the following MS parameters: ion spray voltage −4500 V, at 375 °C, nebulizer gas 55 psi, heater gas 34, curtain gas 40 psi, interface heater 100 °C and collision gas 10 psi. Collision energy was maintained at −70 eV for the duration of the run. MRM transition related parameters were optimized, monitoring $m/z = 499-99$ (SO_3F^-) and $m/z = 499-80$ (SO_3^-). Following the analysis by triple quadrupole MS, several of the extracts were reanalyzed using an MDS Sciex QStar (QqToF), at 10 000 mass resolution and a −70 eV collision energy in negative ESI mode in order to determine the exact mass of the interfering compounds observed in the 499−80 transition. The LC conditions were the same as outlined above. The concentrations of L-PFOS were quantified based on a ^{13}C-PFOS internal standard (Wellington Laboratories, Guelph, ON, Canada).

In order to understand more clearly the bioaccumulation of PFOS in the aquatic food web, and potential differences between benthic and pelagic species, we estimated L-PFOS and branched PFOS concentrations in abiotic and biotic samples from Lake Ontario. Isomer results based on quantification with the L-PFOS standard were adjusted using the response factors for individual isomers reported by Riddell et al. (*26*).

The efficiency of methanol extraction and influence of the sample matrix on recoveries was investigated by spiking (in triplicate) sediment, arctic char muscle, and zooplankton samples with technical PFOS and examining isomer to total PFOS ratios and recoveries in each matrix following extraction with the method of Tomy et al. (*26*). Results (SI Tables S2 and S3) showed no effect of matrix on the ratios with either the m/z 499 to 80 or m/z 499 to 99 transition and average recoveries of L-PFOS of 98−102% (SI Table S3).

Bioacumulation and Biomagnification Factors. The bioaccumulation factor (BAF; [organisms]/[water]; L/kg wet weight) and biomagnification factor (BMF; [predator]/[prey]) were calculated for organisms in order to compare the bioaccumulation potential of branched versus linear PFOS. A second method determined trophic level corrected BMF for individual species: $BMF_{TL} = [predator]/[prey]/(TL_{predator}/$

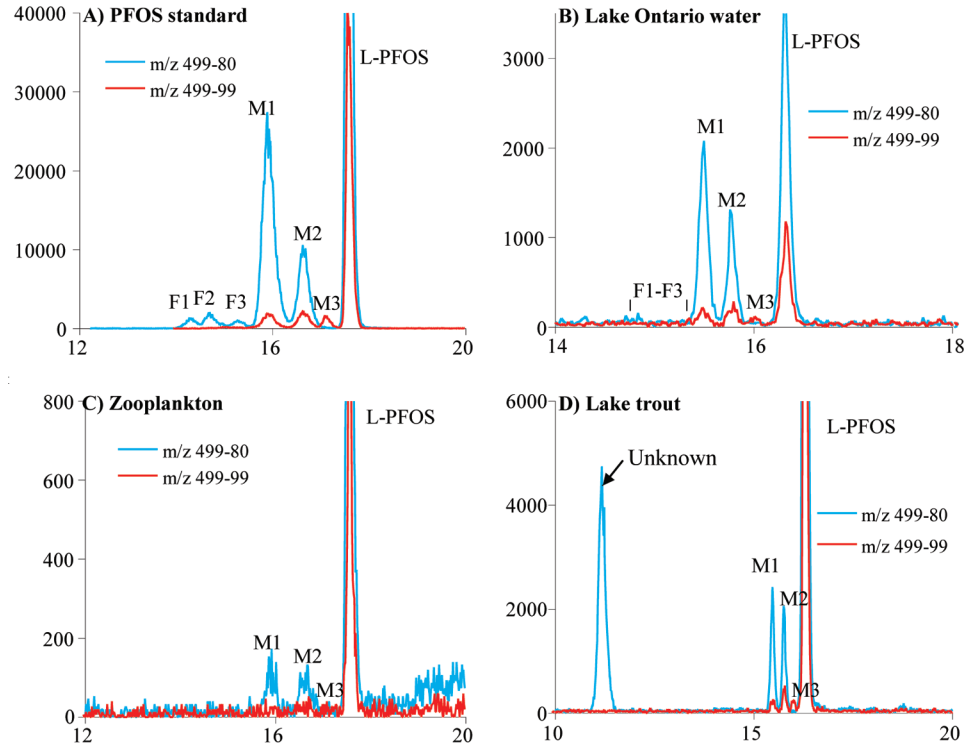

FIGURE 1. Chromatograms of (A) PFOS technical standard, (B) water (C) zooplankton, and (D) lake trout from Lake Ontario showing L-PFOS, monomethyl-PFOS, and dimethyl-PFOS isomers.

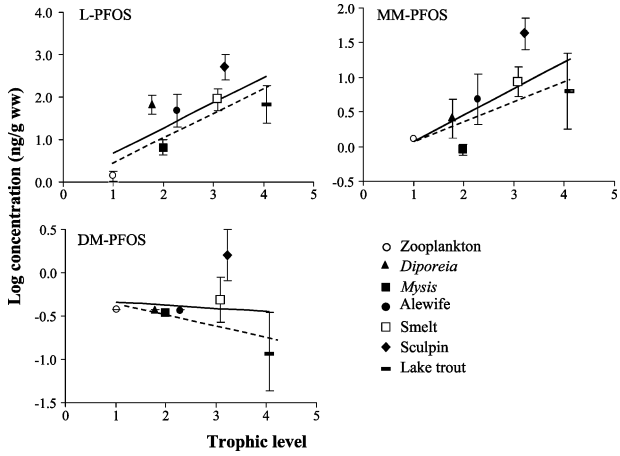

FIGURE 2. Log concentration (ng/g ww) of L-PFOS, MM-PFOS, and DM-PFOS isomers in organisms from Lake Ontario versus trophic level. Symbols represent mean concentration ± 95% confidence intervals. Solid lines represent the regression of log concentration vs trophic level for all organisms; dashed lines with benthic feeders (diporeia and sculpin) omitted.

TL_{prey}) (*27*). All concentrations are on a wet weight basis. The trophic levels of organisms were calculated based on $\delta^{15}N$ in the same manner as Martin et al. (*21*); $\delta^{15}N$ is given in SI Table S1. The trophic magnification factors (TMFs) were estimated based on the relationship between trophic level and log PFOS isomer concentrations (TMF = antilog of the regression slope) (*27*). Nondetectable concentrations were replaced with 1/2 the detection limit of 0.98 ng/g ww (for L-PFOS) in order to calculate means.

Results and Discussion

PFOS Standard. Six PFOS peaks, in addition to the linear PFOS (L-PFOS), were chromatographically resolved from the technical PFOS standard (Figures 1A and 22). The molecular structures of the major PFOS isomers are shown in SI Table S3. Three of these isomers were identified as dimethyl PFOS (DM-PFOS; labeled as F1 to F3; Figure 1A) based on their relative retention times (*13*); these isomers were detected with the *m/z* 499 to 80 transition. Based on ref *13*, we deduced three perfluoro monomethyl isomers, labeled as M1-PFOS to M3-PFOS. The M3 peak was identified as 1-CF_3-PFOS, the M2 peak is 6-CF_3-PFOS, and M1 is likely a coelution of 3-CF_3-, 4-CF_3-, and 5-CF_3-PFOS. The M3 isomer was only detected with the *m/z* 499 to 99 transition (Figure 1A), while all other isomers were best detected with 499 to 80 transition. The proportion of PFOS isomers (i.e., 76% of L-PFOS, 20% of monomethylated isomers (MM-PFOS) and 3.6% of DM-PFOS) detected in the standard is similar to the results reported by Langlois and Oehme (*13*) and Arsenault et al. (*9*).

Water and Sediment. The mean total PFOS concentration (5.9 ng/L) detected in water from Lake Ontario is consistent with other recent reports which show mean concentrations of 4.9 ng/L (cited in (*24*)) to 6.3 ng/L (*28*). The PFOS isomer pattern in bulk water samples from Lake Ontario was similar to PFOS technical standard but with different proportions (Table 1; SI Figure S2A and B). L-PFOS predominated in water (Figure 1B) with mean proportions (% of L-PFOS on the total sum of linear and branched isomers) ranging from 43 to 56% (compared to 77% for the standard) depending on the ion transition monitored. An enrichment of MM-PFOS (Sum of M1, M2, and M3) was observed in both water samples (43 to 57%; Table 1). These proportions (range for *m/z* 80 and 99 for M1 = 17−21% and M2 = 22−28%; M3 only detected at *m/z* 99 = 3.9−8.0%) are as twice as high as what found in the PFOS standard (19.6% for MM-PFOS). DM-PFOS isomers were detected (*m/z* 80; 1−2%) in only one sample at low peak areas (SI Figure S2B).

Invertebrates and Fish. L-PFOS was the predominant isomer detected in sediment samples (81−89%; Table 1) with proportions higher than the PFOS standard and water samples which suggest that the linear isomer is more strongly associated with sediment. No major differences were observed in the PFOS isomer pattern between layer 1 (0−1 cm

TABLE 1. Percentage (%) of PFOS Isomers (L-PFOS; M1, M2, M3 = MM-PFOS) Detected in Abiotic and Biotic Samples Collected from Lake Ontario (m/z 80 and 99). Dimethyl-PFOS Isomers Are Reported As Total DM-PFOS Due to the High Proportions of Non-Detectable Values. Results for Isomers Are Adjusted for Instrumental Response after Riddell et al. (*27*)

sample	*N*	L-PFOS %	M1%	M2%	M3%	total MM-PFOS %	total DM PFOS%
PFOS standard	3	76.9 ± 0.09	5.1 ± 0.18	10.6 ± 0.28	3.9 ± 0.20	19.6 ± 0.18	3.58 ± 0.12
water	4	43−56	17−21	22−28	3.9−8.0	43−57	1.0−2.0
sediment	9	81−89	2.2−5.9	4.6−10	2.7−4.4	11−19	0[a]
zooplankton	6	95−100	0.4−3.0	0.1−1.0	0	0.4−3.0	0
Mysis	3	91−92	1.7−2.4	3.9−5.2	0	7.6−8.4	0
Diporeia	5	95−96	0.4−0.6	2.0−2.8	0.7−1.1	3.1−4.1	0
alewife	4	90−91	2.3−2.4	4.2−4.5	2.5−2.8	9.1−9.6	0
smelt	6	88−92	2.4−4.2	4.2−7.1	0.5−0.9	7.2−12	0.4−0.5
sculpin	3	91−92	1.8−2.3	4.6−4.8	0.9−1.1	7.4−8.3	0.2−0.3
lake trout	5	88−93	2.5−4.1	3.8−7.1	0.9−1.1	6.9−12	0.2−0.3

[a] Zero indicates that the isomer was not detected.

depth) and layer 2 (1−2 cm) of sediment samples. Slightly lower intensity of MM-PFOS (11−19%) was detected in all sediment samples compared to the technical standard. No DM-PFOS isomers were observed (SI Figure S2B). It was impossible to compare these results with other data as no other reference of the pattern of PFOS isomer contamination in water and sediment could be found in the scientific literature.

L-PFOS was the only isomer detected in zooplankton samples at *m*/*z* 99 (Figure 1C) while M1 and M2 were detected at low count intensity (*m*/*z* 80) in three of the four zooplankton samples (data not shown). The same pattern, at similar proportions, was observed for *Mysis* where L-PFOS was predominant (Table 1, SI Figure S2A); MM-PFOS (M1 and M2) could be detected at *m*/*z* 80 but no dimethyl branched isomers were observed (SI Figure S2B). In *Diporeia*, linear and monomethyl isomers were detected in both samples at both transitions (SI Figure S2A and B), however DM-PFOS was absent.

The ratio of each isomer group found in invertebrates (high proportion of L-PFOS followed by lower presence of MM-PFOS) was similar to the pattern of contamination observed in sediment rather than water. Zooplankton feed exclusively on phytoplankton, while *Mysis* feed primarly on phytoplankton, sediment/detritus, and zooplankton, and *Diporeia* prefer sediment/detritus (*29*). Thus zooplankton achieved a similar isomer pattern as *Diporeia* despite lack of sediment contact. The results suggest that the predominance of L-PFOS in sediment and invertebrates is related to greater sorption of the linear isomer and that both the upper sediment layers and the invertebrates are close to a chemical equilibrium partitioning with the ambient water. This would be in line with the bioaccumulation of other halogenated compounds such as PCBs in invertebrates for which, although to some extent still controversial, recent field and laboratory studies supported the equilibrium partitioning approach (*30*).

An unidentified peak was observed in fish and invertebrate extracts at the retention time of 11.4 min with an exact mass of *m*/*z* 498.2864 (Figure 1D). Previous studies (*31, 32*) suggest that the contaminant is taurodeoxycholate, a bile salt, with a similar mass as PFOS (with a difference of approximately 0.64 amu) and the same MS/MS transition (*20*). Further discussion of this peak is provided in the Supporting Information.

The results of the analysis of four species of fish from Lake Ontario showed that L-PFOS predominated in all samples (Table 1, and SI Figure S2A and B). MM-PFOS were found in all fish species at higher proportions than in invertebrates. M2 (*m*/*z* 99) and M1 (*m*/*z* 80) were the main MM-PFOS detected in fish. DM-PFOS isomers were only found at low intensity in three species of fish with smelt and sculpin demonstrating the largest proportions of all analyzed species (0.5 and 0.3%, respectively; *m*/*z* 80; SI Figure S2B, Table 1). Overall, in all organisms investigated in this study, the linear isomer represented a higher proportion (88−100%) of total PFOS (sum of linear and branched for either *m*/*z* 80 or 99) compared to technical PFOS (77%).

Similar predominance of linear isomers was observed for perfluorocarboxylates in liver samples of polar bears from Greenland and Canada although this could be due to input of fluorotelomer related linear perfluorocarboxylates (*18*). High percentages of L-PFOS were also reported for human serum and plasma from Sweden, Australia, and the UK (58−70%), as well as for Canadian human serum (∼80%) (*19, 20*). In both studies, also the presence of monosubstituted- and disubstituted-PFOS isomers was confirmed. Based on these results, the pattern of PFOS contamination in human seems to be more similar to PFOS technical standard compared to the proportions of isomers observed in the aquatic environment.

Bioaccumulation and Biomagnification of PFOS Isomers. The concentrations of total PFOS found in organisms are generally similar to the results reported by Martin et al. (*21*). L-PFOS and MM-PFOS are bioaccumulating in the lake Ontario food web as indicated by BMFs and trophic level corrected BMFs (BMF_{TL}) greater than 1 (Table 2) and BAFs for all PFOS isomers in the thousands. As a consequence of the enrichment of branched PFOS isomers in water, the BAFs calculated for total PFOS (as done in previous studies where no differentiation of individual isomers was performed) are lower than the BAFs of L-PFOS, the dominating isomer in the biotic samples (Table 2). Most obvious is this effect for zooplankton, where the linear isomer predominated (95−100%). The opposite effect can be observed for the lake trout:prey biomagnification factor due to the stronger retention of L-PFOS in the food web. However, this effect is much less pronounced apart from zooplankton for which the BMF is about 12.5% higher for total PFOS. Note though that zooplankton is of minor importance in the lake trout's diet compared to the other prey organisms. BMFs for M1, M2, M3, and sum of MM-PFOS, except for lake trout:smelt and lake trout:sculpin, were also > 1. The BMF_{TL} also showed bioaccumulation of L-PFOS and MM-PFOS for lake trout: invertebrates with factors lower than uncorrected BMFs (Table 2). BMF_{TL}s, were often close to or below 1 for forage fish, which are the main prey items of lake trout. These results suggest that the linear and monoperfluoromethyl branched isomers biomagnify in the Lake Ontario food web and support observations from previous studies (SI Table S4) (*33, 34*). High BMFs were observed for the benthic sculpin:*Diporeia* compared to other pelagic organisms (Table 2). Elevated PFOS concentrations were also reported by Martin et al. (*21*) for

TABLE 2. Bioaccumulation (BAF), Biomagnification (BMF), Trophic Level Corrected BMF (BMF_{TL}) and Trophic Magnification factor (TMF) of PFOS Isomers in a Lake Ontario food web[a]

	L-PFOS	M1	M2	M3	MM-PFOS (M1+M2+M3)	DM-PFOS[b]	sum PFOS
BAF (L/kg)							
zooplankton:water	650	–[c]	–	–	–	–	240
Mysis:water	3000	75	290	–	170	–	1200
Diporeia:water	32 000	200	1580	1270	960	–	13 000
alewife:water	24 000	640	2100	3470	1800	–	9800
smelt:water	45 000	1520	4600	1710	3200	–	19 000
sculpin:water	234 000	5400	22 500	11 950	14 600	–	95 000
lake trout:water	34 000	1270	4040	2580	2900	–	16 000
BMF							
lake trout: zooplankton	60	–	–	–	–	–	66
lake trout: *mysis*	12	17	14	–	17	–	13
lake trout: *diporeia*	1.2	6.4	2.5	2	3.0	–	1.2
lake trout: alewife	1.6	2	1.9	0.7	1.6	–	1.6
lake trout: smelt	0.84	0.8	0.9	1.5	0.91	0.25	0.84
lake trout:sculpin	0.16	0.2	0.2	0.2	0.20	0.09	0.17
sculpin:d*iporeia*	9.0	27	14	9.4	15	–	7.5
BMF_{TL}							
lake trout: zooplankton	15	–	–	–	–	–	16
lake trout: *mysis*	6.0	8.3	6.9	–	8.4	–	6.2
lake trout: *diporeia*	0.51	2.8	1.1	0.89	1.3	–	0.5
lake trout: alewife	0.89	1.1	1.1	0.42	0.90	–	0.9
lake trout: smelt	0.64	0.64	0.67	1.1	0.69	0.19	0.64
lake trout:sculpin	0.13	0.19	0.14	0.17	0.16	0.07	0.13
sculpin:d*iporeia*	0.25	15	7.8	5.2	8.4	–	4.1
TMF[b,e] (±std error)							
including benthic organisms	3.7 ± 0.94	2.7 ± 0.50	2.3 ± 0.43	1.5 ± 0.21	3.0 ± 0.59	0.87 ± 0.12	3.8 ± 0.98
excluding benthic organisms	3.9 ± 0.78	2.3 ± 0.41	2.0 ± 0.34	1.3 ± 0.15	2.8 ± 0.52	0.77 ± 0.09	4.2 ± 0.87

[a] Results based on the *m/z* 499 to *m/z* 80 transition. [b] Dimethyl-PFOS are reported as total F1, F2, F3 due to the high proportions of nondetectable values. [c] Dash indicates factor could not be calculated due to nondetectable values. Nondetectable concentrations were replaced with half the method detection limit. [e] All TMFs are statistically significant ($P < 0.05$; $n = 24$ or 32) except for DM-PFOS with benthic organisms included.

these two species leading the authors to suggest that sediment was a major source of contamination in the Lake Ontario food web.

Trophic Magnification Factors (TMFs). TMFs for PFOS isomers in the Lake Ontario food web (Table 2; Figure 2) were above 1 with the highest factor observed for L-PFOS (TMF=3.9 ± 0.78). TMFs for the individual MM-PFOS M1, M2, and M3 were respectively 2.3 ± 0.41, 2.0 ± 0.34, and 1.3 ± 0.15, with the benthic organisms with high PFOS concentrations excluded. The TMF for total sum of MM-PFOS was 2.8 ± 0.52 compared to a negative TMF of 0.77 ± 0.09 for DM-PFOS (Figure 2). The relationships between log M1, M2, M3, MM-PFOS concentrations and trophic level of organisms were statistically significant ($P < 0.05$). The TMF results with all biota were very similar although the fit of the regression of log concentrations vs TL was not as good due to high concentrations in sculpin (Table 2).

The absence or low proportions of MM- and DM-PFOS in this food web and, on the other hand, the positive TMFs for linear and MM-PFOS isomers suggest that differences in partitioning and pharmacokinetics are both playing a role in PFOS bioaccumulation. A recent study conducted on a western Canadian Arctic marine food web suggested different pharmacokinetic behavior of PFOS isomers based on the report of a 50% proportion of branched PFOS isomers and 50% of L-PFOS in Arctic cod homogenates compared to only 4% of branched isomers in blood and liver of their bearded and ringed seal predators (*35*). In general, results from the present study and data collected for human and other wildlife corroborate the observations made by Loveless et al. (*17*) in an experimental dosing study in rodents where it was suggested that branched PFOA has absorption differences or a more rapid elimination compared to the linear isomers. De Silva et al. (*36, 37*) reported a significant faster elimination of branched perfluorocarboxylate isomers in fish with enhanced concentrations of the more water soluble branched isomers in urine of rats but found no differences for L-PFOS and MM-PFOS isomers. In the present study, however, the similarity in the PFOS isomer profile between sediment and organisms also suggests that sediment is a source of PFOS contamination in this Lake Ontario food web and/or that the partitioning into organic material in general is favored for the linear isomer. The very low proportions of MM-PFOS in zooplankton, despite significant amounts in water, points to large differences in partitioning properties of linear vs branched isomers.

Based on the BMFs and TMFs found for PFOS isomers, the concentration trend through the different trophic levels, and comparison to technical PFOS mixture, DM-PFOS isomers seem to have distinctly different bioaccumulation characteristics compared to L- and MM- isomers. The differences in toxicokinetics for linear and perfluorodimethyl branched PFOS isomers and the different partitioning properties for branched vs L-PFOS need to be taken into account in toxicological and environmental studies. The differences in environmental behavior of the isomers imply that as fresh sources decline, the ultimate fate of PFOS will be for only the linear isomer to remain, at least in the biosphere.

Supporting Information Available

A map of the sampling area, detailed information on the abiotic and biotic samples, estimated concentrations of L-PFOS and branched-PFOS in water, sediment, and organisms from lake Ontario, the molecular structures of the major PFOS isomers, and a review of BAFs and BMFs of total PFOS available in the literature. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication

The first paragraph of the Results and Discussion section was modified in the version published ASAP November 14, 2008; the corrected version published ASAP December 11, 2008.

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