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Isomer-Specific Trophic Transfer of Perfluorocarboxylic Acids in the Marine Food Web of Liaodong Bay, North China

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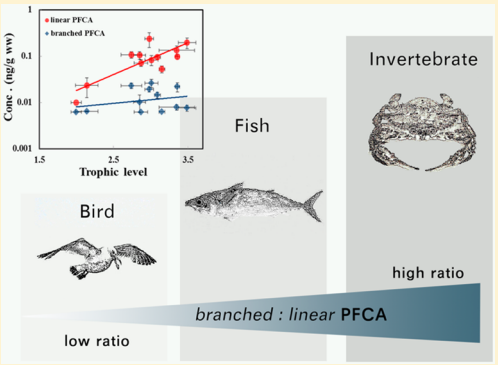
Supporting Information

ABSTRACT: Trophic transfers of perfluorocarboxylic acids (PFCAs) have been well studied in aquatic food webs; however, most studies examined PFCAs as single compounds without differentiating isomers. In this study, an in-port derivatization GC-MS method was used to determine PFCA (perfluorooctanoic acid, PFOA; perfluorononanoic acid, PFNA; perfluorodecanoate acid, PFDA; perfluoroundecanoate acid, PFUnDA; perfluorododecanoate acid, PFDoDA; perfluorotridecanoate acid, PFTriDA, and perfluorotetradecanoate acid, PFTeDA) structural isomers in 11 marine species including benthic invertebrates, fishes, and gulls collected in November 2006 from Liaodong Bay in China. The total concentrations of linear PFCAs were 0.35−1.10, 0.93−2.61, and 2.13−2.69 ng/g ww, and the corresponding percentages of branched PFCAs to linear PFCAs were 6.6−15.5%, 4.2−9.9%, and 4.5−6.0% in invertebrates, fishes, and birds, respectively. Except for linear PFOA, significant positive relationships were found between the concentrations of all the target linear PFCAs and trophic levels, and the trophic magnification factors (TMFs) ranged from 1.90 to 4.88. Positive correlations between the concentrations of branched PFCAs isomers and trophic levels were also observed but were without statistical significance. The relatively high biomagnification of linear isomers of PFCAs would lead to low percentages of branched PFCAs to total PFCAs in organisms at high trophic levels. This study for the first time clarified isomer-specific trophic transfers of PFCAs in a marine food web.



INTRODUCTION

Perfluoroalkyl acids (PFAAs) including perfluorosulfonates (PFSAs) and perfluorocarboxylic acids (PFCAs) are widely used in the manufacturing of stain repellents, surface coatings, firefighting foams, insecticides, and cleaners. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are the most extensively studied PFAs and have been detected in blood and tissues of wildlife and humans globally, even in the remote Arctic regions together with other related perfluoro-chemicals.[1−9] Recent studies demonstrated that the toxicities of branched PFOA in exposed rats and mice were different from the linear forms,[10] and thus the isomer-specific environmental fates are of concern for assessing the ecological and human exposure risks.

Industrial synthesis of PFAAs is conducted primarily by two routes: electrochemical fluorination (ECF) and telomerization. From 1947 to 2002, PFOS, PFOA, and other perfluoroalkyl-containing compounds were produced largely by ECF.[11] ECF products are a mixture of structural isomers predominantly composed of the linear perfluoroalkyl chain (∼70−80%) with smaller quantities of branched chain isomers (∼20−30%). Among the branched isomers of ECF PFOA, the isopropyl branch isomer is the most abundant isomer which accounts for 9%, while internal CF_3 branched PFOA isomers including the *3m*-, *4m*-, and *5m*-PFOA collectively consist of 13%.[12] In 2002, 3M voluntarily ceased production of PFOA by the ECF method, and since then PFOA production has been based primarily on telomerization and the PFOA product is typically linear, possibly with isopropyl geometry.[11,13] Besides the direct discharging of PFOA, linear PFOA can be transformed from the precursors such as fluorotelomer alcohols (FTOHs) and perfluoroalkyl phosphoric acids (PAPs) via abiotic and biotic reactions in the environment.[14−17] Therefore, the relatively low percentages of branched PFCAs in biological samples have been attributed to additional input from an exclusively linear isomer source such as telomerization and transformation from their precursors,[18−23] while the percentage of branched isomers in the isomer profile may be confounded by different trophic transfers of structural isomers as exemplified by PFOS in previous studies.[24] Several studies have reported the trophic transfer of perfluorinated compounds (PFCs) in aquatic food webs, especially for PFOS and PFCAs with eight to 12 carbons.[5,6,9,25−29] However, these studies took PFCAs as single compounds without differentiating its isomers, and, also, sparse information is available for the fractionation of the PFCAs isomers along the food web.

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Table 1. Molecular Formula, Relative Retention Times (RRTs) and Relative Abundances of the Fragments Ions of Derivatized Linear PFCAs Obtained from Full Scan MS with an NCI Source

			relative abundance of ions (m/z amu)				
compound	molecular formula of derivatives	RRT	[M-158]	[M-120]	[M-92]	[M-76]	[M-20]
n-PFOA	$C_7F_{15}CO_2C_4H_9$	9.45	28	73	100	21	29
n-PFNA	$C_8F_{17}CO_2C_4H_9$	11.18	33	3	100	23	26
n-PFDA	$C_9F_{19}CO_2C_4H_9$	12.95	47	60	100	27	24
n-PFUnDA	$C_{10}F_{21}CO_2C_4H_9$	14.72	46	48	100	30	20
n-PFDoDA	$C_{11}F_{23}CO_2C_4H_9$	16.71	73	47	100	46	20
n-PFTriDA	$C_{12}F_{25}CO_2C_4H_9$	17.76	74	39	100	36	18
n-PFTeDA	$C_{13}F_{27}CO_2C_4H_9$	18.45	78	31	100	50	0

An in-port derivatization using tetrabutylammonium hydrogen sulfate (TBAS) followed by gas chromatography−mass spectrometry (GC-MS) analysis has shown greater potential for separation of PFOS isomers with greater sensitivity.[30] In this study, we for the first time applied the sensitive in-port TBAS derivatization GC-MS method to the simultaneous determination of PFCAs isomers in the biological samples from the Liaodong Bay food web in China. The main objective of this study was to explore the concentrations of PFCAs isomers with eight to 14 carbons in biological samples from Liaodong Bay and to evaluate trophic transfers of PFCAs isomers in marine organisms.

MATERIALS AND METHODS

Chemicals and Reagents. The isomer standards of PFOA and perfluorononanoic acid (PFNA) including two linear isomers (*n*-PFOA and *n*-PFNA, >98%) and 5 branched isomers (*3m*-PFOA, *4m*-PFOA, *5m*-PFOA, *iso*-PFOA, and *iso*-PFNA, >90%), standards of linear PFCAs including perfluorodecanoate acid (PFDA, >98%), perfluoroundecanoate acid (PFUnDA, >98%), perfluorododecanoate acid (PFDoDA, >98%), perfluorotridecanoate acid (PFTriDA, >98%), perfluorotetradecanoate acid (PFTeDA, >98%), and their corresponding stable isotope labeled standards including $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, and $^{13}C_2$-PFDoDA were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Sep-Pak Plus AC-2 and Oasis WAX (6 cm^3, 150 mg, 30 μm) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, USA). TBAS (99%) was purchased from J&K Scientific Ltd. (Beijing, China). Methanol and acetonitrile (HPLC grade) were purchased from Fisher Chemicals (New Jersey, USA). Ammonia solution (28−30%) was purchased from Alfa Aesar (Massachusetts, USA), and ethyl ether (HPLC grade) was purchased from Burdick & Jackson (Michigan, USA). Water was obtained from purification of distilled water by a Milli-Q Synthesis water purification system (Millipore, Bedford, MA, USA).

Sample Collection. Liaodong Bay is located in the northern region of the Bohai Sea, northern China, with an approximate area of 10,000 km^2 and maximum depth of 32 m. Components of the aquatic food web from Liaodong Bay were collected in November 2006 (40°42N; 121°46E) as described previously.[31,32] The food web included two species of mollusk, the short-necked clam (*Ruditapes philippinarum*) and rock shell (*Rapana venosa*), one crustacean, Chinese mitten-handed crab (*Eriocheir sinensis H. Milne-Eswards*), seven fishes, the red-eye mullet (*Liza hematocheila*), small yellow croaker (*Pseudosciaena polyactis*), China anchovy (*Thrissa kammalensis*), Japanese Spanish mackerel (*Scomberomrus niphonius*), half-smooth tongue-sole (*Cynoglossus semilaevis*), flathead fish (*Platycephalus indicus*), and black spot-fed bass (*Lateolabrax japonicas*), and one species of seabird, the black-tailed gull (*Larus crassirostris*) which consists of black-tailed gulls and juvenile black-tailed gulls. As shown in Figure S1, seabirds were sampled along the coast of Liaodong Bay (40°52N; 121°51E) in November 2006. Both black-tailed gulls and juvenile black-tailed gulls are resident seabirds in Liaodong Bay and build their nests on the coast and feed mostly on insects, crustaceans, and fish.[33] Invertebrates and fishes were caught with a bottom trawler, and seabirds were collected before their winter migration commenced. All samples were stored at −20 °C prior to analysis. The concentrations of the 7 PFCAs and their corresponding isomers were measured in the whole bodies of invertebrates (n = 3 for each species) and in both muscle and liver tissues of fishes (n = 3 for each species) and seabirds (n = 3 for black-tailed gull, n = 4 for juvenile black-tailed gulls).

Extraction and Cleanup of Biological Samples. The sample preparation process included extraction of target compounds using acetonitrile and cleanup using WAX cartridges followed by AC activated charcoal cartridges. In brief, approximately 1.0−1.5 g wet weight (ww) of homogenized tissue was transferred to a 15 mL polypropylene (PP) centrifuge tube. Fifty microliters (50 μL) of 50 μg/L mass-labeled internal standards $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, and $^{13}C_2$-PFDoDA were added to the sample. The sample was extracted with 5 mL of acetonitrile by shaking for 20 min at 300 rpm. After centrifugation at 4000 rpm for 15 min, the supernatant was transferred to a new 15 mL PP tube and then diluted with 6 mL of pure water. The extract solution was passed through a WAX cartridge, which was preconditioned with 6 mL of methanol, followed by 6 mL of ultrapure water at a flow rate of 1−2 drops/s. After the cartridge was washed with 5 mL of distilled water and rinsed with 4 mL of methanol, the target PFCAs were eluted with 6 mL of methanol containing 0.5% NH_4OH. The extraction solution was passed through the Plus AC-2 cartridge and then dried under gentle nitrogen stream for in-port derivatization.

Sample Preparation for in-Port Derivatization. The extracts were derivatized by TBAS according to the method for analyzing PFOS isomers.[30] Briefly, 0.4 g of TBAS and 4 mL of diethyl ether were mixed by vortex mixer for 1 min and then sonicated for 1 h to ensure the dissolution of TBAS. Next, the upper phase (TBAS in diethyl ether) was diluted with 4 mL of ethyl ether serving as the in-port derivatization reagent solution. The dried extracts were reconstituted with 50 μL of diluted TBAS solution. After vortex mixing for 1 min and ultrasonic treatment for 2 h, the samples were analyzed by gas chromatography with negative chemical ionization mass spectrometry (GC-NCI-MS).

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Table 2. Mean Biological Parameters and Concentrations of PFCAs in Organisms (pg/g wet weight) Collected from Liaodong Bay, North China[a]

species	RP	ESME	RV	LH	PP	TK	SN	CS	PI	LJ	J-LC	LC
TL	2 ± 0.07	2.74 ± 0.14	2.87 ± 0.09	2.14 ± 0.15	2.85 ± 0.08	2.98 ± 0.06	3.01 ± 0.09	3.09 ± 0.04	3.15 ± 0.04	3.36 ± 0.03	3.35 ± 0.44	3.49 ± 0.12
n	3	3	3	3	3	3	3	3	3	3	4	3
length (cm)				38 ± 1.7	27 ± 2.3	14 ± 0.58	47 ± 1.2	30 ± 1.7	33 ± 2.3	78 ± 1.2	52 ± 4.0	45 ± 8.5
weight (g)				671 ± 31	168 ± 31	16 ± 1.2	525 ± 12	170 ± 12	175 ± 58	3540 ± 170	998 ± 334	615 ± 341
n-PFOA	129	143	336	101	102	62	50	251	71	145	326	372
	(116−138)	(112−161)	(297−370)	(85−115)	(76−116)	(47−74)	(36−65)	(216−285)	(69−74)	(90−186)	(150−443)	(197−482)
iso-PFOA	ND	ND	81	12.8	13.4	ND	ND	55	13.0	22	40	30
			(72−86)	(12.8−12.9)	(13.1−13.7)			(54−56)	(12.9−13.0)	(12−27)	(12−79)	(26−51)
n-PFNA	66	183	106	117	85	64	91	169	181	151	185	326
	(61−69)	(123−226)	(101−109)	(99−133)	(65−122)	(51−74)	(47−136)	(146−193)	(131−236)	(140−158)	(108−245)	(212−470)
iso-PFNA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-PFDA	54	234	182	276	214	170	336	331	278	260	489	541
	(49−57)	(205−275)	(164−202)	(233−314)	(149−265)	(145−191)	(284−380)	(320−342)	(165−401)	(208−300)	(247−868)	(154−805)
iso-PFDA	ND	ND	ND	10	6	7.3	7.1	18.0	8.1	7.2	36	40
				(8−16)	(6−7)	(7.0−7.5)	(7.1−7.2)	(17.9−18.1)	(7.8−8.4)	(6.9−7.4)	(31−74)	(14−74)
n-PFUnDA	24	97	101	182	346	472	675	272	197	338	250	374
	(22−25)	(77−115)	(98−103)	(154−208)	(140−453)	(372−583)	(440−907)	(260−283)	(157−244)	(306−373)	(149−347)	(191−468)
iso-PFUnDA	ND	ND	ND	9	ND	ND	12	20	ND	6.7	12	11
				(8−10)			(7−13)	(20−21)		(6.6−6.8)	(8−18)	(6−18)
n-PFDoDA	24	142	172	185	515	825	870	414	213	544	414	493
	(21−24)	(131−162)	(157−185)	(168−211)	(425−566)	(642−929)	(56−117)	(387−440)	(136−297)	(490−602)	(324−514)	(247−751)
iso-PFDoDA	ND	ND	53	ND	36	50	101	54	8	11	16	16
			(50−57)		(28−49)	(42−55)	(68−118)	(51−56)	(7−9)	(10−12)	(6−20)	(ND-23)
n-PFTriDA	43	149	140	56	440	405	526	233	197	468	341	405
	(33−51)	(136−174)	(135−147)	(45−62)	(426−463)	(332−452)	(506−546)	(204−262)	(190−208)	(440−483)	(112−654)	(221−545)
iso-PFTriDA	ND	ND	ND	ND	ND	7.3	19	ND	ND	9.6	9	7
						(7.2−7.5)	(18−21)			(9.4−9.8)	(6−15)	(ND-9)
n-PFTeDA	ND	112	74	24	109	250	86	100	54	102	140	204
		(97−129)	(64−88)	(12−32)	(87−128)	(187−298)	(70−111)	(93−106)	(47−64)	(92−118)	(101−182)	(155−258)
iso-PFTeDA	ND	24	ND	6.7	11	20	27	15	ND	23	8	8
		(19−28)		(6.6−6.8)	(9−13)	(18−22)	(21−32)	(13−17)		(17−26)	(7−9)	(7−9)

[a]RP = short-necked clam (Ruditapes philippinarum); ESME = Chinese mitten-handed crab (Eriocheir sinensis H. Milne-Eswards); RV = rock shell (Rapana venosa); LH = redeye mullet (Liza hematocheila); PP = small yellow croaker (Pseudosciaena polyactis); TK = China anchovy (Thrissa kammalensis); SN = Japanese spanish mackerel (Scomberomrus niphonius); CS = half-smooth tongue-sole (Cynoglossus semilaevis); PI = flathead fish (Platycephalus indicus); LJ = black spotfed bass (Lateolabrax japonicas); LC = black-tailed gull (Larus crassirostris); J-LC = juvenile black-tailed gull (Larus crassirostris). TL, trophic level; ND, not detected. All values were indicated by mean (range). Whole body was used to determine PFCAs isomers.

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GC/MS Determination. In-port TBAS derivatization coupled with GC-MS analysis was performed using a GC with NCI-MS detector (Shimadzu QP 2010 plus). Chromatographic separation was achieved on a DB-5MS capillary column (60 m × 0.25 mm × 0.1 μm film thickness; J&W Scientific). The carrier gas was helium at a constant flow rate of 3.0 mL/min, and the injection volume was 3 μL. A splitless injector was used and held at 300 °C. The temperature program was from 40 °C (2 min) to 90 °C (3 min) at the rate of 4 °C/min and then increased to 300 °C (5 min) at the rate of 50 °C/min. Ionization was performed in NCI mode using methane as reagent gas. The interface and ion temperatures were maintained at 285 and 210 °C, respectively. Individual standard of PFCAs was prepared and injected into GC/MS operating in the full scan mode (m/z 50−850) to get the fragments ions of derivatized PFCAs. Selected ion-monitoring mode (SIM) was used for quantitative analysis, and the ions at m/z $[M\text{-}20]^-$, $[M\text{-}76]^-$, and $[M\text{-}92]^-$ were monitored (Table 1).

Quality Assurance and Quality Control (QA/QC). Identification of the linear PFCAs and branched PFOA in biological samples was accomplished by comparing the retention time and the relative abundance of monitored ions with corresponding standards. Quantification of the linear PFCAs and branched PFOA and PFNA isomers was achieved using an internal standard method with calibration against standard solutions. The method was also used to determine 5 isomers of other PFCAs. Since other branched PFCAs isomers were not commercially available, we assumed any peaks appearing at the same m/z as the linear PFCAs to be branched isomers, and the elution time and order of PFOA isomers were used to identify the potential PFCAs. Identification of PFCAs was accomplished by monitoring three fragments ions, $[M\text{-}20]^-$, $[M\text{-}76]^-$, and $[M\text{-}92]^-$, which were the same as those for linear PFCAs with standards. Considering the different instrument sensitivity of isomers, we assumed the relative instrument responses between linear isomers and branched isomers of PFCAs without standards to be the same as PFOA, and the concentrations of those branched isomers were quantified using the relative sensitivity of PFOA isomers according to eq 1

$$C_{\text{branched}} = \text{Area}_{\text{branched}}/\text{Area}_{\text{linear}} \times \text{Area}_{\text{linear\_PFOA}} /\text{Area}_{\text{branched\_PFOA}} \times C_{\text{linear}} \quad (1)$$

where C_{branched} is the calculated concentrations of branched isomers in biological samples, $\text{Area}_{\text{branched}}$ is the peak area of branched isomers in biological samples, $\text{Area}_{\text{linear}}$ is the peak area of linear isomers of corresponding PFCAs, $\text{Area}_{\text{linear\_PFOA}}$ is the area of linear PFOA, and $\text{Area}_{\text{branched\_PFOA}}$ is the peak area of isomers of PFOA with the same concentration as linear PFOA; while C_{linear} is the concentrations of corresponding linear PFCAs.

Procedure blank experiments were performed along with each batch of samples. Standard injections were done among two or three sample injections, and derivatization reagent injections were done after each standard injection to monitor background contamination.

The compound-specific matrix spiking recoveries were determined by triplicate analysis of invertebrate homogenate, vertebrate muscle, and liver which spiked with 50, 100, and 150 ng/g of mixed standards respectively, which were about 3−5-fold higher than the concentrations shown in the unspiked tissue matrixes. In all kinds of samples, mixed internal standards at 50 ng/mL for each were added. To assess the instrument detection limits (IDLs), analysis of derivatized 2.0 pg PFCAs standards was conducted. The IDL was defined as the concentration producing a peak with a S/N ratio of 3. As for PFOA with detectable blank contamination, the method detection limits (MDLs) were defined as the mean blank +3 times standard deviation, and the MDLs of other PFCAs in each tissue matrix were defined as three times the noise. Concentrations of target analytes were determined based on calibration curves that were generated using concentration series of 0.5, 2, 5, 10, 20, 40, 80, and 160 ng/mL, which showed strong linearity (correlation coefficients >0.99).

Data Analysis. Different from lipophilic pollutants, PFCAs are proteinophilic and are generally found to have the highest concentrations in the liver.[25] In previous studies, the liver or plasma of mammals and muscle tissues in species occupying low trophic levels from a food web have been used to estimate the TMF values of PFCAs, leading to an overestimation of the biomagnification factor for these compounds.[6,34] According to previous studies,[9] PFCAs concentrations in the liver were 10−20-fold higher than that in other organs and muscle although the different PFCA homologues may have a different tissue distribution. However, when the body fractions of the tissues were considered, the liver had only a minor contribution, while other organs such as the kidney lost importance with less than 1% of the total burden.[9,35] Therefore, in the present study, the liver and muscle were analyzed to estimate whole body concentration for fishes and gulls (eq 2), and whole body of invertebrates were analyzed. A similar calculation has been used to estimate whole body concentration in the terrestrial food chain[35]

$$C_{\text{wholebody}} = C_{\text{liver}} \times f_{\text{liver}} + C_{\text{muscle}} \times (1 - f_{\text{liver}}) \quad (2)$$

where C_{muscle} and C_{liver} are the concentrations of muscle and liver, respectively, and f_{liver} is the mass fraction of this tissue in the whole body. For those results lower than the MDL, half of the MDL was assigned.

Concentrations of PFCAs in the whole body were used in the TMF calculation by eq 3

$$\text{Log PFCAs concentration} = a + b\text{TL} \quad (3)$$

where trophic levels, determined by stable nitrogen isotopes, ranged from 2.0 to 3.75 in all individual organisms (Table 2) which have been reported in our previous study,[31,32] and the details are given in the Supporting Information. The b in eq 1 was used to calculate TMF (eq 4)

$$\text{TMF} = 10^b \quad (4)$$

All data analyses such as linear regression were performed with SPSS 15.0. Statistical significance was defined as $p < 0.05$.

RESULTS AND DISCUSSION

Derivatization and Method Validation. An in-port TBAS derivatization followed by GC-NCI-MS analysis has been used to identify PFOS isomers in previous studies.[29] The present paper for the first time applied this method to the simultaneous determination of PFCAs isomers to achieve high analytical sensitivity and short analytical time. Only linear standards for PFCAs except for PFOA and PFNA could be commercially obtained. In the MS spectra of linear PFCAs including linear PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, and PFTeDA, all molecular ions $[M\text{-}H]^-$ of TBAS

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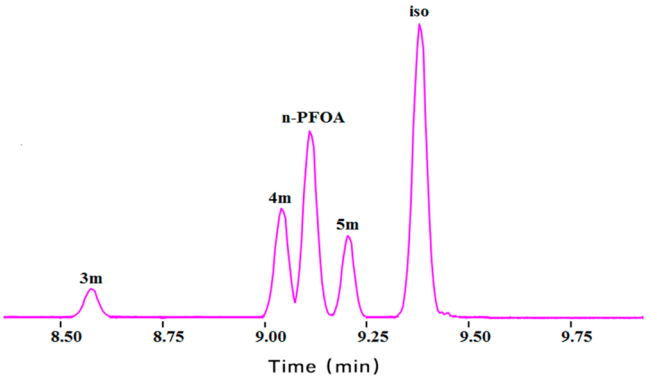

Figure 1. GC-MS(NCI) determination of individual standards of PFOA isomers including *3m*-, *4m*-, *5m*-, *iso*-, and *n*-PFOA. The concentration of each isomer standard was 50 ng/mL.

Table 3. Parameters of Regression Analyses between Logarithm of PFCAs Concentration in Whole Body and Trophic Levels and Trophic Magnification Factors (TMFs)

	TMF	r^2	*p*
n-PFOA	1.57	0.092	0.339
iso-PFOA	2.15	0.226	0.118
n-PFNA	1.90	0.363	**0.038**
n-PFDA	2.61	0.544	**0.006**
iso-PFDA	1.78	0.176	0.174
n-PFUnDA	3.76	0.459	**0.015**
n-PFDoDA	4.88	0.534	**0.007**
iso-PFDoDA	2.13	0.119	0.273
n-PFTriDA	4.78	0.731	**<0.001**
n-PFTeDA	4.87	0.674	**0.001**
iso-PFTeDA	1.42	0.079	0.376

derivatives for target compounds produced the major product ions, $[M\text{-}HF_3\text{-}CO_2C_4H_8(158)]^-$, $[M\text{-}HF\text{-}CO_2C_4H_8(120)]^-$, $[M\text{-}HF\text{-}OC_4H_8(92)]^-$, $[M\text{-}HF\text{-}C_4H_8(76)]^-$, and $[M\text{-}HF(20)]^-$ (Table 1). Such fragmentation pattern of the backbone is similar to that of TBAS derivatized PFOS, but without detection of TBAS group at *m/z* 137 which is the most abundant fragments of PFOS derivative.[30] As exemplified by the MS spectrum of *n*-PFOA, the ion at *m/z* 378 ($[M\text{-}92]^-$) shows the highest relative abundance which was used for quantitative determination of linear PFCAs, and, together with ions at *m/z* 394 ($[M\text{-}76]^-$) and *m/z* 450 ($[M\text{-}20]^-$), these three ions were chosen as monitoring ions. Of the seven target PFCAs, only PFOA and PFNA have commercially obtainable isomer standards including two linear isomer (*n*-PFOA and *n*-PFNA) and five branched isomers, *3m*-PFOA ($F[CF_2]_4CF[CF_3]CF_2COOH$), *4m*-PFOA ($F[CF_2]_3CF[CF_3]CF_2CF_2COOH$), *5m*-PFOA ($F[CF_2]_2CF[CF_3]CF_2CF_2CF_2COOH$), *iso*-PFOA ($[CF_3]_2CF[CF_2]_4COOH$), and *iso*-PFNA ($[CF_3]_3CF[CF_2]_4COOH$). The in-port derivatization GC-MS method for separating and determining the isomers of PFOA was validated. The five isomers were fully separated, and the instrument response showed isomeric discrimination. The instrument response of *n*-PFOA was 5.6, 2.0, 1.7, and 0.6 times higher than *3m*-PFOA, *4m*-PFOA, *5m*-PFOA, and *iso*-PFOA, respectively (Figure 1). The IDLs of *3m*-PFOA, *n*-PFOA, *4m*-PFOA, *5m*-PFOA, *iso*-PFOA, *n*-PFNA, *iso*-PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, and PFTeDA were 1.68, 0.24, 0.48, 0.41, 0.15, 0.2, 0.12, 0.3, 0.18, 0.32, 0.18, and 0.4 ng/mL, respectively. For those isopropyl isomers of PFCAs except for PFOA and PFNA without authentic standards, we assumed that instrument response factors between linear and isopropyl isomers were the same as that between linear and isopropyl PFOA. Thus, the IDLs of these branched isomers were calculated to be 0.18, 0.11, 0.19, 0.11, and 0.24 ng/mL for *iso*-PFDA, *iso*-PFUnDA, *iso*-PFDoDA, *iso*-PFTriDA, and *iso*-PFTeDA, respectively.

A WAX SPE cartridge can effectively reduce interferences in complex bioligical matrixes which have been widely used for previous PFCs analysis.[30] In the present study, we found out that the instrument was heavily contaminated, and the response decreased about 4−7-fold after several sample injections. Therefore, additional cleanup steps are necessary to eliminate potential interferences. We found out that an AC-2 activated charcoal cartridge was able to further reduce interferences of biological samples. By applying our method that incorporated cleanup by WAX and AC-2 cartridges, no obvious response decrease was observed. The compound-specific matrix spiking recoveries were determined for each tissue by triplicates, and

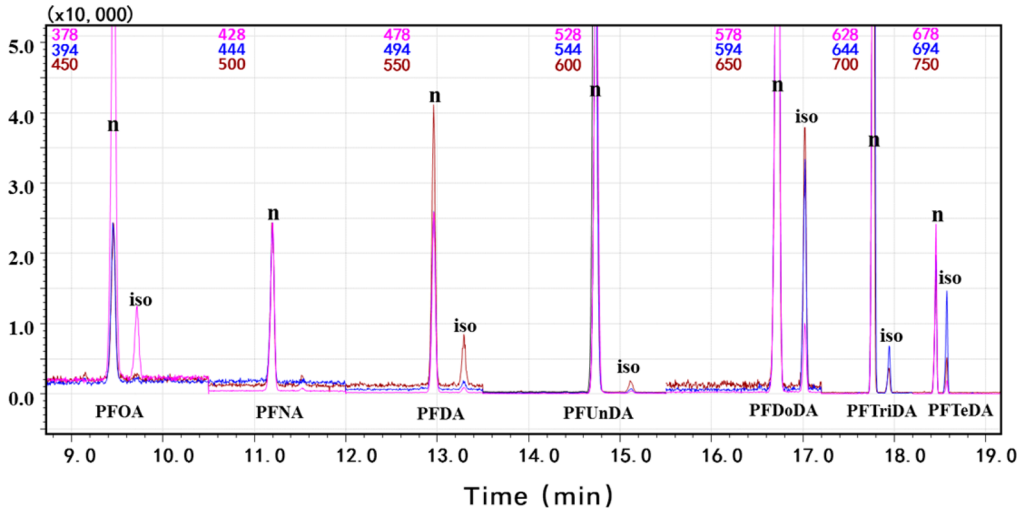

Figure 2. GC-MS(NCI) chromatogram of PFCAs isomers in biota samples in Liaodong Bay. Peaks labeled with "n" correspond to linear isomers and peaks labeled with "iso" are ascribed to branched isomers.

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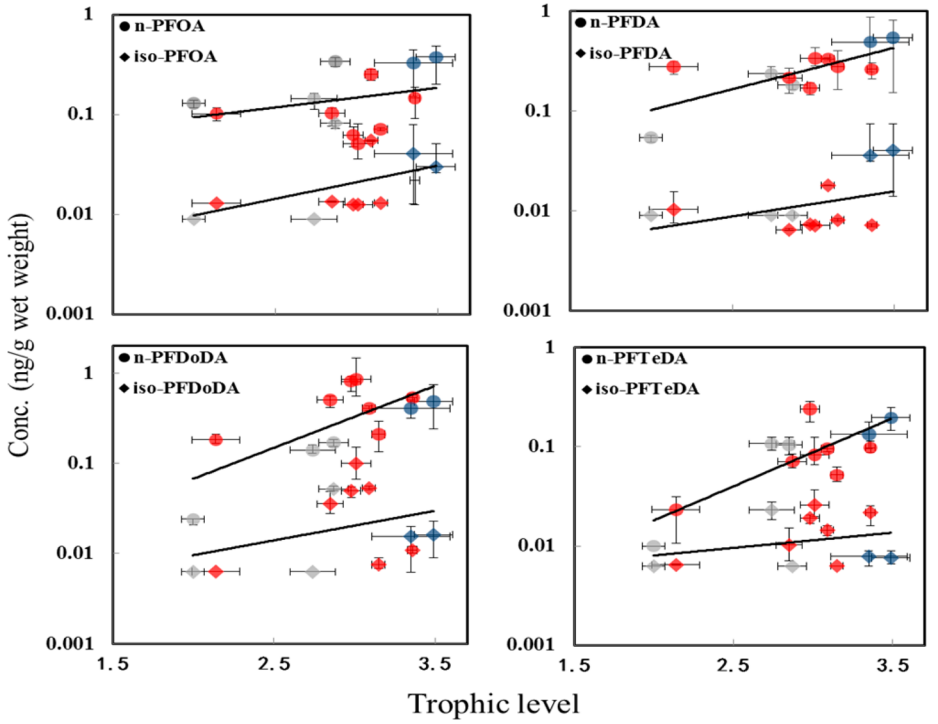

Figure 3. Relationships between log-transformed concentrations of PFCAs (ng/g ww) and trophic levels in organisms from Liaodong Bay. Horizontal error bar indicated ± standard deviation. Vertical error bar indicated range of concentration. Gray, red, and blue represented invertebrates, fish, and gulls, respectively. Regression based on the mean concentrations of PFCAs in each species.

the values for five isomers of PFOA and other linear PFCAs except for PFDA ranged from 74% to 111%. The recoveries of their stable isotope surrogate standards ranged from 68% to 117% (Table S1). For PFDA, matrix enhancement was observed, and its spiking recoveries were 131% in the muscle and 141% in the liver, which were similar to those (118% in the muscle and 134% in the liver) of its surrogate, $^{13}C_2$-PFDA. The relative recoveries were 111% for muscle and 105% for liver, and thus the quantitation should be accurate by the use of surrogate standard. For those branched isomers without authentic standards, the actual recoveries in the biological matrixes were unknown and based on the responses of corresponding linear standards. The MDLs of 3*m*-, 4*m*-, 5*m*-, *iso*-, and *n*-PFOA isomers were 0.17, 0.06, 0.05, 0.02, and 0.03 ng/g ww, respectively. For *iso*- and *n*-PFNA, the MDLs were 0.01 and 0.02 ng/g ww, respectively. As for all other PFCAs, the MDLs ranged from 0.02 to 0.03 ng/g ww. It should be noted that the analytical time of the present method was 26 min, which was much shorter than previously reported GC/MS (more than 75 min).[19,20] The analysis time of the present method is also shorter than previously reported LC-MS/MS using the PFP column for PFCAs analysis.[5] Due to lack of authentic standards for branched isomers of PFCAs except for PFOA and PFNA, we assumed that instrument response factors between linear and isopropyl isomers were the same as that between linear and isopropyl PFOA. As exemplified by PFNA in Figure S2, the instrument response factor between linear and *iso*-PFNA was 0.60 ± 0.05, similar to that (0.61 ± 0.04) between linear and *iso*-PFOA, suggesting that the assumption described above would be reasonable.

Concentrations of PFCAs Isomers in Aquatic Organisms. The concentrations of PFCAs isomers detected in the livers and muscles of 7 fish species and one gull species including black-tailed gulls and juvenile black-tailed gulls were listed in Tables S2 and S3, and the concentrations in the whole body of all species are listed in Table 2.

Linear PFCAs. The concentrations of PFCAs were determined in both liver and muscle samples to estimate the whole-body concentrations as conducted in previous studies.[33] All linear PFCAs were detected in the livers of fish and gulls. Of 7 *n*-PFCAs, *n*-PFOA (4.3 ng/g wet weight (ww)), *n*-PFNA(4.4 ng/g ww), and *n*-PFDA (5.5 ng/g ww) showed the relatively high concentrations in the livers of black-tailed gulls, while other *n*-PFCAs showed the highest concentrations in the livers of China anchovy which was 6.3 ng/g ww for *n*-PFUnDA, 10 ng/g ww for *n*-PFDoDA, 11 ng/g ww for *n*-PFTriDA, and 3.5 ng/g ww for *n*-PFTeDA. Considering its relatively low trophic level, the highest detected concentration of most PFCAs in China anchovy is unexpected but accordant with our previous studies,[32,36] which may be due to the high lipid content of the fish species compared to other organisms. As for the most often reported *n*-PFCAs, the concentration of *n*-PFOA and *n*-PFNA in gull liver was higher than that in Chinese pond heron liver (0.76 ng/g ww for *n*-PFOA and 2.7 ng/g ww for *n*-PFNA), but the reverse was the case for *n*-PFDA (8.8 ng/g ww).[26] All linear PFCAs were also detected in the muscles of fishes and gulls with much lower concentrations. Of 7 *n*-PFCAs, *n*-PFOA, *n*-PFDA, and *n*-PFTeDA showed the highest concentrations in the muscles of gulls (ranged from 0.21 ng/g ww for *n*-PFOA to 0.34 ng/g ww for *n*-PFDA). Concentrations of *n*-PFCAs ranged from 0.023 ng/g ww for *n*-PFTeDA in redeye mullet to 0.79 ng/g for *n*-PFDoDA in Japanese spanish mackerel in the muscles of fish which were comparable to the levels in fish muscles from an Arctic marine food web.[25] The concentration distribution between muscle and liver varied for the different PFCA homologues and isomers, and, generally, PFCAs concentrations in the muscle were 2.3-fold (*iso*-PFOA) to 13-fold (*n*-PFTriDA) lower than those in the liver. Such extreme

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preference of PFCAs for liver has been attributed to the fact that PFCAs bind preferentially to certain proteins in the blood and liver.[37,38] In spite of higher concentrations in liver, the liver contributed minor to the whole body PFCAs amounts when the respective body fractions of the tissues are considered, since the mass fraction of liver in the whole body is limited to about 2−4%. Thus, we estimated the concentration in the whole body of fishes and gulls according to eq 1, and *n*-PFOA, *n*-PFNA, and *n*-PFDA showed the highest concentrations in the whole body of gulls (ranged from 0.32 ng/g ww for *n*-PFNA to 0.54 ng/g ww for *n*-PFDA).

In the whole body of invertebrates from Liaodong Bay, longer-chain PFCAs showed much lower concentrations (ranged from 0.024 ng/g ww to 0.18 ng/g ww) than those of gulls and fishes. Especially, all *n*-PFCAs showed the lowest concentrations (ranged from for 0.024 ng/g ww *n*-PFUnDA to 0.054 ng/g ww for *n*-PFDA) in one invertebrate, short-necked clam, which was at the lowest tropical level of the studied food web. However, relatively high concentrations of *n*-PFOA was observed in invertebrates (ranged from 0.13 ng/g ww to 0.33 ng/g ww), and the greatest concentration of *n*-PFOA (0.33 ng/g ww) was found in another kind of invertebrate rock shell, higher than all of the investigated fish species. This is consistent with Lake Ontario biological samples in which diporeia, another kind of burrowing benthic invertebrate, has the greatest concentration of PFOA in the food web.[5]

Branched PFCAs. Branched PFCAs were less frequently detected in the liver samples with detection frequency of 68%. Among the four branched isomers of PFOA, only *iso*-PFOA (0.030−0.26 ng/g) was detected in the marine species, which was reasonable given that *iso*-PFOA is the most prevalent branched isomer in ECF PFOA. The concentrations of branched PFCAs may be slightly overestimated due to the relatively low purity (>90%) of the commercial standard. It was reported that the most dominant isomer in the 3 M ECF PFOA product was *n*-PFOA (78%), followed by *iso*-PFOA (10.1%), *4m*-PFOA (3.90%), and *5m*-PFOA (3.12%). The concentration of branched PFNA in all biological samples from Liaodong Bay was below its MDL, and this phenomenon was also observed in most Lake Ontario biological samples.[23] Similar to PFOA, a single branched isomer was observed for the longer chain PFCAs from PFDA to PFTeDA in the livers of fishes and gulls as shown in Figure 2. It should be noted that all the peaks showed similar relative retention time to their corresponding linear isomers, and peaks were observed for selected monitoring ions. Based on the information, it was hypothesized that these isomers corresponded to the isopropyl isomers and that the same strategy of using retention time and monitoring ions to postulate branched isomers has also been adopted in a previous study.[23]

It is interesting to note that an even−odd pattern for the profile of *iso*-isomers was observed which was opposite to the trend of *n*-PFCAs previously observed in the livers of polar bears[18] and Chinese sturgeon.[39] The concentration of *iso*-PFCAs with an even chain was always higher than the preceding odd-numbered *iso*-PFCAs. For example, in the livers of black spotfed bass, the concentration of *iso*-PFOA (0.17 ng/g ww) was higher than that of the preceding *iso*-PFNA (<MDL), *iso*-PFDA (0.050 ng/g ww) was higher than *iso*-PFUnDA (0.028 ng/g ww), and *iso*-PFDoDA (0.23 ng/g ww) was greater than *iso*-PFTriDA (0.032 ng/g ww) (Figure S3). This even−odd pattern for *iso*-PFCAs was also reported in Arctic samples including sediment,[40] polar bears,[41] and seals.[20] The even-chain *iso*-PFCAs with higher concentration may be due to the preferential emission of these compounds in technical products.

Similar to that in the livers, only *iso*-PFCAs were detected in the muscles with less detection frequency. The detection frequency for *iso*-PFOA, *iso*-PFDoDA, and *iso*-PFTeDA was 55%, 44%, and 55%, respectively; *iso*-PFDA was only detected in redeye mullet (8.8 pg/g) and half-smooth tongue-sole (15 pg/g); *iso*-PFUnDA was only detected in Japanese spanish mackerel (12 pg/g) and half-smooth tongue-sole (21 pg/g); and *iso*-PFTriDA was only detected in Japanese spanish mackerel (19 pg/g), while *iso*-PFNA in all muscle was below the limit of detection. While the *iso*-PFCAs with even number carbons were generally detected (>77%) in the whole body of fishes and gulls, only *iso*-PFOA (81 pg/g) and *iso*-PFDoDA (53 pg/g) were detected in rock shell and *iso*-PFTeDA (24 pg/g) in Chinese mitten-handed crab.

The percentages of branched PFCAs to linear PFCAs were calculated to better characterize the relative contributions of PFCAs isomers. The percentages in the invertebrates were in the range of 6.6−15.5%, higher than those (4.2−9.9%) in fishes and in gulls (4.5−6.0%), showing trophic level-dependent decrease. The percentage in fish species were comparable to the levels in trout (2−10%) in Lake Ontario foodweb.[23]

Trophic Transfer of PFCAs Isomers in the Food Web. Trophic transfers of PFCAs isomers in the food web of Liaodong Bay were investigated to assess their biomagnifications. Linear regression was used to evaluate the association between PFCAs concentrations and trophic levels. Among seven linear PFCAs, all *n*-PFCAs displayed a positive linear relationship with trophic levels, and statistical significance ($p < 0.05$) was found for all *n*-PFCAs (p values ranged from <0.001 to 0.038) except for *n*-PFOA ($p = 0.34$) (Table 3). The TMFs were calculated for these compounds and were all greater than 1 (TMF = 1.90 for *n*-PFDA, 2.61 for *n*-PFDA, 3.76 for *n*-PFUnDA, 4.88 for *n*-PFDoDA, 4.78 for *n*-PFTriDA, and 4.87 for *n*-PFTeDA), indicating their biomagnification (Figures 3and S4). The TMFs of linear PFCAs generally displayed an increasing trend with increasing carbon chain length and then peaked at PFDoDA, which is consistent with the results observed in Ontario and Arctic marine food webs.[5,6] The TMFs of PFDA and PFUnDA in the present paper were lower than those (4.18 for PFDA and 4.79 for PFUnDA) in Canadian Arctic marine food web, but the TMFs of PFDoDA and PFTeDA were higher than those (2.96 for PFDoDA and 1.97 for PFTeDA) in the aforementioned study.[25] One paper reported the TMF (2.45) of PFTriDA in the food web of Lake Ontario in Canada which were lower than that (4.78) in the present paper.[26] In Arctic marine food web, high trophic level (TL > 5) organisms including marine mammals were engaged, and liver or plasma concentrations in mammals and muscle tissue concentrations in other species were used for estimating the TMF values.[25] In the present paper, the highest TL in the current study was 3.49 for black-tailed gulls, and whole body concentrations for all species were used to calculate TMFs. Such differences may lead to different TMF values as well described in previous studies.[6,34]

For *iso*-PFCAs, the TMF was calculated only when the detection frequency was higher than 70% as used in our previous study.[36] Different from *n*-PFCAs, no significant biomagification was found for any branched PFCAs isomers, although the positive correlation between the concentrations of *iso*-isomers of target PFCAs and trophic levels were generally observed (Figure 3). Previous studies have indicated faster

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clearance of branched PFOA compared to *n*-PFOA in fishes and rats.[42−44] Therefore, the significant biomagnification of *n*-PFCAs may be due to their preferential bioaccumulation. Alternatively, metabolism of FTOHs may be another potential reason since FTOHs were produced via telomerization, and therefore *n*-PFCAs could be preferentially produced from FTOHs.[14−17] We detected FTOHs concentrations in sediment samples from the same investigated region with total FTOHs concentrations from 0.19 to 0.52 ng/g dry weight (dw).[45] Since all the branched PFCAs isomers except for *iso*-PFOA and *iso*-PFNA were not commercially available, as mentioned above, we quantified the concentrations of *iso*-PFCAs using the standards of *n*-PFCAs after adjusting the relative response in GC-MS using PFOA isomers assuming that instrument response factors between linear and isopropyl isomers were the same as that between linear and isopropyl PFOA. While the reasonability of such assumption was proven by the fact that the ratio between *iso*-PFNA and *n*-PFNA was very close to that between *iso*-PFOA and *n*-PFNA, there are the uncertainties on quantification of the concentrations for other *iso*-PFCAs detected in the present study. However, the TMFs of *iso*-PFCAs based on the relative increase of concentration per trophic levels were accurate and presented for the first time. The TMF values of PFCAs were also calculated after excluding gulls species, and significance was also found for *n*-PFDA (TMF = 2.17, $p = 0.05$), *n*-PFUnDA (TMF = 4.60, $p = 0.03$), *n*-PFDoDA (TMF = 6.32, $p = 0.01$), *n*-PFTriDA (TMF = 5.78, $p = 0.001$), and *n*-PFTeDA (TMF = 5.04, $p = 0.007$) except for *n*-PFNA (TMF = 1.48, $p = 0.2$). For *n*-PFOA and all branched PFCAs, the TMF regressions are not significant with or without bird data.

Overall, this study clarified the isomer-specific trophic transfers of PFCAs in the marine food web. The relative high biomagnification of linear isomers would lead to a higher percentage of linear PFCAs in organisms with increasing trophic level. Since the toxicities of linear PFCAs were demonstrated higher than branched forms in recent studies,[10] PFCAs may pose higher ecological risks for organisms at higher trophic level.

■ ASSOCIATED CONTENT

Supporting Information

Figures and Tables addressing (1) Stable nitrogen isotope analysis and calculations of trophic level; (2) Method Detection Limits and Recoveries ($n = 3$) of PFCAs in Biological Samples; (3) Mass Fraction of Liver in the Whole Body and Concentrations of PFCAs in Livers of 7 Fish Species and One Species of Gull; (4) Concentrations of PFCAs in Muscle (pg/g wet weight) of 7 Fish Species and One Species of Gull; (5) Location of sampling sites; (6) GC-MS(NCI) determination of individual standards of *n*- and *iso*-PFNA; (7) Calibration curves of linear PFCAs; (8) Concentrations of *iso*-PFCAs in livers of fishes; (9) Relationships between log-transformed concentrations of *n*-PFNA, *n*-PFUnDA, and *n*-PFTriDA (ng/g ww) and trophic levels in organisms from Liaodong Bay. 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.

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■ REFERENCES

(1) Giesy, J. P.; Kannan, K. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* **2001**, *35*, 1339−1342.

(2) Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, P. D.; Helle, E.; Nyman, M.; Giesy, J. P. Accumulation of perfluorooctane sulfonate in marine mammals. *Environ. Sci. Technol.* **2001**, *35*, 1593−1598.

(3) Olsen, G. W.; Hansen, K. J.; Stevenson, L. A.; Burris, J. M.; Mandel, J. H. Human donor liver and serum concentrations of perfluorooctanesulfonate and other perfluorochemicals. *Environ. Sci. Technol.* **2003**, *37*, 888−891.

(4) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C.; Mabury, S. A. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environ. Sci. Technol.* **2004**, *38*, 373−380.

(5) Martin, J. W.; Whittle, D. M.; Muir, D. C.; Mabury, S. A. Perfluoroalkyl contaminants in a food web from Lake Ontario. *Environ. Sci. Technol.* **2004**, *38*, 5379−5385.

(6) Tomy, G. T.; Budakowski, W.; Halldorson, T.; Helm, P. A.; Stern, G. A.; Friesen, K.; Pepper, K.; Tittlemier, S. A.; Fisk, A. T. Fluorinated organic compounds in an eastern Arctic marine food web. *Environ. Sci. Technol.* **2004**, *38*, 6475−6481.

(7) Smithwick, M.; Mabury, S. A.; Solomon, K. R.; Sonne, C.; Martin, J. W.; Born, E. W.; Dietz, R.; Derocher, A. E.; Letcher, R. J.; Evans, T. J. Circumpolar study of perfluoroalkyl contaminants in polar bears (Ursus maritimus). *Environ. Sci. Technol.* **2005**, *39*, 5517−5523.

(8) Van de Vijver, K. I.; Hoff, P.; Das, K.; Brasseur, S.; Van Dongen, W.; Esmans, E.; Reijnders, P.; Blust, R.; De Coen, W. Tissue distribution of perfluorinated chemicals in harbor seals (*Phocavitulina*) from the Dutch Wadden Sea. *Environ. Sci. Technol.* **2005**, *39*, 6978−6984.

(9) Houde, M.; Bujas, T. A.; Small, J.; Wells, R. S.; Fair, P. A.; Bossart, G. D.; Solomon, K. R.; Muir, D. C. Biomagnification of perfluoroalkyl compounds in the bottlenose dolphin (Tursiops truncatus) food web. *Environ. Sci. Technol.* **2006**, *40*, 4138−4144.

(10) Loveless, S.; Finlay, C.; Everds, N.; Frame, S.; Gillies, P.; O'Connor, J.; Powley, C.; Kennedy, G. Comparative responses of rats and mice exposed to linear/branched, linear, or branched ammonium perfluorooctanoate (APFO). *Toxicology* **2006**, *220* (2−3), 203−217.

(11) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32−44.

(12) Stevenson, L. *Comparative analysis of fluorochemicals*; United States Environmental Protection Agency Public Docket, 2002; AR-2261150.

(13) Benskin, J. P.; Yeung, L. W. Y.; Yamashita, N.; Taniyasu, S.; Lam, P. K. S.; Martin, J. W. Perfluorinated acid isomer profiling in water and quantitative assessment of manufacturing source. *Environ. Sci. Technol.* **2010**, *44*, 9049−9054.

(14) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38*, 3316−3321.

(15) Vesine, E.; Bossoutrot, V.; Mellouki, A.; Le Bras, G.; Wenger, J.; Sidebottom, H. Kinetic and mechanistic study of OH- and Cl-initiated oxidation of two unsaturated HFCs: $C_4F_9CH_5CH_2$ and $C_6F_{13}CH_5CH_2$. *J. Phys. Chem. A* **2000**, *104*, 8512−8520.

DOI: 10.1021/es504445x
Environ. Sci. Technol. 2015, 49, 1453−1461

(16) Dinglasan, M. J. A.; Ye, Y.; Edwards, E. A.; Mabury, S. A. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. *Environ. Sci. Technol.* **2004**, *38*, 2857−2864.
(17) Martin, J. W.; Mabury, S. A.; O'Brien, P. J. Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes. *Chem.-Biol. Interact.* **2005**, *155*, 165−180.
(18) Houde, M.; Wells, R. S.; Fair, P. A.; Bossart, G. D.; Hohn, A. A.; Rowles, T. K.; Sweeney, J. C.; Solomon, K. R.; Muir, D. C. G. Polyfluoroalkyl compounds in free-ranging bottlenose dolphins (*Tursiops truncatus*) from the Gulf of Mexico and the Atlantic Ocean. *Environ. Sci. Technol.* **2005**, *39*, 6591−6598.
(19) De Silva, A. O.; Mabury, S. A. Isolating isomers of perfluorocarboxylates in polar bears (*Ursus maritimus*) from two geographical locations. *Environ. Sci. Technol.* **2004**, *38*, 6538−6545.
(20) Butt, C. M.; Muir, D. C. G.; Stirling, I.; Kwan, M.; Mabury, S. A. Rapid response of arctic ringed seals to changes in perfluoroalkyl production. *Environ. Sci. Technol.* **2007**, *41*, 42−49.
(21) De Silva, A. O.; Mabury, S. A. Isomer distribution of perfluorocarboxylates in human blood: Potential correlation to source. *Environ. Sci. Technol.* **2006**, *40*, 2903−2909.
(22) Furdui, V. I.; Stock, N. L.; Ellis, D. A.; Butt, C. M.; Whittle, D. M.; Crozier, P. W.; Reiner, E. J.; Muir, D. C. G.; Mabury, S. A. Spatial distribution of perfluoroalkyl contaminants in lake trout from the Great Lakes. *Environ. Sci. Technol.* **2007**, *41*, 1554−1559.
(23) De Silva, A. O.; Muir, D. C. G.; Mabury, S. A. Distribution of perfluorocarboxylate isomers in select samples from the North American environment. *Environ. Toxicol. Chem.* **2009**, *28*, 1801−1814.
(24) Houde, M.; Czub, G.; Small, J. M.; Backus, S.; Wang, X. W.; Alaee, M.; Muir, D. C. G. Fractionation and bioaccumulation of perfluorooctane sulfonate (PFOS) isomers in a Lake Ontario food web. *Environ. Sci. Technol.* **2008**, *42*, 9397−9403.
(25) Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Surridge, B.; Hoover, D.; Grace, R.; Gobas, F. A. P. C. Perfluoroalkyl Contaminants in an Arctic Marine Food Web: Trophic Magnification and Wildlife Exposure. *Environ. Sci. Technol.* **2009**, *43*, 4037−4043.
(26) Loi, E. I. H.; Yeung, L. W. Y.; Taniyasu, S.; Lam, P. K. S.; Kannan, K.; Yamashita, N. Trophic magnification of poly-and perfluorinated compounds in a subtropical food web. *Environ. Sci. Technol.* **2011**, *45*, 5506−5513.
(27) Martin, J. W.; Whittle, D. M.; Muir, D. C. G.; Mabury, S. A. Perfluoroalkyl contaminants in a food web from Lake Ontario. *Environ. Sci. Technol.* **2004**, *38*, 5379−5385.
(28) Powley, C. R.; George, S. W.; Russell, M. H.; Hoke, R. A.; Buck, R. C. Polyfluorinated chemicals in a spatially and temporally integrated food web in the Western Arctic. *Chemosphere* **2008**, *70*, 664−672.
(29) Tomy, G. T.; Pleskach, K.; Ferguson, S. H.; Hare, J.; Stern, G.; MacInnis, G.; Marvin, C. H.; Loseto, L. Trophodynamics of some PFCs and BFRs in a western Canadian Arctic marine food web. *Environ. Sci. Technol.* **2009**, *43*, 4076−4081.
(30) Chu, S. G.; Letcher, R. J. Linear and branched perfluorooctane sulfonate isomers in technical product and environmental samples by in-port derivatization-gas chromatography-mass spectrometry. *Anal. Chem.* **2009**, *81*, 4256−4262.
(31) Zhang, K.; Wan, Y.; Jones, P. D.; Wiseman, S.; Giesy, J. P.; Hu, J. Y. Occurrences and fates of hydroxylated polybrominated diphenyl ethers in marine sediments in relation to trophodynamics. *Environ. Sci. Technol.* **2012**, *46*, 2148−2155.
(32) Zhang, K.; Wan, Y.; An, L. H.; Hu, J. Y. Trophodynamics of polybrominated diphenyl ethers and methoxylated polybrominated diphenyl ethers in a marine food web. *Environ. Toxicol. Chem.* **2010**, *29*, 2792−2799.
(33) Deqi, T. *Manual of the Wildlife in the Area Around Huludao*; Northeast Forestry University Press: Harbin, Heilongjiang Province, China, 2002.
(34) Kannan, K.; Tao, L.; Sinclair, E.; Pastva, S. D.; Jude, D. J.; Giesy, J. P. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. *Arch. Environ. Contam. Toxicol.* **2005**, *48*, 559−566.
(35) Muller, C. E.; De Silva, A. O.; Small, J.; Williamson, M.; Wang, X.; Morris, A.; Katz, S.; Gamberg, M.; Muir, D. C. G. Biomagnification of perfluorinated compounds in a remote terrestrial food chain: lichen−caribou−wolf. *Environ. Sci. Technol.* **2011**, *45*, 8665−8673.
(36) Peng, H.; Wan, Y.; Zhang, K.; Sun, J. X.; Hu, J. Y. Trophic transfer of dechloranes in the marine food web of Liaodong Bay, north China. *Environ. Sci. Technol.* **2014**, *48*, 5458−5466.
(37) Han, X.; Snow, T. A.; Kemper, R. A.; Jepson, G. W. Binding of perfluorooctanoic acid to rat and human plasma proteins. *Chem. Res. Toxicol.* **2003**, *16*, 775−781.
(38) Jones, P. D.; Hu, W.; De Coen, W.; Newsted, J. L.; Giesy, J. P. Binding of perfluorinated fatty acids to serum proteins. *Environ. Toxicol. Chem.* **2003**, *22*, 2639−2649.
(39) Peng, H.; Wei, Q. W.; Wan, Y.; Giesy, J. P.; Li, L. X.; Hu, J. Y. Tissue distribution and maternal transfer of poly- and perfluorinated compounds in Chinese Sturgeon (*Acipenser sinensis*): implications for reproductive risk. *Environ. Sci. Technol.* **2010**, *44*, 1868−1874.
(40) Stock, N. L.; Furdui, V. I.; Muir, D. C. G.; Mabury, S. A. Perfluoroalkyl contaminants in the Canadian Arctic: evidence of atmospheric transport and local contamination. *Environ. Sci. Technol.* **2007**, *41*, 3529−3536.
(41) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C. G.; Mabury, S. A. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environ. Sci. Technol.* **2004**, *38*, 373−380.
(42) De Silva, A. O.; Tseng, P. J.; Mabury, S. A. Toxicokinetics of perfluorocarboxylate isomers in rainbow trout. *Environ. Toxicol. Chem.* **2009**, *28*, 330−337.
(43) Benskin, J. P.; De Silva, A. O.; Martin, L. J.; Arsenault, G.; McCrindle, R.; Riddell, N.; Mabury, S. A.; Martin, J. W. Disposition of perfluorinated acid isomers in Sprague-Dawley rats; Part 1 Single dose. *Environ. Toxicol. Chem.* **2009**, *28*, 542−554.
(44) De Silva, A. O.; Benskin, J. P.; Martin, L. J.; Arsenault, G.; McCrindle, R.; Riddell, N.; Martin, J. W.; Mabury, S. A. Disposition of perfluorinated acid isomers in Sprague-Dawley rats. Part 2. Subchronic dose. *Environ. Toxicol. Chem.* **2009**, *28*, 555−567.
(45) Peng, H.; Hu, K.; Zhao, F. R.; Hu, J. Y. Derivatization method for sensitive determination of fluorotelomer alcohols in sediment by liquid chromatography-electrospray tandem mass spectrometry. *J. Chromatogr. A* **2013**, *1288*, 48−53.

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