

Fluorine Mass Balance and Suspect Screening in Marine Mammals from the Northern Hemisphere

Supporting Information

Kyra M. Spaan^{1}, Carmen van Noordenburg¹, Merle M. Plassmann¹, Lara Schultes¹, Susan Shaw², Michelle Berger², Mads Peter Heide-Jørgensen³, Aqqalu Rosing-Asvid³, Sandra M. Granquist^{4,5}, Rune Dietz⁶, Christian Sonne⁶, Frank Rigét⁶, Anna Roos^{3,7}, Jonathan P. Benskin^{1*}*

¹Department of Environmental Science, Stockholm University, Svante Arrhenius Väg 8, 106 91, Stockholm, Sweden.

²Shaw Institute, P.O. Box 1652, Blue Hill, ME 04614

³Greenland Institute of Natural Resources, Nuuk, Greenland

⁴Marine and Freshwater Research Institute, Skúlagata 4, 101 Reykjavík, Iceland.

⁵The Icelandic Seal Center, Brekkugata 2, 530 Hvammstangi, Iceland

⁶Aarhus University, Department of Bioscience, Arctic Research Centre (ARC), Frederiksborgvej 399, PO Box 358, DK-4000 Roskilde, Denmark

⁷Department of Environmental Research and Monitoring, Swedish Museum of Natural History, Box 50007, 104 05 Stockholm, Sweden

*Corresponding authors:

Kyra.Spaan@aces.su.se

Jon.Benskin@aces.su.se

Number of Pages: 38

Number of Figures: 13

Number of Tables: 10

Chemicals and Reagents

Methanol (99.8%, LiChrosolv®) and ammonium acetate (98%) were purchased from Merck (Darmstadt, Germany). Acetonitrile ($\geq 99.9\%$, Chromasolv™) was obtained from Honeywell (France). Water was purified by a millipore water purification system and had a resistance <18 M Ω /cm (Milli-Q water). Fluoride standard (1000 mg/L) was obtained from Thermo Scientific. EnviCarb (Supelclean™) was obtained from Sigma Aldrich. Stainless steel beads (4.8 mm) were purchased from Next Advance©. Certified NIST serum (SRM 1957) was used for quality control. For CIC analysis, argon and oxygen gases were of purity grade 5.0 and the certified reference material (CRM) clay (BCR-461) was purchased from Sigma Aldrich.

Sample preparation

Targeted analysis

The extraction method was based on the method described by Powley et al. (2005) and was performed as follows. For each sample about 0.5 g of liver was thawed at room temperature and 50 μ l of internal standard (IS) solution (20 pg/ μ l) was added to each sample prior to extraction. Extraction was performed by adding 4 ml acetonitrile (ACN) together with 7-8 beads (stainless steel \varnothing 4.8 mm); thereafter the samples were homogenized in a bead blender (SPEX SamplePrep 1600 MiniG®) for 5 min at 1500 rpm. The samples were then centrifuged at 2000 rpm for 5 min (Centrifuge 5810, Eppendorf, Hamburg) and the supernatant was transferred to a new 13 ml PP-tube. The precipitate was extracted one more time by adding another 4 ml ACN, and vortexing, blending, and centrifuging again. The supernatant was added to the existing tube with the previous supernatant. The combined extracts were concentrated to ~ 1 ml under a stream of nitrogen in a water bath at 40 °C (TurboVap LV Evaporator, Biotage). The concentrated extracts were weighed and added to a 1.7 ml Eppendorf tube containing 25 mg EnviCarb and 50 μ l acetic acid. The tubes were vortexed and centrifuged for 10 min at 10 000 rpm (Galaxy 14D, Microcentrifuge, VWR). Then 500 μ l of the supernatant were transferred to another Eppendorf tube. To this 50 μ l recovery standard (RS) solution (20 pg/ μ l $^{13}\text{C}_8$ -PFOA and $^{13}\text{C}_8$ -PFOS) and 500 μ l NH_4OAc (4 mM in water) were added and the extracts were stored at -20 °C until analysis. On the day of analysis, the extract was adjusted to room temperature, vortex-mixed and transferred to an LC vial.

Clean-up step test

Two clean-up steps were evaluated for their potential to remove inorganic fluorine and recovery of target analytes: 1) a solid phase extraction (SPE)-based clean-up, and 2) an EnviCarb-based clean-up. The SPE extraction method was based on Miyake et al.² and the EnviCarb extraction on Powley et al.¹ Fish muscle samples were spiked with 250 ng PFOS (~162 ng F) and 500 ng NaF. Method blanks showed high concentrations for the SPE clean-up with high variation, while the method blanks for the EnviCarb clean-up step were rather low and consistent. The unspiked samples showed similar concentrations for both methods, however EnviCarb showed a bit higher deviation. PFOS and NaF recoveries were calculated according to the following formula:

$$Recovery (\%) = \frac{\text{Measured spike (ng F)} - \text{Measured no spike (ng F)}}{\text{Spiked concentration (ng F)}} \times 100\%$$

PFOS recovery was high for both methods, i.e. 96% and 92% for SPE and EnviCarb, respectively. Both extraction methods aim to remove inorganic fluorine, such as NaF, and get as low recovery as possible. NaF recovery was 12.5% and -0.2% for SPE and EnviCarb, respectively. Only the EnviCarb method was able to remove the inorganic fluorine effectively. After this extraction method comparison, EnviCarb was found to be the best suitable to use for analysis of the real samples, since this approach resulted in lower method blanks and more efficient removal of inorganic fluorine and was therefore considered the most suitable clean-up method.

Total and extractable organofluorine

A similar extraction procedure was applied to the liver samples prior to analysis with the CIC. Since the CIC measures the total fluorine concentration, no internal standards were added, also no NH₄OAc was added in the end. The final extracts (~ 1 ml) were split into two parts, in order to have a replicate of each sample. Also, since the sample boats have limited sample space, the final split extracts were concentrated to ~200 µl under a stream of nitrogen.

Instrumental Analysis

Targeted analysis

The system was operated in negative ion electrospray ionization (ESI-) mode. The source and desolvation temperatures were set at 150 °C and 350 °C, respectively. The desolvation and cone gas flows (nitrogen) were set at 650 L/h and 150 L/h, respectively. The capillary voltage was set at 1.0 kV. Qualification and quantification were carried out using MassLynx 4.1 (Waters).

Quantification was performed using internal standards via a 9-point calibration curve ranging from 0.008 to 150 ng/ml (linear, 1/x weighting). Precursor and product ions are presented in Table S7. Analytes lacking an analogous labeled standard were quantified using the IS with the closest retention time and the data quality was defined as semi-quantitative (semiQ). Branched isomers were quantified using the calibration curve of the linear isomer.

Total and extractable organofluorine analysis

Measurements of total fluorine (TF) and extractable organofluorine (EOF) were carried out using a Thermo-Mitsubishi CIC using previously described methods.^{3,4} Briefly, extracts (~200 µl for samples and 100 µl for standards) were placed in a ceramic sample boat containing glass wool (for fluid dispersion), while neat liver material (~100 mg) was weighed directly into the sample boat. The samples were combusted slowly in a horizontal furnace (HF-210, Mitsubishi) at 1100 °C under a flow of oxygen (400 ml/min), argon (200 ml/min), and argon mixed with water vapor (100 ml/min) for approximately 5 minutes. Combustion gases were absorbed in MilliQ water during the entire length of the combustion process using a gas absorber unit (GA-210, Mitsubishi). A 200 µl aliquot of the absorption solution was subsequently injected onto an ion chromatograph (Dionex Integrion HPIC, Thermo Fisher Scientific) equipped with an anion exchange column (2 × 50 mm guard column (Dionex IonPac AS19-4µm) and 2 × 250 mm analytical column (Dionex IonPac AS19-4µm) operated at 30 °C. Chromatographic separation was achieved by running a gradient of aqueous hydroxide mobile phase ramping from 8 mM to 100 mM at a flow rate of 0.25 ml/min (Table S8), and fluoride was detected using a conductivity detector. Quantification was carried out using a standard calibration curve prepared at 0.05 to 100 µg F/ml. The calibration curve showed very good linearity with $R^2 > 0.98$. The mean fluoride concentration in the method blanks was subtracted from the samples. The method detection limit (MDL) was defined as the mean concentration plus three times the standard deviation in the method blanks.

Suspect screening

Suspect screening was carried out using a Dionex Ultimate 3000 liquid chromatograph coupled to a Q Exactive HF Orbitrap (Thermo Scientific), based on a previously described method.⁵ The flow rate was held constant at 0.4 ml per minute throughout the run. The mobile phases and eluent program used for non-target/suspect screening were the same as those used for target analysis (i.e.

by UPLC-MS/MS). The instrument was run in negative ion, full scan (200-1200 m/z) data dependent acquisition (DDA) MS/MS mode (50-1200 m/z). The resolution was set to 120 000 (15 000 for MS/MS), the automatic gain control (AGC) was set to 3e6, and other instrumental parameters are presented in Table S11. Briefly, CL = 5 is assigned when only the exact mass is known. CL = 4 is used when the unknown analyte ion can be assigned an unambiguous formula, but no structural information is available. CL = 3 represents tentative candidates whose possible structure can be proposed but lack sufficient information to assign an exact structure. CL = 2a represents probable structures by comparing to library spectra where spectrum-structure is unambiguous. CL = 2b can be assigned when no standard or literature information is available for confirmation and there is only diagnostic evidence. Finally, CL = 1 represents confirmed structures, that match a reference standard with MS, MS/MS and RT.

Quality Control

Targeted analysis

Limits of quantification (LOQs) were determined by the lowest calibration concentration that showed a well-shaped peak with intensity $>1e3$ and signal-to-noise (S/N) >3 . For compounds that were not present in the calibration standard, but that were detected in the samples (PFPeDA, PFHpS, and branched isomers), the LOQ from the corresponding standard was used. For compounds where method blank contamination was observed (PFBS, PFOS, and FOSAA), the LOQ was determined as the average of the quantified concentrations in the method blanks plus ten times the standard deviation. The compound-specific LOQs are listed in Table S6.

Method accuracy and precision for most substances was very good, with percent recoveries ranging from 73-130% and standard deviations ranging from 3-30% (Figure S2). The exceptions were for PFHxDA, PFOcDA, 4:2 FTSA, and 8:2 FTSA, which showed very high recoveries (278%, 397%, 212%, and 227%, respectively), while HFPO-DA, 3:3 FTCA, 5:3 FTCA, and 7:3 FTCA showed very low recoveries (22%, 34%, 55%, and 53%, respectively). These deviating recoveries are likely due to matrix effects, which were not accounted for because of the absence of an exactly matching isotopically-labeled internal standard. Nevertheless, the targets with very high recoveries were included in the analysis, since their concentrations in the samples were so low (<1 ng/g, ww). The targets with low recoveries were also included in the analysis, albeit

measured concentrations may be underreported. Finally, the method was externally validated by analyzing a standard reference material (SRM) sample of NIST serum 1957. Results are presented in Table S9 and were generally in good agreement with certified values and prior measurements of this material by other researchers.

Total and extractable organofluorine

All boats were baked out prior to sample combustion to minimize background contamination. Each run started and ended with a calibration curve and after every 8-10 samples, a blank and a mid-level calibration standard were analyzed for quality control. The removal efficiency of inorganic fluoride was tested by spiking a range of known concentrations of NaF (0.25, 0.5, 0.75, 1, and 2 µg) into liver tissue followed by extraction (Figure S3). Furthermore, recovery of organic fluoride was determined by spiking PFOS (0.08, 0.13, 0.25, 0.5, and 1 µg/ml) to liver tissue and performing the extraction (Figure S4). CIC analysis of both the extracted liver residue and the EnviCarb used for clean-up showed that the inorganic fluoride remained in the extracted liver; in other words, it was not extracted during the initial acetonitrile extraction step. The obtained recovery for PFOS was used to correct the measured concentrations of EOF in real samples. In theory, since the recovery is different for each target analyte, the recovery should be determined for each individual compound. However, practically this would mean a large number of experiments and therefore only the recovery for the most abundant compound, PFOS, was assessed here.

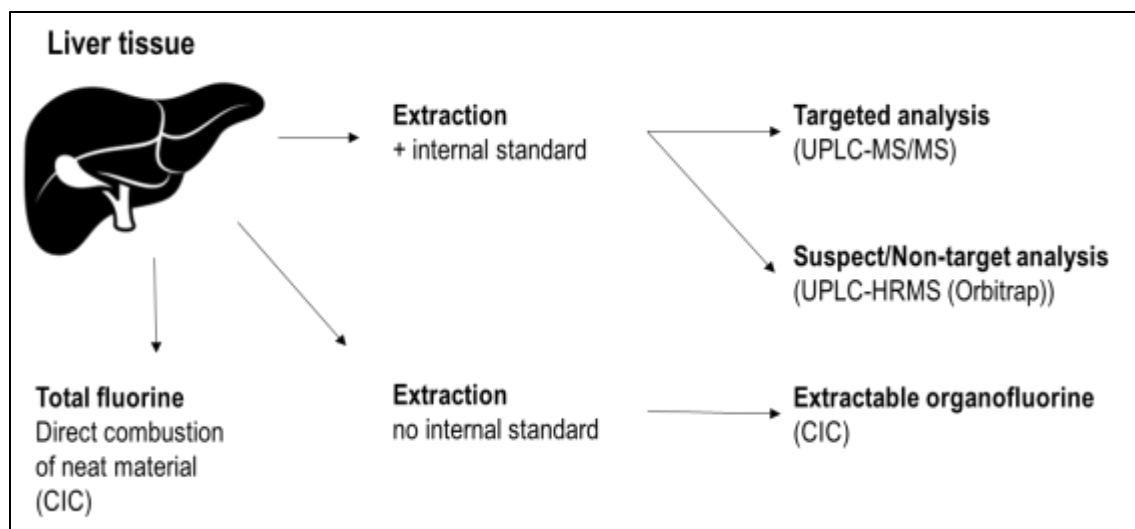


Figure S1. Diagram of the experimental design.

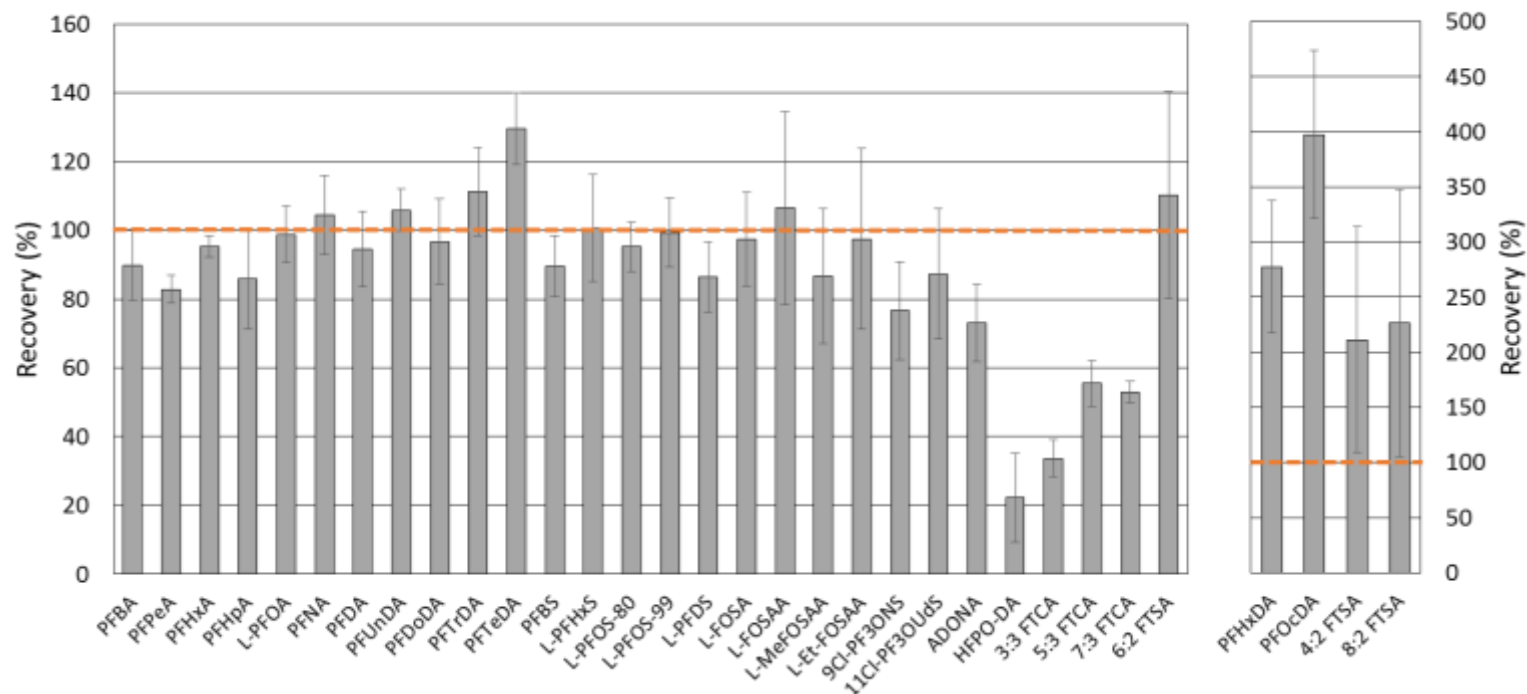


Figure S2. Recovery \pm standard deviation (%) of native compounds spiked in seal samples ($n=4$). Right panel shows severe over-recovery of four targets, attributable to matrix-induced ionization enhancement.

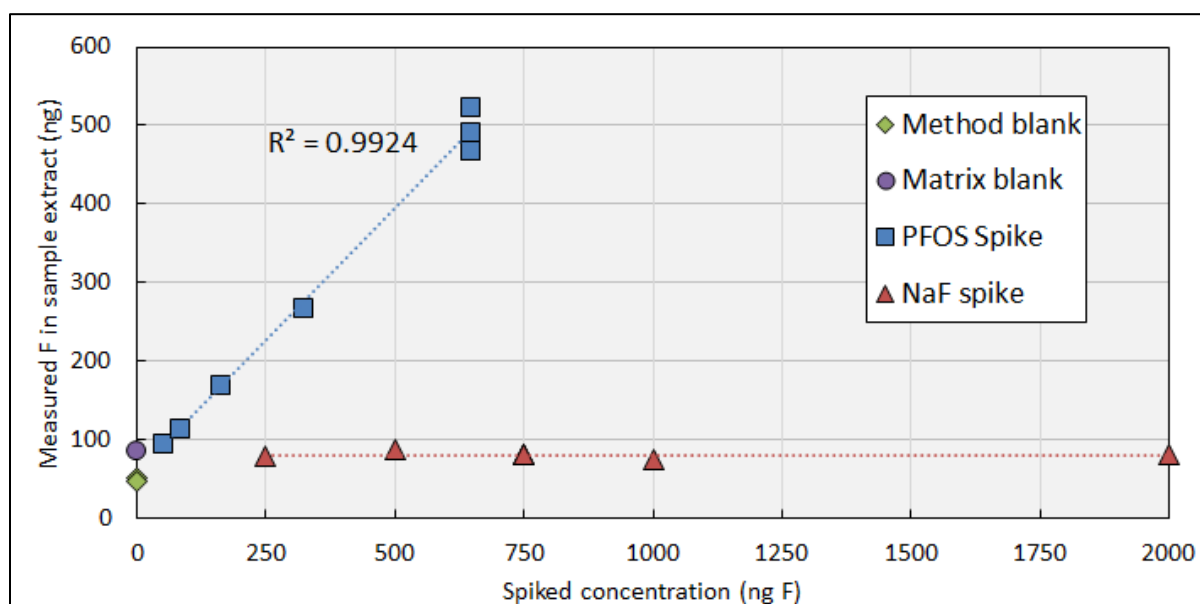


Figure S3. Results from spike/recovery experiments for CIC analysis. Comparison between PFOS- and NaF-spiked samples.

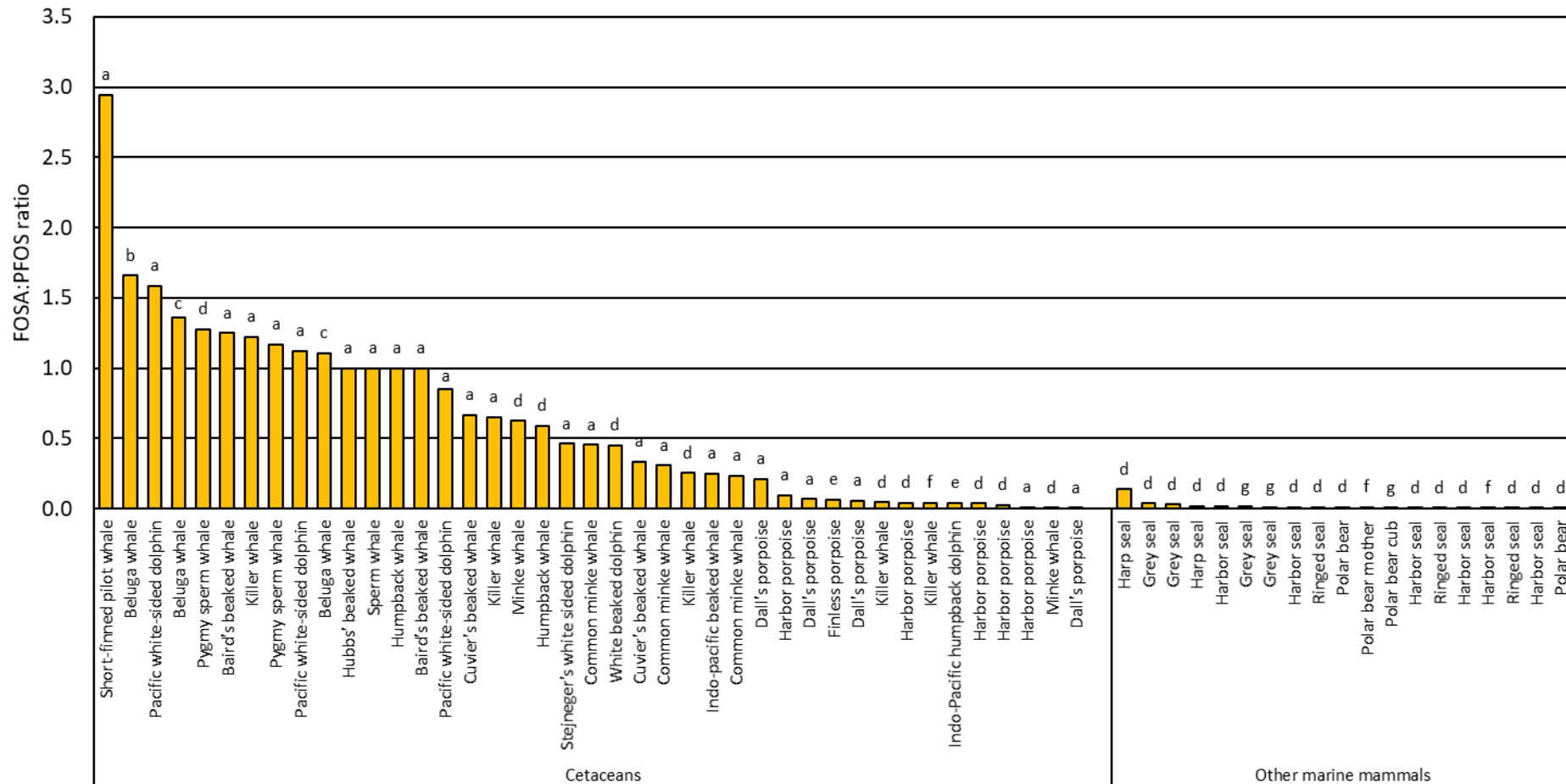


Figure S4. Overview on the FOSA:PFOS ratio for cetaceans and other marine mammals from literature as well as from the present study. ^aFujii et al.⁶, ^bTomy et al.⁷, ^cKelly et al.⁸, ^dPresent study, ^eYeung et al.⁹, ^fGebbink et al.¹⁰, ^gShaw et al.¹¹

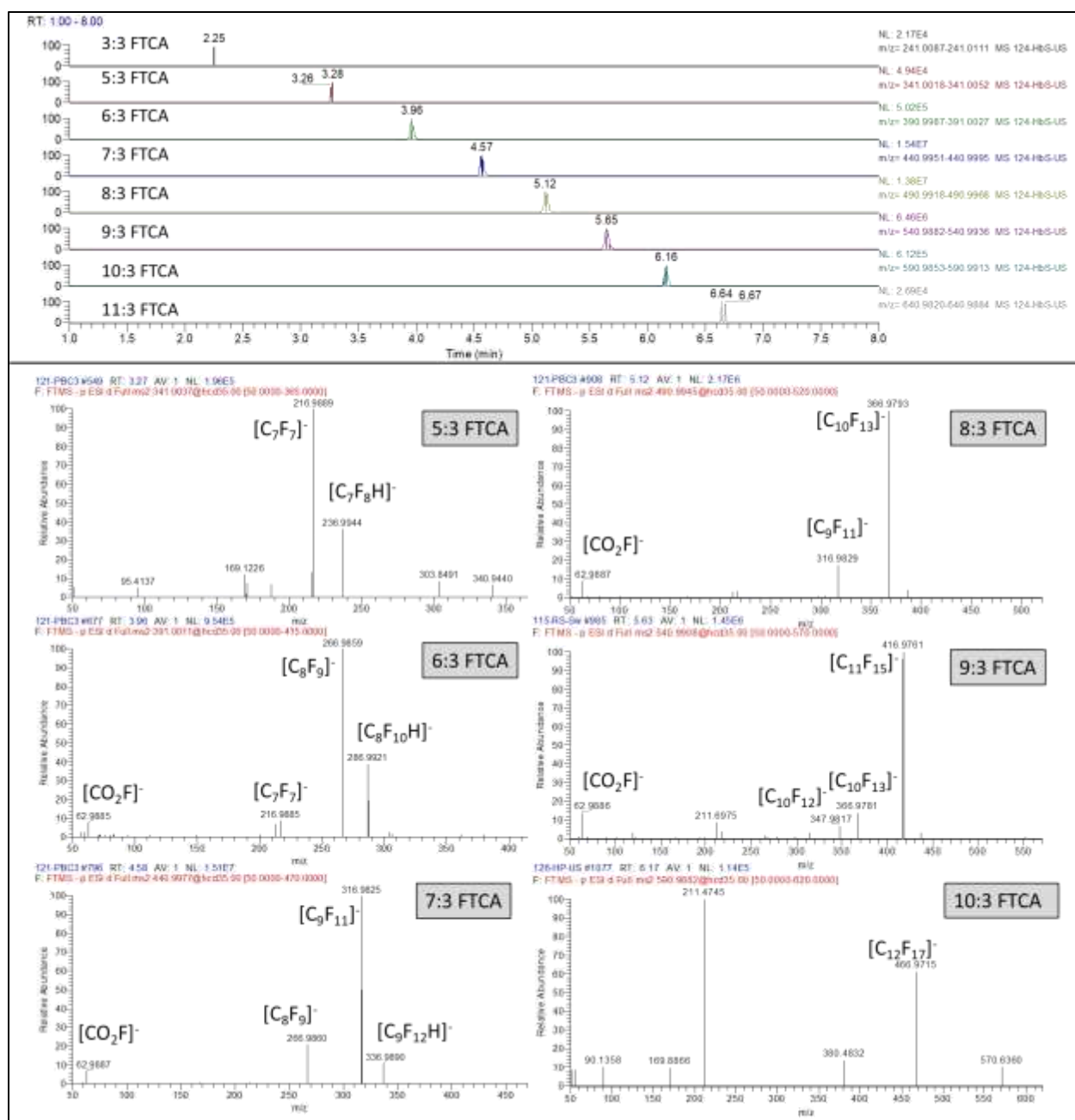


Figure S5. Above the EICs for x:3 FTCAs (class 3) observed in harbor seal from the US are shown. MS/MS spectra including the molecular formulas belonging to the most common peaks.

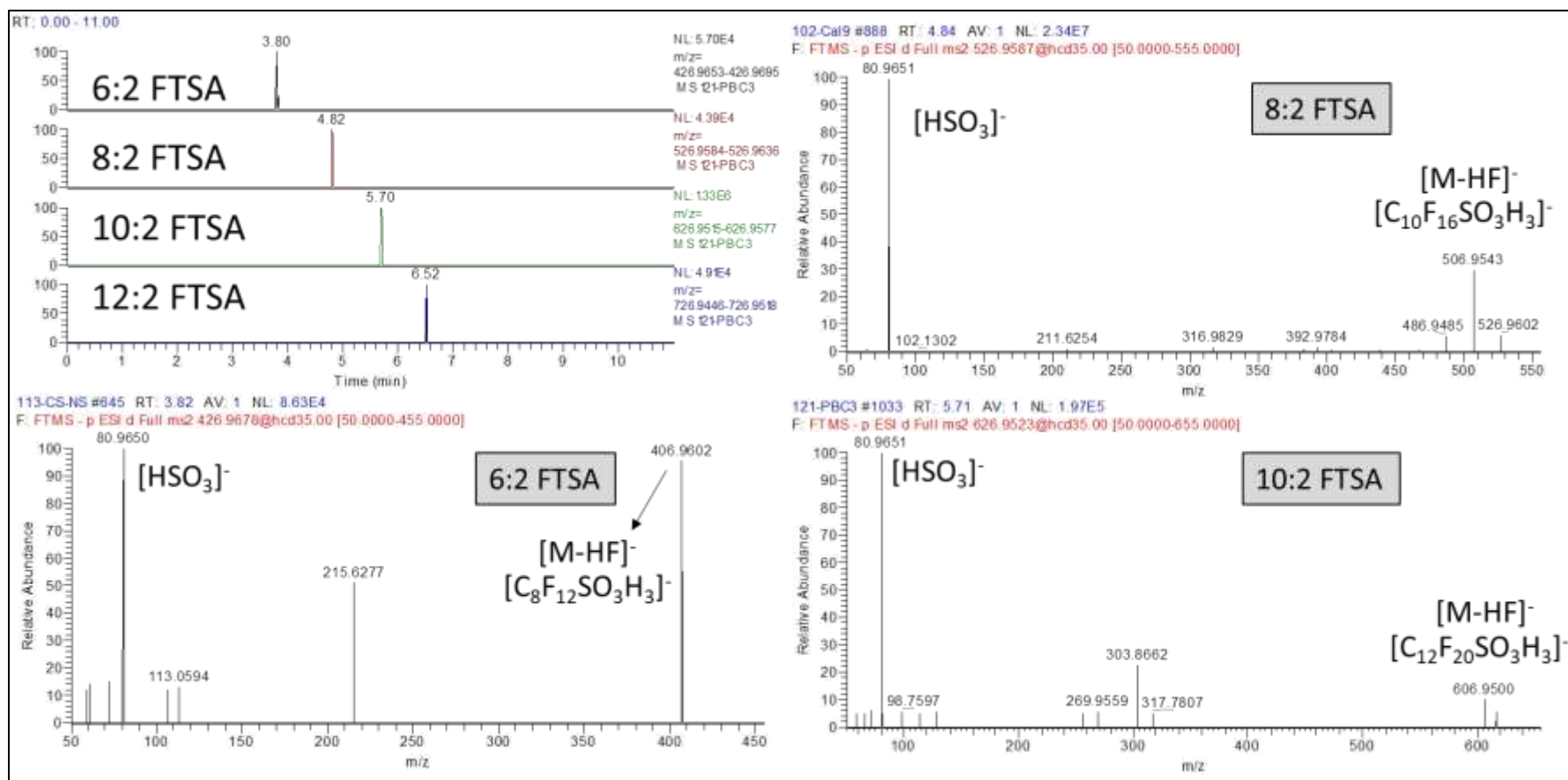


Figure S6. EICs of x:2 FTSA (class 4) in polar bear cub sample. MS/MS spectra from 6:2 FTSA (grey seal from Sweden), 8:2 FTSA (calibration standard), and 10:2 FTSA (polar bear cub) are shown with molecular formulas assigned to the most common peaks.

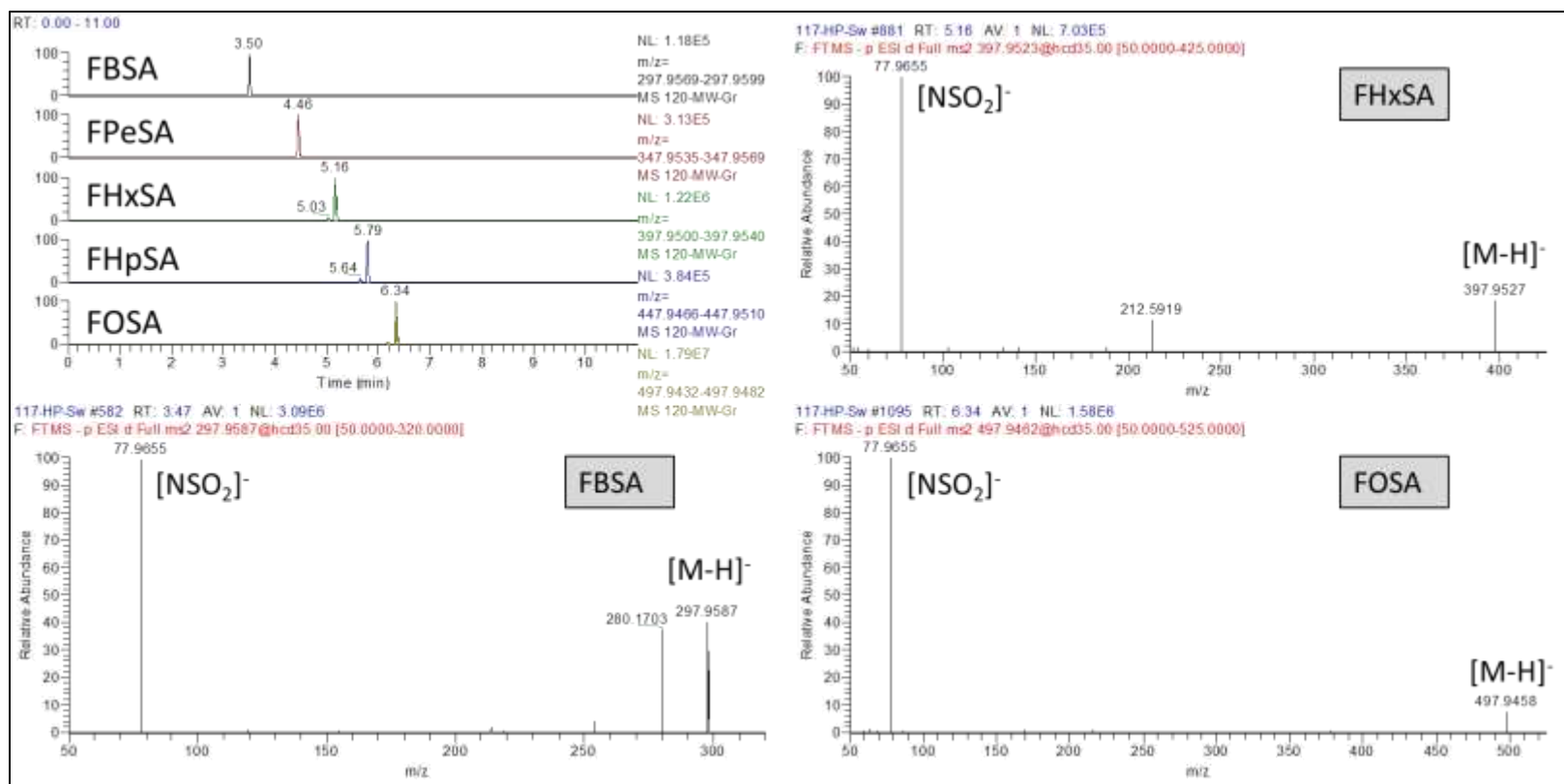


Figure S7. EICs of FASAs (class 5) in minke whale from Greenland. MS/MS spectra for FBSA, FHxSA, and FOSA (harbor porpoise from Sweden) are shown.

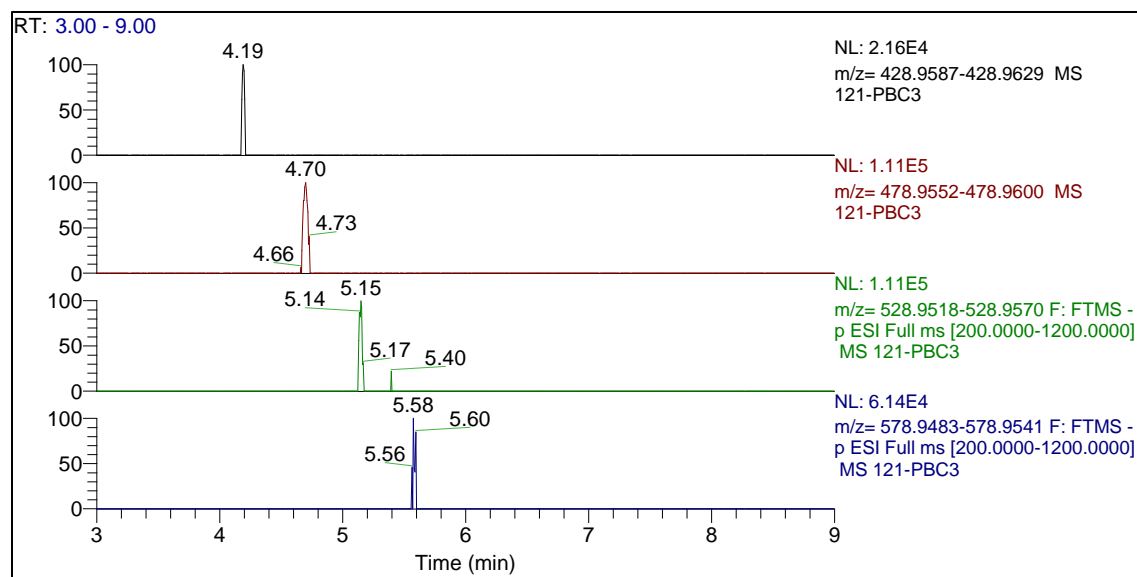


Figure S8. EICs for PFECAs (class 8) in polar bear cub sample. No MS/MS spectra were available.

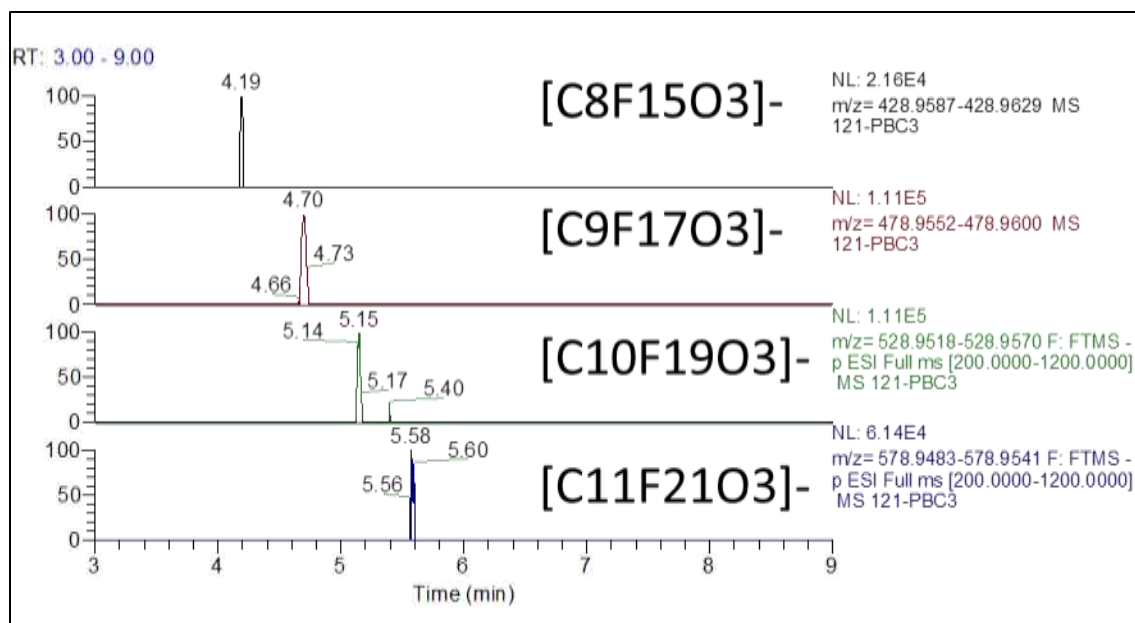


Figure S9. EICs for PFECAs (class 8) in polar bear cub sample. No MS/MS spectra were available.

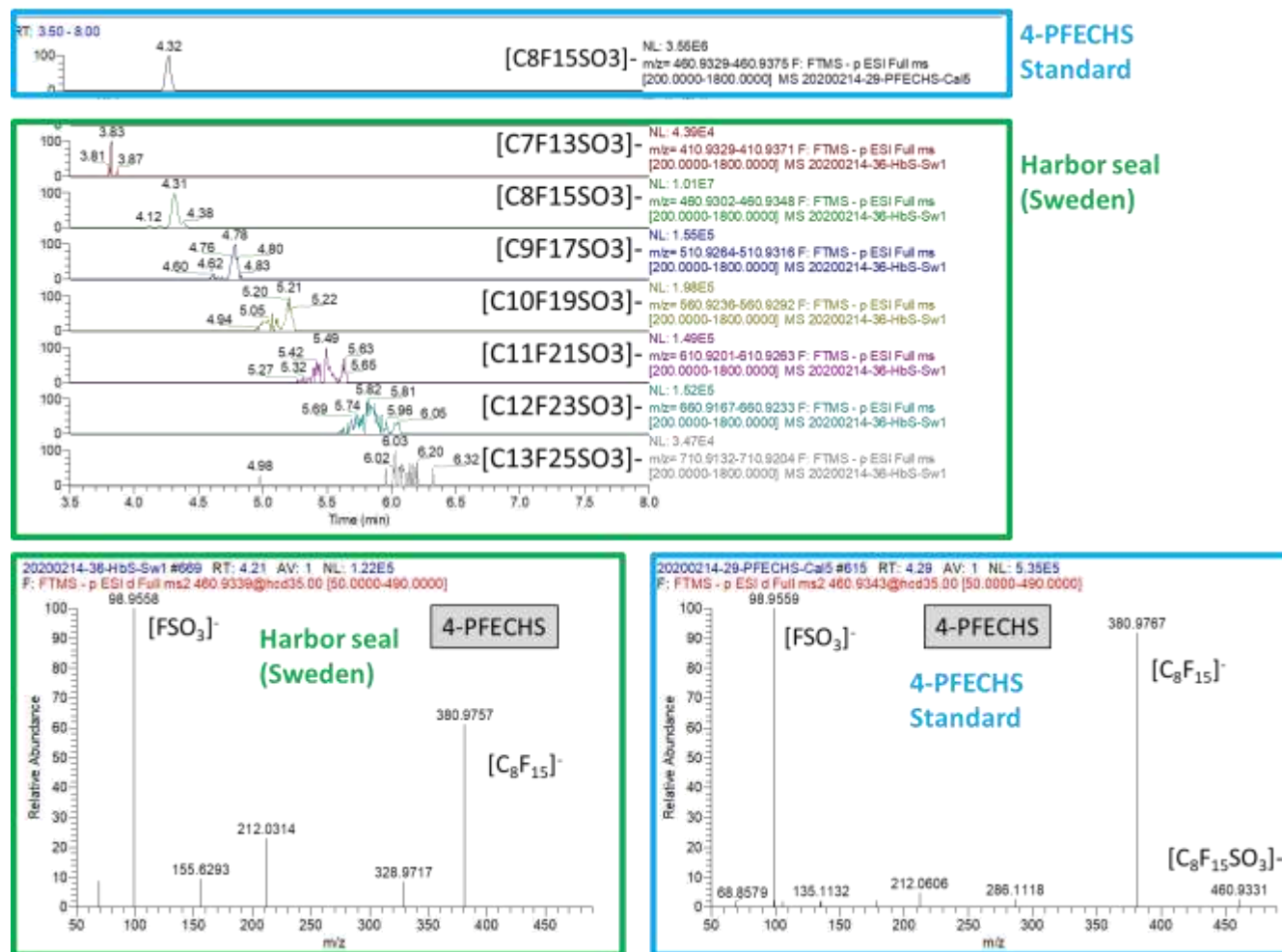


Figure S10. EICs for double-bond/cyclic PFSA (class 9) in harbor seal sample from Sweden, as well as the MS/MS spectrum for 4-PFECHS in harbor seal from Sweden as well as for the purchased 4-PFECHS standard.

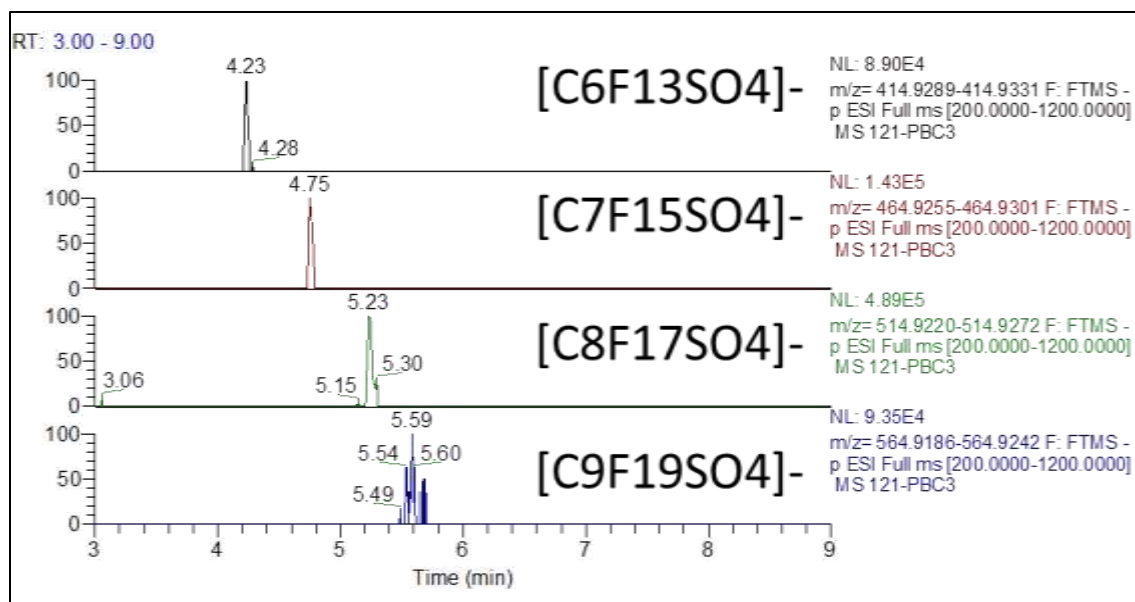


Figure S11. EICs of ether-PFSAs (class 10) in polar bear cub sample. No MS/MS spectra were available.

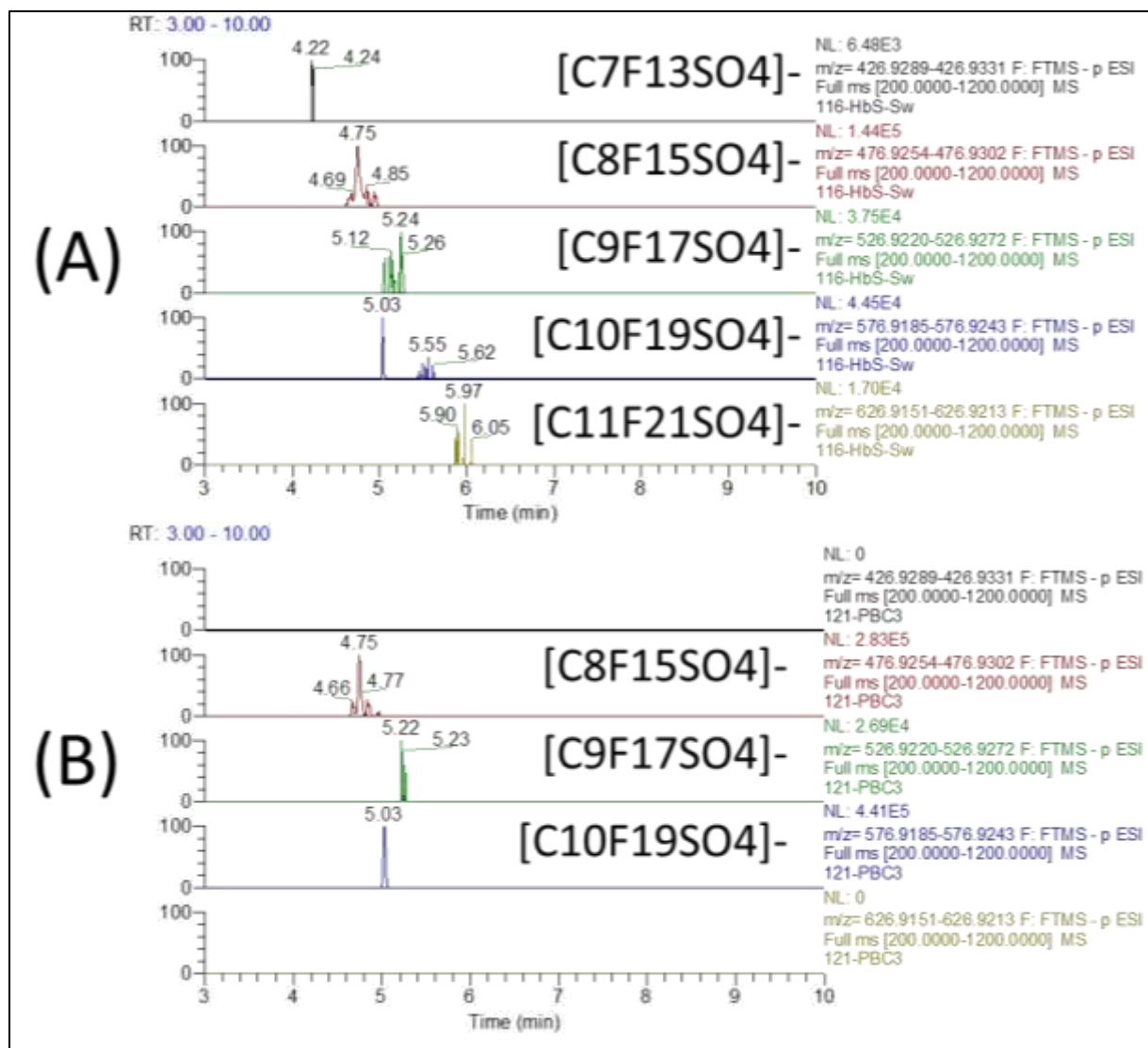


Figure S12. EICs of enol-ether-, cyclic- ether- or carbonyl- PFSA (class 11) in (A) harbor seal from Sweden and (B) polar bear cub.

No MS/MS spectra were available.

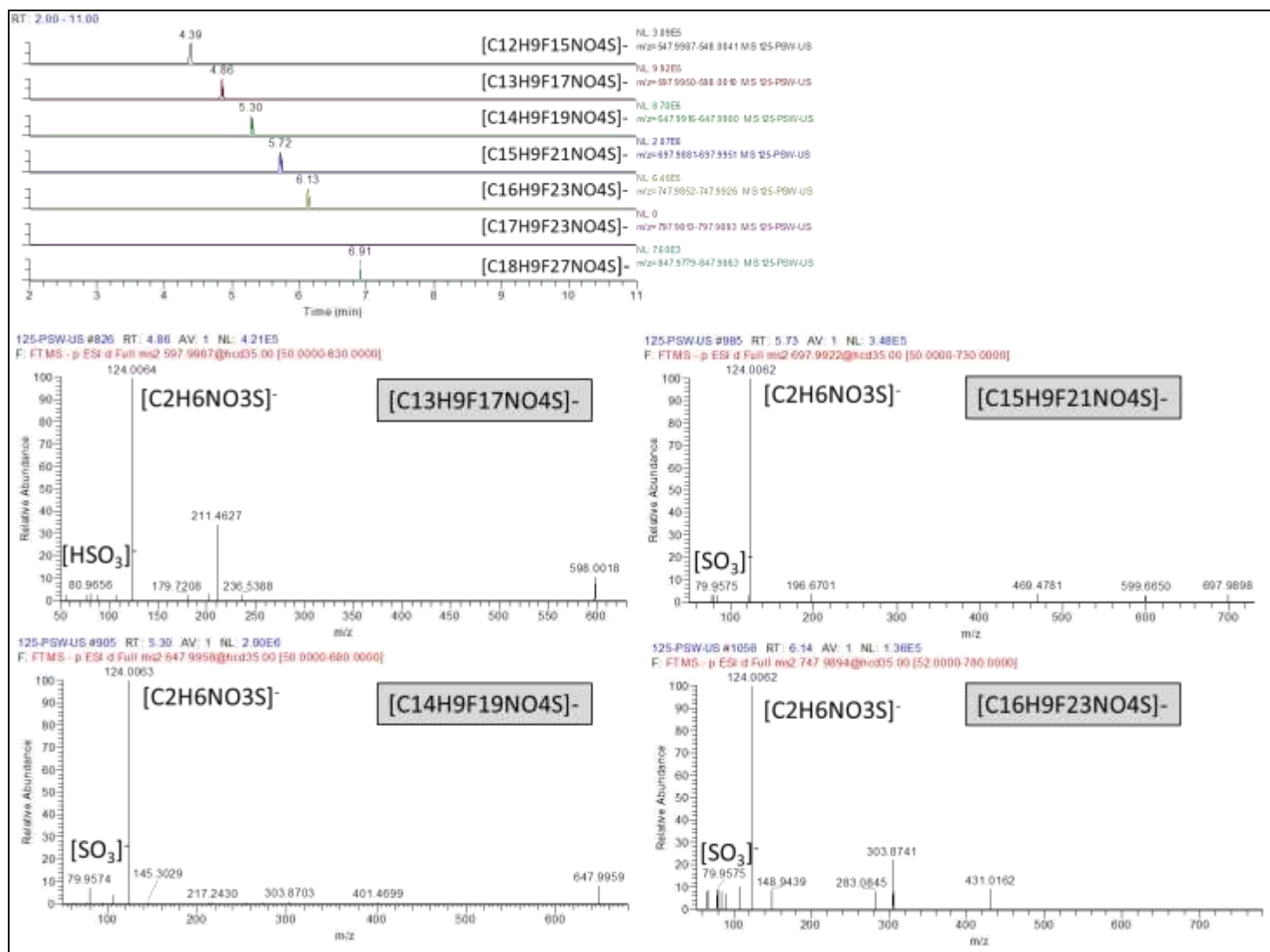


Figure S13. EICs for unknowns (class 12) in pygmy sperm whale. MS/MS spectra for four compounds within class 12 with molecular formulas assigned to the most common fragments.

Table S1. Detailed overview on the marine mammals that were assessed in this study.

<i>Sampled by</i>	<i>IDs</i>	<i>Specie</i>	<i>Latin name</i>	<i>Year</i>	<i>Age</i>	<i>Sex (M/F)</i>	<i>Location</i>	<i>Weight (kg)</i>	<i>Length (cm)</i>	
Susan Shaw and Michelle Berger	MH 00670 HG, #7	Grey seal	<i>Halichoerus grypus</i>	2000	Adult	M	Narragansett Bay, RI, US	136	190	Pooled
	MH 01830 HG, #17	Grey seal	<i>Halichoerus grypus</i>	2001	Pup	M	Narragansett Bay, RI, US	22.73	99	
	NY 308404 HG, #245	Grey seal	<i>Halichoerus grypus</i>	2004	Pup	F	E Long Island, NY, US	21.7	97.2	
	MH 02637 HG, #314	Grey seal	<i>Halichoerus grypus</i>	2002	Pup	F	S Massachusetts, US	18.2	96	
	CCSN 02243 HG, #320	Grey seal	<i>Halichoerus grypus</i>	2002	Subadult	M	Massachusetts, US	136.4	181	
	MH 00543F PV, 21	Harbor seal	<i>Phoca vitulina</i>	2000	Fetus	F	Massachusetts Bay, US	6.4	64	Pooled
	COA020730PV, #133	Harbor seal	<i>Phoca vitulina</i>	2002	Adult	F	Midcoast, ME, US	54.55	140	
	COA060622PV, #285	Harbor seal	<i>Phoca vitulina</i>	2006	Adult	M	Midcoast, ME, US	63.6	157	
	COA060705PV, #333	Harbor seal	<i>Phoca vitulina</i>	2006	Pup	F	E Maine, US	14.2	85	
	COA080717PV-01, #352	Harbor seal	<i>Phoca vitulina</i>	2008	Yearling	M	Midcoast, ME, US	16.6	100	
	COA060619PP, #287	Harbor porpoise	<i>Phocoena phocoena</i>	2006	Calf	F	E Maine, US	9.9	81	Pooled
	COA060713PP, #289	Harbor porpoise	<i>Phocoena phocoena</i>	2006	Adult	F	Midcoast, ME, US	54.5	145	
	COA060905PP, #340	Harbor porpoise	<i>Phocoena phocoena</i>	2006	Calf	M	E Maine, US	11.8	97	
	COA101005PP, #392	Harbor porpoise	<i>Phocoena phocoena</i>	2010	Juvenile	M	E Maine, US	18.2	116.5	
	COA121030PP, #410	Harbor porpoise	<i>Phocoena phocoena</i>	2012	Juvenile	M	Midcoast, ME, US	23.3	126.8	
	COA071003KB, #358	Pygmy sperm whale	<i>Kogia breviceps</i>	2007	Calf	F	Midcoast, ME	35	135	
Anna Roos, Mads Peter Heide- Jørgensen, Aqqalu Rosling-Asvid, Kristin Laidre	PAX16/0331	Harp seal	<i>Pagophilus groenlandicus</i>	2016	Adult (pregnant)	F	Nuuk (Kobbefjord) (West Greenland)	93	145	
	PAX16/0329	Ringed seal	<i>Pusa hispida</i>	2013	-	-	Illulissat (North-West Greenland)	-	-	Pooled
		Ringed seal	<i>Pusa hispida</i>	2013	-	-	Illulissat (North-West Greenland)	-	-	
		Ringed seal	<i>Pusa hispida</i>	2013	-	-	Illulissat (North-West Greenland)	-	-	
		Ringed seal	<i>Pusa hispida</i>	2013	-	-	Illulissat (North-West Greenland)	-	-	
		Ringed seal	<i>Pusa hispida</i>	2013	-	-	Illulissat (North-West Greenland)	-	-	
	PAX16/0327	Harbor porpoise	<i>Phocoena phocoena</i>	2009	-	-	Maniitsoq, West Greenland	-	-	Pooled
		Harbor porpoise	<i>Phocoena phocoena</i>	2009	-	-	Maniitsoq, West Greenland	-	-	
		Harbor porpoise	<i>Phocoena phocoena</i>	2009	-	-	Maniitsoq, West Greenland	-	-	
		Harbor porpoise	<i>Phocoena phocoena</i>	2009	-	-	Maniitsoq, West Greenland	-	-	
		Harbor Porpoise	<i>Phocoena phocoena</i>	2009	-	-	Maniitsoq, West Greenland	-	-	

	PAX16/0328	Humpback whale	<i>Megaptera novaeangliae</i>	2011	-	-	Nuuk (West Greenland)	-	-	Pooled
		Humpback whale	<i>Megaptera novaeangliae</i>	2013	-	-	Nuuk (West Greenland)	-	-	
	PAX15/0326	Minke whale	<i>Balaenoptera acutorostrata</i>	2000	-	F	Qasigianniguit (West Greenland)	-	-	Pooled
		Minke whale	<i>Balaenoptera acutorostrata</i>	-	-	-	Arsuk (West Greenland)	-	-	
		Polar bear	<i>Ursus maritimus</i>	2013	Mother	F	Tasiilaq (East Greenland)	-	-	
		Polar bear	<i>Ursus maritimus</i>	2013	Cub	-	Tasiilaq (East Greenland)	-	-	
	PAX16/0330	White beaked dolphin	<i>Lagenorhynchus albirostris</i>	2016	-	-	Tasiilaq-Kulusuc (East Greenland)	-	-	
Sandra Granquist		Minke whale	<i>Balaenoptera acutorostrata</i>	2017	Fetus		Tasiilaq, East Greenland	-	-	
		Killer whale	<i>Orcinus orca</i>	2017	3	F	Tasiilaq, East Greenland	-	-	
	050510-L-FH1	Grey seal	<i>Halichoerus grypus</i>	2010	-	-	Iceland	-	-	Pooled
	210510-Ú-SGB7	Grey seal	<i>Halichoerus grypus</i>	2010	-	-	Iceland	-	-	
	210510-Ú-SGB2	Grey seal	<i>Halichoerus grypus</i>	2010	-	-	Iceland	-	-	
	210510-Ú-SGB3	Grey seal	<i>Halichoerus grypus</i>	2010	-	-	Iceland	-	-	
	060709-Ú-GIB6	Grey seal	<i>Halichoerus grypus</i>	2009	-	F	Breiðafjörður (Iceland)	52.5	-	
	060709-L-DB4	Harbor seal	<i>Phoca vitulina</i>	2009	0	F	Barðaströnd (Iceland)	29.5	-	Pooled
	180609-L-SJH1	Harbor seal	<i>Phoca vitulina</i>	2009	1	F	Skagaströnd (Iceland)	42	-	
	080510-L-SJH1	Harbor seal	<i>Phoca vitulina</i>	2010	0	M	Húnaflói (Iceland)	25.5	-	
	080510-L-SJH2	Harbor seal	<i>Phoca vitulina</i>	2010	0	M	Húnaflói (Iceland)	32.5	-	
	060709-L-DB3	Harbor seal	<i>Phoca vitulina</i>	2009	1	M	Barðaströnd (Iceland)	36.5	-	
	200409-V-GP3	Harp seal	<i>Pagophilus groenlandicus</i>	2009	11	F	Þistilfjörður (Iceland)	104.5	-	Pooled
	140410-V-ELS8	Harp seal	<i>Pagophilus groenlandicus</i>	2010	-	-	Iceland	-	-	
	200409-V-JSH10	Harp seal	<i>Pagophilus groenlandicus</i>	2009	7	F	Húnaflói (Iceland)	82.5	-	
	140410-V-ELS4	Harp seal	<i>Pagophilus groenlandicus</i>	2010	-	-	Iceland	-	-	
	080510-V-SH2	Harp seal	<i>Pagophilus groenlandicus</i>	2010	-	-	Iceland	-	-	
Rune Dietz, Frank Rigét?, Christian	46701	Ringed seal	<i>Pusa hispida</i>	2012	-	-	Ittoqq/Scoresby Sound, E Greenland	-	-	Pooled
	46702	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			
	46703	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			

Sonne and Aqqalu Rosing-Asvid	46706	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			
	46709	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			
	46711	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			
	46712	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			
	46714	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			
	46717	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			
	46726	Ringed seal	<i>Pusa hispida</i>	2012			Ittoqq/Scoresby Sound, E Greenland			
	35143	Killer whale	<i>Orcinus orca</i>	2013	Ad	F	Tasilaq/Ammassalik, East Greenland	-	-	Pooled
	35144	Killer whale	<i>Orcinus orca</i>	2013	SubAd	M	Tasilaq/Ammassalik, East Greenland			
	48732	Killer whale	<i>Orcinus orca</i>	2013	Ad	M	Tasilaq/Ammassalik, East Greenland			
	48733	Killer whale	<i>Orcinus orca</i>	2013	Ad	F	Tasilaq/Ammassalik, East Greenland			
	48734	Killer whale	<i>Orcinus orca</i>	2013	Fetus	M	Tasilaq/Ammassalik, East Greenland			
	48735	Killer whale	<i>Orcinus orca</i>	2013	SubAd	F	Tasilaq/Ammassalik, East Greenland			
	46752	Polar bear	<i>Ursus maritimus</i>	2012	10	M	Ittoqq/Scoresby Sound, E Greenland	-	-	Pooled
	46753	Polar bear	<i>Ursus maritimus</i>	2012	6	M	Ittoqq/Scoresby Sound, E Greenland			
	46754	Polar bear	<i>Ursus maritimus</i>	2201	7	F	Ittoqq/Scoresby Sound, E Greenland			
	46755	Polar bear	<i>Ursus maritimus</i>	2012	5	F	Ittoqq/Scoresby Sound, E Greenland			
	46756	Polar bear	<i>Ursus maritimus</i>	2012	2	F	Ittoqq/Scoresby Sound, E Greenland			
	46758	Polar bear	<i>Ursus maritimus</i>	2012	5	M	Ittoqq/Scoresby Sound, E Greenland			
	46759	Polar bear	<i>Ursus maritimus</i>	2012	5	M	Ittoqq/Scoresby Sound, E Greenland			
	46760	Polar bear	<i>Ursus maritimus</i>	2012	3	M	Ittoqq/Scoresby Sound, E Greenland			
Anna Roos	A2012/05463	Grey seal	<i>Halichoerus grypus</i>	2012	Yearling	M	Sweden	117	34.2	Pooled
	A2013/05230	Grey seal	<i>Halichoerus grypus</i>	2013	Yearling	M	Sweden	113	34	
	A2015/05571	Grey seal	<i>Halichoerus grypus</i>	2015	21	M	Sweden	145	-	
	A2015/05614	Grey seal	<i>Halichoerus grypus</i>	2015	12	F	Sweden	115	-	
	A2016/05270	Grey seal	<i>Halichoerus grypus</i>	2016	1	M	Sweden	50.4	-	
	A2015/05387	Harbor seal	<i>Phoca vitulina</i>	2015	Yearling	F	Sweden	18.9	94	Pooled
	A2015/05390	Harbor seal	<i>Phoca vitulina</i>	2015	Yearling	M	Sweden	19.7	97	
	A2016/05109	Harbor seal	<i>Phoca vitulina</i>	2015	Adult	M	Sweden	105	-	
	A2016/05167	Harbor seal	<i>Phoca vitulina</i>	2015	Adult	F	Sweden	75	-	
	A2016/05316	Harbor seal	<i>Phoca vitulina</i>	2015	Yearling	F	Sweden	75	-	

A2014/05650	Ringed seal	<i>Phoca hispida</i>	2014	23	F	Northern Baltic	-	-	Pooled
A2015/05591	Ringed seal	<i>Phoca hispida</i>	2015	Adult	M	Northern Baltic	-	-	
A2016/05110	Ringed seal	<i>Phoca hispida</i>	2015	Yearling	M	Northern Baltic	31.8	100.5	
A2016/05126	Ringed seal	<i>Phoca hispida</i>	2015	Adult	F	Northern Baltic	41.6	132	
A2016/05133	Ringed seal	<i>Phoca hispida</i>	2015	Yearling	F	Northern Baltic	37.1	108	
A2015/05283	Harbor porpoise	<i>Phocoena phocoena</i>	2011	Adult	M	Southern Baltic	-	145	Pooled
A2016/05526	Harbor porpoise	<i>Phocoena phocoena</i>	2016	Subadult	M	Southern Baltic	-	124	
A2016/05528	Harbor porpoise	<i>Phocoena phocoena</i>	-	Juvenile	F	Southern Baltic	-	114	
A2016/05637	Harbor porpoise	<i>Phocoena phocoena</i>	2016	Adult	M	Southern Baltic	43	141.5	
C2012/00009	Harbor porpoise	<i>Phocoena phocoena</i>	2011	Adult	M	Southern Baltic	45	154.5	
A2016/05633 liver 3439	Grey seal	<i>Halichoerus grypus</i>	2016	(pregnant)	F	Sweden - Gävleborgs län	-	-	

Table S2. Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) numbers for export permissions.

CITES nr	Species	Name
17GL1167082	Polar bear	Anna Roos
17GL1167083	Harbor porpoise	Anna Roos
17GL1167084	Humpback whale	Anna Roos
17GL1167085	Minke whale	Anna Roos
17GL1167088	Killer whale	Anna Roos
17GL1167090	Humpback whale	Anna Roos
17GL1167098	White beaked dolphins, East Greenland	Anna Roos
17US18692C/9	Pygmy sperm whale	Susan Shaw and Michelle Berger
17US18692C/9	Harbor porpoise	Susan Shaw and Michelle Berger

Table S3. Target compounds according to their compound class, acronyms, and molecular formula.

	Name	Acronym	Molecular formula
PFCAs	Perfluorobutanoic acid	PFBA	C ₄ F ₇ O ₂ H
	Perfluoropentanoic acid	PFPeA	C ₅ F ₉ O ₂ H
	Perfluorohexanoic acid	PFHxA	C ₆ F ₁₁ O ₂ H
	Perfluoroheptanoic acid	PFHpA	C ₇ F ₁₃ O ₂ H
	Perfluorooctanoic acid	PFOA ^{L+Br}	C ₈ F ₁₅ O ₂ H
	Perfluorononanoic acid	PFNA	C ₉ F ₁₇ O ₂ H
	Perfluorodecanoic acid	PFDA	C ₁₀ F ₁₉ O ₂ H
	Perfluoroundecanoic acid	PFUnDA	C ₁₁ F ₂₁ O ₂ H
	Perfluorododecanoic acid	PFDoDA	C ₁₂ F ₂₃ O ₂ H
	Perfluorotridecanoic acid	PFTTrDA	C ₁₃ F ₂₅ O ₂ H
	Perfluorotetradecanoic acid	PFTeDA	C ₁₄ F ₂₇ O ₂ H
	Perfluoropentadecanoic acid	PFPeDA	C ₁₅ F ₂₉ O ₂ H
	Perfluorohexadecanoic acid	PFHxDA	C ₁₆ F ₃₁ O ₂ H
	Perfluorooctadecanoic acid	PFOcDA	C ₁₈ F ₃₅ O ₂ H
PFSAs	Perfluorobutane sulfonic acid	PFBS	C ₄ F ₉ SO ₃ H
	Perfluoropentane sulfonic acid	PFPeS	C ₅ F ₁₁ SO ₃ H
	Perfluorohexane sulfonic acid	PFHxS ^{L+Br}	C ₆ F ₁₃ SO ₃ H
	Perfluoroheptane sulfonic acid	PFHpS	C ₇ F ₁₅ SO ₃ H
	Perfluorooctane sulfonic acid	PFOS ^{L+Br}	C ₈ F ₁₇ SO ₃ H
	Perfluorononane sulfonic acid	PFNS	C ₉ F ₁₉ SO ₃ H
	Perfluorodecane sulfonic acid	PFDS ^{L+Br}	C ₁₀ F ₂₁ SO ₃ H

	Perfluoroundecane sulfonic acid	PFUnDS	C ₁₁ F ₂₃ SO ₃ H
FASA(A)s	Perfluorooctane sulfonamide	FOSA ^{L+Br}	C ₈ F ₁₇ SO ₂ NH ₂
	Perfluorooctane sulfonamidoacetic acid	FOSAA ^{L+Br}	C ₁₀ F ₁₇ SO ₄ NH ₅
	N-Methyl perfluorooctane sulfonamidoacetic acid	MeFOSAA ^{L+Br}	C ₁₁ F ₁₇ SO ₄ NH ₇
	N-Ethyl perfluorooctane sulfonamidoacetic acid	EtFOSAA ^{L+Br}	C ₁₂ F ₁₇ SO ₄ NH ₉
Cl- PFESA	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	C ₈ F ₁₆ SO ₄ ClH
	11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	C ₁₀ F ₂₀ SO ₄ ClH
PFECAs	Ammonium dodecafluoro-3H-4,8-dioxanonanoate	ADONA	C ₇ F ₁₂ NO ₄ H ₅
	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid	HFPO-DA (GenX)	C ₆ F ₁₁ O ₃ H
n:3 FTCA	3:3 fluorotelomer carboxylic acid	3:3 FTCA	C ₆ F ₇ O ₂ H ₅
	5:3 fluorotelomer carboxylic acid	5:3 FTCA	C ₈ F ₁₁ O ₂ H ₅
	7:3 fluorotelomer carboxylic acid	7:3 FTCA	C ₁₀ F ₁₅ O ₂ H ₅
n:2 FTSA	1H,1H,2H,2H-perfluorohexane sulfonate	4:2 FTSA	C ₆ F ₉ SO ₃ H ₅
	1H,1H,2H,2H-perfluorooctane sulfonate	6:2 FTSA	C ₈ F ₁₃ SO ₃ H ₅
	1H,1H,2H,2H-perfluorodecane sulfonate	8:2 FTSA	C ₁₀ F ₁₇ SO ₃ H ₅

^{L+Br} = both linear and branched isomers are analyzed.

Table S4. Target analytes with their quantification and qualifications ions as well as the internal standard used for quantification. L indicates linear ions, and br indicates branched ions. All ISs were purchased from Wellington Laboratories (Guelph, Canada).

Target Analyte	Average RT (min)	Precursor ion	Quantitative product ion	Qualitative product ion	IS	IS transition	Quantification standard	Data quality ¹
PFBA	0.66	213	169	149	¹³ C ₄ -PFBA	217/172	PFBA	Q
PFPeA	1.46	263	219	169	¹³ C ₂ -PFHxA	266/222	PFPeA	Q
PFHxA	2.19	313	269	119	¹³ C ₂ -PFHxA	315/270	PFHxA	Q
PFHpA	2.63	363	319	169	¹³ C ₄ -PFOA	367/322	PFHpA	semiQ
L-PFOA	2.98	413	369	169	¹³ C ₄ -PFOA	417/372	PFOA	Q
br-PFOA	2.92	413	369	169	¹³ C ₄ -PFOA	417/372	PFOA	semiQ
PFNA	3.30	463	419	219	¹³ C ₅ -PFNA	468/423	PFNA	Q
PFDA	3.58	513	469	269	¹³ C ₂ -PFDA	515/470	PFDA	Q
PFUnDA	3.87	563	519	269	¹³ C ₂ -PFUnDA	565/520	PFUnDA	Q
PFDODA	4.14	613	569	169	¹³ C ₂ -PFDODA	615/570	PFDODA	Q
PFTTrDA	4.40	662.9	619	169	¹³ C ₂ -PFDODA	615/570	PFTTrDA	semiQ
PFTeDA	4.65	712.9	669	169	¹³ C ₂ -PFDODA	615/570	PFTeDA	semiQ
PFPeDA	4.90	762.9	719	169	¹³ C ₂ -PFDODA	615/570	PFHxDA	semiQ
PFHxDA	5.15	813	769	169	¹³ C ₂ -PFDODA	615/570	PFHxDA	semiQ
PFOcDA	5.59	913	869	169	¹³ C ₂ -PFDODA	615/570	PFOcDA	semiQ
PFBS	2.12	298.9	80	99	¹⁸ O ₂ -PFHxS	403/84	PFBS	Q
PFPeS-80	2.57 ²	348.9	80	99	¹⁸ O ₂ -PFHxS	403/84	PFHxS	semiQ
PFPeS-99	2.57 ²	348.9	99	80	¹⁸ O ₂ -PFHxS	403/84	PFHxS	semiQ
L-PFHxS	3.02	398.9	80	99	¹⁸ O ₂ -PFHxS	403/84	PFHxS	Q

br-PFHxS	2.97	399	80	99	¹⁸ O ₂ -PFHxS	403/84	PFHxS	semiQ
PFHpS-80	3.36	448.9	80	99	¹⁸ O ₂ -PFHxS	403/84	PFHxS	semiQ
PFHpS-99	3.36	448.9	99	80	¹⁸ O ₂ -PFHxS	403/84	PFHxS	semiQ
L-PFOS-80	3.66	498.9	80	99	¹³ C ₄ -PFOS	503/80	PFOS	Q
br-PFOS-80	3.57	498.9	80	99	¹³ C ₄ -PFOS	503/80	PFOS	semiQ
L-PFOS-99	3.66	498.9	99	80	¹³ C ₄ -PFOS	503/80	PFOS	Q
br-PFOS-99	3.57	498.9	99	80	¹³ C ₄ -PFOS	503/80	PFOS	semiQ
PFNS-80	3.83	548.9	80	99	¹³ C ₄ -PFOS	503/80	PFOS	semiQ
PFNS-99	3.83	548.9	99	80	¹³ C ₄ -PFOS	503/80	PFOS	semiQ
L-PFDS	4.23	598.9	80	99	¹³ C ₄ -PFOS	503/80	PFDS	Q
br-PFDS	4.17	598.9	80	99	¹³ C ₄ -PFOS	503/80	PFDS	semiQ
PFUnDS-80	4.63 ²	648.9	80	99	¹³ C ₄ -PFOS	503/80	PFDS	semiQ
PFUnDS-99	4.63 ²	648.9	99	80	¹³ C ₄ -PFOS	503/80	PFDS	semiQ
L-FOSA	4.40	497.9	78	169	¹³ C ₈ -FOSA	506/78	FOSA	Q
br-FOSA	4.34	497.9	78	169	¹³ C ₈ -FOSA	506/78	FOSA	semiQ
L-FOSAA	3.49	555.9	498	419	D ₃ -MeFOSAA	573/419	FOSAA	Q
br-FOSAA	3.44	555.9	498	419	D ₃ -MeFOSAA	573/419	FOSAA	semiQ
L-MeFOSAA	3.62	570	419	483	D ₃ -MeFOSAA	573/419	MeFOSAA	Q
br-MeFOSAA	3.56	570	419	483	D ₃ -MeFOSAA	573/419	MeFOSAA	semiQ
L-EtFOSAA	3.74	584	419	526	D ₅ -EtFOSAA	589/419	EtFOSAA	Q
br-EtFOSAA	3.69	584	419	526	D ₅ -EtFOSAA	589/419	EtFOSAA	semiQ
9Cl-PF3ONS	3.86	531	351	83	¹³ C ₄ -PFOS	503/80	9Cl-PF3ONS	semiQ
11Cl-PF3OUdS	4.42	631	451	83	¹³ C ₄ -PFOS	503/80	11Cl-PF3OUdS	semiQ

ADONA	2.75	377	251	85	¹³ C ₄ -PFOS	503/80	ADONA	semiQ
HFPO-DA	2.36	329	169	185	¹³ C ₄ -PFOA	417/372	HFPO-DA	semiQ
3:3 FTCA	0.95	241	117	177	¹³ C ₄ -PFOA	417/372	3:3 FTCA	semiQ
5:3 FTCA	2.50	341	237	217	¹³ C ₄ -PFOA	417/372	5:3 FTCA	semiQ
7:3 FTCA	3.30	441	337	148	¹³ C ₄ -PFOA	417/372	7:3 FTCA	semiQ
4:2 FTSA	2.03	327	307	80.6	¹³ C ₂ -6:2 FTSA	429/409	4:2 FTSA	semiQ
6:2 FTSA	2.86	427	407	80.6	¹³ C ₂ -6:2 FTSA	429/409	6:2 FTSA	Q
8:2 FTSA	3.46	527	507	80.6	¹³ C ₂ -6:2 FTSA	429/409	8:2 FTSA	semiQ
¹³C₈-PFOA³	2.98	421	376					
¹³C₈-PFOS³	3.66	507	80					

¹ Q = quantitative, semiQ = semi-quantitative for compounds lacking authentic standards and/or analogous ISs.

² Estimated retention time, based on retention times of adjacent PFSA.

³ ¹³C₈-PFOA and ¹³C₈-PFOS were used as recovery internal standards.

Table S5. Mobile phase gradient program for targeted analysis. Flow rate was 0.4 ml/min, column temperature 50°C, injection volume 5 µl.

Time (min)	Mobile phase A ¹ (%)	Mobile phase B ² (%)
0.0	90	10
0.5	90	10
5.0	20	80
5.1	0	100
8.0	0	100
10.0	90	10

¹Mobile phase A: 90% water and 10% acetonitrile containing 2 mM ammonium acetate. ²Mobile phase B: 99% acetonitrile and 1% water containing 2 mM ammonium acetate.

Table S6. Limit of quantification (LOQ) for all compounds determined by the lowest calibration concentration.

Compound	LOQ (ng/g)	Compound	LOQ (ng/g)	Compound	LOQ (ng/g)
PFBA	0.814	PFOcDA	15.1	L-FOSAA ^a	1.16
PFPeA	0.290	PFBS ^a	2.37	L-MeFOSAA	0.826
PFHxA	0.290	L-PFHxS	0.014	L-Et-FOSAA	0.296
PFHpA	0.290	br-PFHxS ^b	0.014	9Cl-PF3ONS	0.840
L-PFOA	0.290	PFHpS ^b	0.014	11Cl-PF3OUdS	0.042
PFNA	0.290	L-PFOS-80 ^a	5.81	ADONA	0.816
PFDA	0.042	br-PFOS-80 ^a	5.81	HFPO-DA	40.6
PFUnDA	0.290	L-PFOS-99 ^a	6.28	3:3 FTCA	105
PFDoDA	0.290	br-PFOS-99 ^a	6.28	5:3 FTCA	106
PFTTrDA	0.290	L-PFDS	0.040	7:3 FTCA	5.61
PFTeDA	0.814	br-PFDS ^b	0.040	4:2 FTSA	0.820
PFPeDA ^b	0.290	L-FOSA	0.302	6:2 FTSA	0.826
PFHxDA	0.814	br-FOSA ^b	0.302	8:2 FTSA	40.9

^aCompounds that were present in the method blanks and for these the LOQ was determined alternatively by calculating the average contamination concentration plus ten times the standard deviation. ^bCompounds that were not present in the calibration curve, but that were present in the samples.

Table S7. Comparison of NIST serum standard reference material (SRM) 1957, reported reference values, and results from method used in the present study.

Compound	NIST certificate values (ng/g)	Gebbink et al. ¹² (ng/g)	Yeung et al. ¹³ (ng/g)	Present study (ng/g)
PFHpA	0.305 ± 0.036	0.2 ± 0.02	0.2 ± 0.1	<0.29
PFOA	5 ± 0.4	3.86 ± 0.13	4.1 ± 0.3	5.0 ± 0.1
PFNA	0.88 ± 0.068	0.72 ± 0.04	0.8 ± 0.1	0.8 ± 0.2
PFDA	0.39 ± 0.1	0.24 ± 0.01	0.3 ± 0.0	0.3 ± 0.1
PFUnDA	0.174 ± 0.031	0.11 ± 0.01	0.1 ± 0.1	<0.29
PFDoDA	-	0.017 ± 0.003	-	-
PFTTrDA	-	0.009 ± 0.004	-	-
PFHxS	4 ± 0.75	3.25 ± 0.06	4.1 ± 0.5	4.0 ± 0.2
PFOS	21.1 ± 1.2	18.5 ± 0.7	19.3 ± 1.2	18.4 ± 0.5
FOSA	-	0.029 ± 0.007	-	-

“-“ = not detected

Table S8. Eluent program for the ion chromatography part of the CIC analysis.

Time (min)	Concentration OH ⁻ (mM)
0.0	8.0
4.0	8.0
9.9	45.0
10.0	100.0
14.0	100.0
14.1	8.0
20.0	8.0

Table S9. Set-up parameters for the HRMS Orbitrap.

Scan parameters	
Scan typ	Full MS
Scan range	200-1200 m/z
Fragmentation	None or NCE(35) (z=1)
Resolution	120000
Polarity	Negative
Maximum inject time	30/250

HESI source	
Sheath gas flow rate	30
Aux gas flow rate	10
Sweep gas flow rate	0
Spray voltage (kV)	3.70
Capillary temp. (°C)	350
S-lens RF level	55.0
Aux gas heater temp. (°C)	350

Table S10. Concentration (ng/g or ng F/g) of PFAS, EOF and TF for sample from East Greenland and Sweden.

(ng/g)	East Greenland								Sweden				
	Polar bear mother (2013)	Polar bear cub (2013)	Polar bear* (2012)	Killer whale* (2013)	Minke whale (2017)	Killer whale (2017)	Ringed seal* (2012)	White beaked dolphin* (2017)	Harbor seal* (2015)	Ringed seal* (2015)	Grey seal* (2012-2016)	Harbor porpoise* (2011-2016)	Grey seal (2016)
PFHpA	1.5	1.4	1.2	0.5	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29
PFOA (L)	55.3	53.8	27.4	0.7	<0.29	<0.29	0.8	0.5	1.8	10.6	2.1	<0.29	0.7
PFNA	451.1	492.9	333.9	20.2	9.0	4.5	13.7	7.7	24.7	124.8	50.5	3.2	35.9
PFDA	138.8	153.8	116.6	43.5	21.0	10.5	10.9	4.9	14.9	48.6	16.7	7.0	9.2
PFUnDA	252.0	235.3	157.1	168.2	96.3	48.3	24.2	19.3	21.4	45.4	19.3	18.5	7.5
PFDoDA	25.2	22.8	16.5	28.4	11.6	5.8	2.8	1.8	4.2	5.3	2.6	2.7	0.9
PFTTrDA	68.6	63.4	63.4	148.0	30.6	15.3	10.8	8.7	9.8	11.9	8.5	10.4	2.8
PFTeDA	9.0	8.4	5.3	27.3	6.5	3.3	1.2	<0.81	1.3	1.4	0.9	1.9	<0.81
PFPeDA	19.7	17.3	16.2	78.6	12.9	6.5	3.2	2.7	2.1	2.5	0.9	2.0	1.2
PFHxDA	<0.81	<0.81	<0.81	0.9	1.1	<0.81	<0.81	<0.81	<0.81	<0.81	<0.81	<0.81	<0.81
PFBS	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4
PFHxS (L+Br)	20.7	22.3	20.7	2.1	0.9	0.5	0.7	0.9	7.6	3.8	1.2	0.7	0.5
PFHpS	14.9	16.6	19.8	0.6	<0.01	<0.01	0.3	<0.01	2.4	1.2	0.5	0.1	0.3
PFOS (L+Br)	1806.5	1784.3	1864.0	230.3	115.0	57.5	99.7	29.5	857.9	483.4	327.8	146.9	172.1
PFDS (L+Br)	8.8	9.9	5.6	3.1	1.3	0.7	0.2	0.1	2.8	0.8	1.0	0.1	<0.04
FOSA (L+Br)	4.5	3.4	7.8	10.4	29.2	14.6	0.5	13.2	0.7	<0.3	3.7	5.4	5.2
F-53B	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84
5:3 FTCA	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106
7:3 FTCA	1130.8	870.7	959.4	132.5	13.7	12.6	9.2	<5.6	31.1	67.1	6.3	72.5	<5.6

6:2 FTSA	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83
ΣPFCA_s (ng/g)	1021.1	1049.0	737.7	516.3	189.2	94.3	67.8	45.6	80.1	250.4	101.7	45.7	58.2
ΣPFSA_s (ng/g)	1850.8	1833.1	1910.2	236.1	117.3	58.7	100.9	30.5	870.7	489.2	330.5	147.8	172.9
ΣPFAS_s (ng/g)	4007.2	3756.1	3615.1	895.3	349.3	180.2	178.5	89.3	982.5	806.8	442.2	271.4	236.3
ΣTarget PFAS_s (ng F/g)	2648.8	2487.6	2379.3	613.2	238.1	122.6	119.6	60.6	640.3	535.7	291.8	178.5	156.1
EOF (ng F/g)	2015.1	1818.2	3537.5	892.8	112.8	186.1	112.7	<158	358.8	973.2	275.1	<158	153.4
TF (ng F/g)	3164.4	2992.5	5562.9	2635.8	408.1	766.6	815.6	626.2	761.0	1085.6	684.4	743.3	568.7

Table S10 continued. Concentration (ng/g or ng F/g) of PFAS, EOF and TF for sample from US Atlantic coast, Iceland and West Greenland.

	US Atlantic coast				Iceland			West Greenland				
	Harbor porpoise* (2006-2012)	Grey seal* (2000-2004)	Harbor seal* (2000-2008)	Pygmy sperm whale (2007)	Harbor seal* (2009-2010)	Harp seal* (2009-2010)	Grey seal* (2009-2010)	Minke whale* (2000)	Harbor porpoise* (2009)	Humpback whale* (2011-2013)	Ringed seal	Harp seal (2016)
PFHpA	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29
PFOA (L)	<0.29	0.4	1.3	0.9	0.5	<0.29	<0.29	0.4	0.5	<0.29	<0.29	0.4
PFNA	0.5	7.7	4.4	5.8	6.5	6.1	3.1	3.6	3.8	0.9	9.7	5.3
PFDA	5.3	8.8	2.4	1.6	4.2	4.2	1.6	3.6	7.4	5.6	5.9	4.0
PFUnDA	7.6	21.1	5.2	7.9	19.8	11.9	5.2	14.2	28.9	28.7	18.1	10.7
PFDoDA	1.7	4.8	1.1	1.8	2.5	1.6	1.0	1.8	3.6	3.1	2.6	1.2
PFTTrDA	6.8	15.6	7.3	18.8	10.6	7.2	4.5	6.5	14.3	12.7	10.7	4.7
PFTeDA	1.3	2.6	1.4	4.5	1.4	<0.81	<0.81	<0.81	1.8	2.1	1.3	<0.81
PFPeDA	3.4	4.9	4.6	28.0	3.7	3.2	1.7	1.8	6.7	9.2	1.7	1.7
PFHxDA	<0.81	<0.81	<0.81	0.8	<0.81	<0.81	<0.81	<0.81	<0.81	<0.81	<0.81	<0.81
PFBS	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4
PFHxS (L+Br)	0.0	0.9	1.1	0.3	0.3	0.1	0.1	0.7	0.1	0.2	<0.01	0.6
PFHpS	<0.01	0.5	0.3	0.2	0.1	<0.01	<0.01	0.1	0.1	<0.01	<0.01	0.2
PFOS (L+Br)	69.1	168.6	50.0	6.6	37.9	21.3	<5.8	86.0	70.4	21.0	28.1	39.1
PFDS (L+Br)	0.3	8.7	0.6	0.1	0.4	<0.04	<0.04	2.6	0.2	0.6	0.2	0.1
FOSA (L+Br)	3.0	2.2	0.5	8.4	0.6	2.9	<0.3	53.5	1.7	12.3	<0.3	0.8
F-53B	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84

5:3 FTCA	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106
7:3 FTCA	189.0	38.5	193.3	20.6	10.4	<5.6	10.7	<5.6	<5.6	<5.6	<5.6	<5.6
6:2 FTSA	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83	<0.83
ΣPFCAs (ng/g)	26.6	65.9	27.7	70.0	49.2	34.2	16.9	31.9	67.0	62.4	50.0	27.9
ΣPFSAAs (ng/g)	69.5	178.6	52.0	7.1	38.6	21.4	0.1	89.4	70.7	21.8	28.3	40.0
ΣPFASs (ng/g)	288.1	285.2	273.6	106.2	99.0	58.5	27.8	174.9	139.4	96.5	78.3	68.7
ΣTarget PFASs (ng F/g)	188.0	188.8	178.6	73.5	67.1	40.0	19.0	115.3	94.5	66.5	53.7	46.1
EOF (ng F/g)	557.8	666.3	3288.2	293.5	52.5	<71	<71	<158	<158	<158	<158	<158
TF (ng F/g)	1560.3	1433.7	1138.8	559.7	718.5	9196.0	298.2	1474.5	1285.4	1487.8	539.8	811.0

REFERENCES

- (1) Powley, C. R.; George, S. W.; Ryan, T. W.; Buck, R. C. Matrix Effect-Free Analytical Methods for Determination of Perfluorinated Carboxylic Acids in Environmental Matrixes. *Anal. Chem.* **2005**, *77* (19), 6353–6358. <https://doi.org/10.1021/ac0508090>.
- (2) Miyake, Y.; Yamashita, N.; Rostkowski, P.; So, M. K.; Taniyasu, S.; Lam, P. K. S.; Kannan, K. Determination of Trace Levels of Total Fluorine in Water Using Combustion Ion Chromatography for Fluorine: A Mass Balance Approach to Determine Individual Perfluorinated Chemicals in Water. *J. Chromatogr. A* **2007**, *1143* (1–2), 98–104. <https://doi.org/10.1016/j.chroma.2006.12.071>.
- (3) Schultes, L.; Vestergren, R.; Volkova Hellström, K.; Westberg, E.; Jacobson, T.; Benskin, J. P. Per- and Polyfluoroalkyl Substances and Fluorine Mass Balance in Cosmetic Products from the Swedish Market: Implications for Environmental Emissions and Human Exposure. *Environ. Sci. Process. Impacts* **2018**. <https://doi.org/10.1039/C8EM00368H>.
- (4) Schultes, L.; Peaslee, G. F.; Brockman, J. D.; Majumdar, A.; McGuinness, S. R.; Ngwenyama, R. A.; Wilkinson, J. T.; Sandblom, O.; Ngwenyama, R. A.; Benskin, J. P. Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform? *Environ. Sci. Technol. Lett.* **2019**, *6*, 73–78. <https://doi.org/10.1021/acs.estlett.8b00700>.
- (5) Miaz, L. T. Development and Application of UHPLC-Orbitrap Method for Quantitative and Suspect Screening of PFASs in Human Serum, Master's thesis, Stockholm University, 2018.
- (6) Fujii, Y.; Kato, Y.; Kozai, M.; Matsuishi, T.; Harada, K. H.; Koizumi, A.; Kimura, O.; Endo, T.; Haraguchi, K. Different Profiles of Naturally Produced and Anthropogenic Organohalogens in the Livers of Cetaceans from the Sea of Japan and the North Pacific Ocean. *Mar. Pollut. Bull.* **2018**, *136* (August), 230–242. <https://doi.org/10.1016/j.marpolbul.2018.08.051>.
- (7) 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* (24), 6475–6481. <https://doi.org/10.1021/es049620g>.
- (8) 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* (11), 4037–4043. <https://doi.org/10.1021/es9003894>.
- (9) Yeung, L. W. Y.; Miyake, Y.; Li, P.; Taniyasu, S.; Kannan, K.; Guruge, K. S.; Lam, P. K. S.; Yamashita, N. Comparison of Total Fluorine, Extractable Organic Fluorine and Perfluorinated Compounds in the Blood of Wild and Perfluorooctanoate (PFOA)-Exposed Rats: Evidence for the Presence of Other Organofluorine Compounds. *Anal. Chim. Acta* **2009**, *635* (1), 108–114. <https://doi.org/10.1016/j.aca.2009.01.004>.
 - (10) Gebbink, W. A.; Bossi, R.; Rigét, F. F.; Rosing-Asvid, A.; Sonne, C.; Dietz, R. Observation of Emerging Per- and Polyfluoroalkyl Substances (PFASs) in Greenland Marine Mammals. *Chemosphere* **2016**, *144*, 2384–2391. <https://doi.org/10.1016/j.chemosphere.2015.10.116>.
 - (11) Shaw, S.; Berger, M. L.; Brenner, D.; Tao, L.; Wu, Q.; Kannan, K. Specific Accumulation of Perfluorochemicals in Harbor Seals (*Phoca Vitulina Concolor*) from the Northwest Atlantic. *Chemosphere* **2009**, *74* (8), 1037–1043. <https://doi.org/10.1016/j.chemosphere.2008.10.063>.
 - (12) Gebbink, W. A.; Glynn, A.; Darnerud, P. O.; Berger, U. Perfluoroalkyl Acids and Their Precursors in Swedish Food: The Relative Importance of Direct and Indirect Dietary Exposure. *Environ. Pollut.* **2015**, *198*, 108–115. <https://doi.org/10.1016/j.envpol.2014.12.022>.
 - (13) Yeung, L. W. Y.; De Silva, A. O.; Loi, E. I. H.; Marvin, C. H.; Taniyasu, S.; Yamashita, N.; Mabury, S. A.; Muir, D. C. G.; Lam, P. K. S. Perfluoroalkyl Substances and Extractable Organic Fluorine in Surface Sediments and Cores from Lake Ontario. *Environ. Int.* **2013**, *59* (2013), 389–397. <https://doi.org/10.1016/j.envint.2013.06.026>.