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Temporal Shifts in Poly- and Perfluoroalkyl Substances (PFASs) in North Atlantic Pilot Whales Indicate Large Contribution of Atmospheric Precursors

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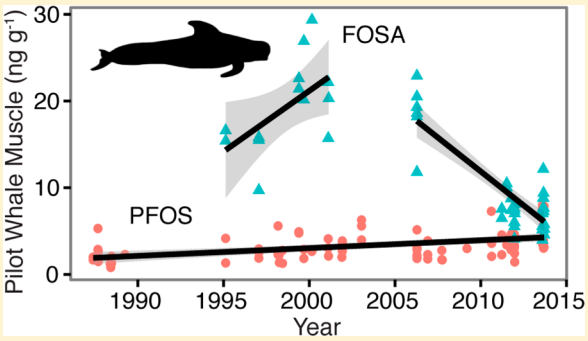
Supporting Information

ABSTRACT: Poly- and perfluoroalkyl substances (PFASs) are persistent, bioaccumulative anthropogenic compounds associated with adverse health impacts on humans and wildlife. PFAS production changed in North America and Europe around the year 2000, but impacts on wildlife appear to vary across species and location. Unlike other mammal species, cetaceans lack the enzyme for transforming an important intermediate precursor (perfluorooctane sulfonamide: FOSA), into a prevalent compound in most wildlife (perfluorooctanesulfonate: PFOS). Thus, their tissue burden differentiates these two compounds while other mammals contain PFOS from both direct exposure and precursor degradation. Here we report temporal trends in 15 PFASs measured in muscle from juvenile male North Atlantic pilot whales (*Globicephala melas*) harvested between 1986 and 2013. FOSA accounted for a peak of 84% of the 15 PFASs around 2000 but declined to 34% in recent years. PFOS and long-chained PFCAs (C9−C13) increased significantly over the whole period (2.8% yr^{-1} to 8.3% yr^{-1}), but FOSA declined by 13% yr^{-1} after 2006. Results from FOSA partitioning and bioaccumulation modeling forced by changes in atmospheric inputs reasonably capture magnitudes and temporal patterns in FOSA concentrations measured in pilot whales. Rapid changes in atmospheric FOSA in polar and subpolar regions around 2000 helps to explain large declines in PFOS exposure for species that metabolize FOSA, including seafood consuming human populations. This work reinforces the importance of accounting for biological exposures to PFAS precursors.



INTRODUCTION

Poly- and perfluoroalkyl substances (PFASs) are widely used persistent anthropogenic chemicals that are accumulating in the global oceans.[1−3] Long-chain PFASs bioaccumulate in aquatic food webs,[4,5] posing risks to apex predators such as whales, seals, and polar bears.[6−8] PFAS exposures have been associated with adverse health effects in humans and wildlife, including immunotoxicity, developmental disorders, and cancer.[9,10] Global regulations and voluntary shifts in chemical manufacturing have changed the source regions and composition of PFASs and precursor compounds released to the environment.[3,11] However, impacts of changing emissions on biological PFAS concentrations and contributions of precursor compounds remain unclear.[11−13]

Exposure analyses focus on two major classes of PFASs, perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) because of their persistence and ubiquity. Between 2000 and 2002, the most prevalent compound, perfluorooctanesulfonate (PFOS), and its precursors were voluntarily phased-out and eventually regulated in North America and Europe.[3] Inconsistent temporal patterns in PFAS concentrations have been measured in marine mammals following this phase out.[6,14] Between 1984 and 2009, trends for perfluorooctanesulfonate (PFOS) and other PFSAs varied

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Table 1. Median Concentrations (ng g^{-1} wet weight) and Number of Samples above Detection Limit (DL) in Parentheses for 15 PFASs Measured in Juvenile Male Pilot Whale Muscle (*Globicephala melas*) between 1986 and 2013 from this Study and from the Faroese Environment Agency (FEA)[41]

Compound	1986−1988	1994−1997	1998−2002	2006−2009	2010−2013	DL (this study)	DL (FEA)
PFBS		<DL (0/5)	<DL (0/11)	<DL (0/10)	<DL (0/29)	0.01	0.09
PFHxS		0.13 (5/5)	0.19 (11/11)	0.11 (5/10)	0.14 (29/29)	0.05	0.03
PFHpS		<DL (1/5)	<DL (2/8)		0.01 (15/29)	0.05	
PFOS	2.0 (13/13)	2.3 (11/11)	3.7 (15/15)	2.8 (15/15)	4.0 (33/33)	0.01	0.01
PFDS		0.06 (5/5)	0.06 (6/11)	<DL (4/10)	0.06 (16/29)	0.01	0.15
FOSA		16 (5/5)	22 (8/8)	19 (7/7)	7.4 (29/29)	0.05	
PFHxA		<DL (0/5)	<DL (0/11)	0.14 (7/10)	<DL (0/29)	0.006	0.06
PFHpA		<DL (0/5)	<DL (0/11)	0.03 (5/10)	<DL (10/29)	0.01	0.06
PFOA		0.17 (5/5)	0.13 (11/11)	0.10 (9/10)0.06	(29/29)	0.006	0.18
PFNA	<DL (3/13)	0.14 (6/11)	0.22 (13/14)	0.29 (13/14)	0.51 (32/33)	0.02	0.06
PFDA	<DL (1/13)	0.18 (5/11)	0.22 (14/15)	0.27 (13/15)	0.73 (32/33)	0.006	0.01
PFUnA	0.5 (9/11)	0.59 (9/11)	0.91 (13/13)	1.6 (15/15)	2.0 (33/33)	0.006	0.02
PFDoA		0.19 (5/5)	0.20 (11/11)0.46	(10/10)	0.38 (29/29)	0.02	0.02
PFTrA	0.53 (1/6)	1.2 (7/7)	1.1 (12/13)	1.4 (13/13)	3.5 (30/31)	0.02	0.01
PFTeA	<DL (0/6)	0.32 (5/7)	0.35 (9/13)	<DL (5/13)	0.84 (28/31)	0.10	0.02

across geographical locations, while long-chained fluorinated carboxylates (PFCAs) in seals, porpoises and dolphins from the Arctic and Subarctic continued to increase by 7−15% per year.[15−17]

Temporal trends in biological concentrations can be confounded by differences in migratory patterns, dietary habits, gender, and age of individuals sampled,[18] as well as varying exposures to precursor compounds.[12,19−21] The suite of PFASs routinely targeted in analytical studies typically comprises a small fraction (<50%) of the environmental burden of total organic fluorine (TOF).[22−24] Relative contributions of neutral volatile atmospheric precursors such as fluorotelomer alcohols (FTOH) and perfluoroalkyl sulfonamides (FASAs) to overall exposures of humans and wildlife are uncertain.[25−29] For humans, the modeled fraction of total PFOS exposures contributed by precursors ranges between 8% and 60%.[19,30] Gebbink et al.[20] reported that precursors contribute minimally to recent (2013−2014) bioaccumulation in a Baltic Sea food web. By contrast, a longitudinal study in fish from the Swedish coast between 1991 and 2011 suggested that exposures from precursors were greater than PFOS prior to year 2001.[31]

Biological exposures to precursor compounds are difficult to measure directly because in vivo biotransformation occurs in many animals, including humans.[19,21,32] One exception is cetaceans, which are missing a key enzyme for metabolism of the commonly observed precursor, perfluorooctane sulfonamide (FOSA), into PFOS.[33−35] FOSA is an intermediate degradation product of other precursors such as the FASA: *N*-ethyl-perfluorooctane sulfonamide (*N*-EtFOSA).[4,36,37] Lack of biotransformation of FOSA by cetaceans provides a unique opportunity to quantify the exposures attributable to this neutral atmospheric precursor.

Here we analyze temporal changes in 15 PFASs in juvenile male North Atlantic pilot whales (*Globicephala melas*) caught in the Faroe Islands between 1986 and 2013 (Figure S2 of the Supporting Information, SI). The Faroe Islands are located in the central North Atlantic (62°N, 7°W), and the traditional diet of the population includes pilot whale.[38] PFASs are generally measured in the liver of marine mammals because contaminants often concentrate there, but measurements in muscle provide a more direct link to human exposure for marine food consuming populations. The main objectives of this work are (1) To gain insight into the responsiveness of North Atlantic marine food-webs to the phase out in North American and European manufacturing of PFOS and its precursors around the year 2000,[3] and (2) to better understand the role of the intermediate precursors in these temporal patterns. We compare measured and modeled temporal changes in FOSA to gain insight into the importance of precursor exposures for shifts in marine food web PFAS burdens.

METHODS

Sample Collection. Pilot whales exhibit a high degree of site-fidelity and have a relatively homogeneous diet consisting mainly of squid.[39,40] We selected muscle tissue for PFAS analysis from 86 pilot whales harvested in the Faroe Islands between 1994 and 2013 and archived by the Faroese Natural History Museum. In addition, we included PFAS data measured in the muscle of 38 juvenile male pilot whales that were previously analyzed by the Faroese Environment Agency to extend our temporal analysis back to 1986.[41] We also collected five squid (*Todarodes sagittatus*) in 2010 from a research vessel off the coast of the Faroe Islands. All samples were frozen after collection and stored in high-density polyethylene bags until analysis.

Muscle samples from 49 of the 86 pilot whales collected for this study were from juvenile males with ages ranging between 5 and 15 years based on length (Figure S1).[42] To assess variability in PFAS concentrations related to gender and size, we also analyzed samples from 9 juvenile females, 20 adult females, and 8 adult males harvested in 2013 to compare to the 16 juvenile males from this year. Adults are defined by lengths >500 cm for males and >378 cm for females.[42] Detailed information on the harvest dates, size, age, and gender of whales included in this study are included in Tables S1 and S2.

PFAS Extraction and Analysis. All whale muscle and squid samples were analyzed for 15 PFASs at Aarhus University, Denmark. Duplicate squid samples were also analyzed by the Faroese Environment Agency, following methods for extraction and quantification described in Ahrens et al.[43] PFASs quantified included: perfluorobutanesulfonic acid (PFBS, four carbon chain length: C-4), perfluorohexanesulfonic acid (PFHxS: C-6), perfluoroheptanesulfonic acid (PFHpS: C-7), PFOS (C-8), perfluorodecanesulfonic acid (PFDS: C-10),

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FOSA (C-8), perfluorohexanoic acid (PFHxA: C-6), perfluoroheptanoic acid (PFHpA: C-7), perfluorooctanoic acid (PFOA: C-8), perfluorononanoic acid (PFNA: C-9), perfluorodecanoic acid (PFDA: C-10), perfluoroundecanoic acid (PFUnA: C-11), perfluorododecanoic acid (PFDoA: C-12), perfluorotridecanoic acid (PFTrA: C-13), and perfluorotetradecanoic acid (PFTeA: C-14).

Approximately 5 g of wet tissue was homogenized and a 1 g aliquot was weighed in a polypropylene tube and spiked with 10 ng of isotopically labeled PFAS mixture (Wellington Laboratories; Guelph, ON, Canada) as an internal standard for quantification (Table S1). Tissues were extracted with 5 mL acetonitrile for 30 min in an ultrasonic bath at 30 °C. Extraction procedures were repeated, and the combined extract was reduced to 2 mL under a stream of nitrogen and 50 μL acetic acid was added. Supelclean ENVI-Carb cartridges (100 mg, 1 mL, 100−400 mesh, Supelco, U.S.A.) were used for cleanup. The cartridges were conditioned with 2 mL acetonitrile followed by 1 mL 20% acetic acid in acetonitrile. The sample extract and 3 mL of methanol were added to the cartridge and directly collected into another vial. The extracts were reduced to dryness under a nitrogen stream and redissolved in 1 mL methanol/2 mM ammonium acetate (50:50, v/v).

Table 1 provides a complete list of the PFASs analyzed and corresponding detection limits for this study. Analysis was performed by liquid chromatography tandem-mass spectrometry (LC−MS/MS) with electrospray ionization in negative mode.[29] Chromatographic separation was performed using a C18 Kinetex column (2.1 × 150 mm^2, Phenomenex, Torrance, CA, U.S.A.) and an Agilent 1200 Series HPLC (Agilent, Palo Alto, CA, U.S.A.). Duplicate squid samples were analyzed on a BEH C-18 column in Water Acquity I-Class UPLC and Waters Xevo TQ-S for improved sensitivity. The ions monitored for each compound can be found in Table S3. Each batch of samples was analyzed with a procedural blank. Method detection limits (MDL) were calculated as three times the standard deviation of procedural blanks. Recoveries ranged from 75% to 128%, which is comparable to previous work (Table S4).[35,44] The relative standard deviation (RSD) of samples run in duplicate ranged from 5 to 24%. RSDs for PFTeA and PFTrA were higher (44%−47%) because of the tendency of longer-chained PFASs to sorb to surfaces during sample preparation and analysis.

For pilot whale data from the Faroese Environment Agency,[41] sample extraction and analysis methods are provided in Rotander et al.[15] Samples were analyzed in two batches and their corresponding detection limits are listed in Table 1. The first batch contained muscle tissue from whales sampled between 1986 and 2010. For this batch, detection limits were higher and frequencies lower than this study for PFBS, PFHxS, PFHpS, PFDS, PFHxA, PFHpA, and PFOA. We therefore excluded these data from subsequent statistical analyses. The second batch included the years 2001/2006 and all compounds had comparable detection limits and frequencies to this work and so were included. Neither batch reported FOSA levels.

Statistical Analysis. All statistical analyses were performed in R version 3.2.2. Five compounds (PFBS, PFHpS, PFDS, PFHpA, and PFHxA) were infrequently detected (6%−52%) and thus removed from subsequent statistical analyses. Detection frequencies for the remaining 10 compounds were all >80%. For compounds that contained samples below the detection-limit (DL), maximum-likelihood estimation was used for inclusion in summary statistics, ANOVA, and regression analyses, as implemented by the NADA package in R.[45] For plotting purposes nondetects are shown as the detection limit multiplied by $1/\sqrt{2}$.[46]

We investigated the occurrence of statistically significant changes in PFAS composition over time using methods for compositional data analysis described in Aitchisen[47] and implemented in the R package *compositions*.[48] This method removes spurious correlations and other constraints inherent in compositional data by applying a log-ratio transformation prior to additional analysis. One-way ANOVA for each compound was used to investigate concentration differences resulting from gender and age as a four-level categorical variable (juvenile/adult, male/female) in whales harvested in the year 2013. We log-transformed concentrations to correct for the observed distribution of PFASs and estimated annual changes in concentrations in juvenile males by the slope of linear regression models for individual compounds.

Environmental Partitioning and Bioaccumulation Model for FOSA. We developed a model for FOSA partitioning and bioaccumulation in whales to simulate expected temporal trends in this neutral precursor compound and quantify the importance of different uptake pathways. Changing atmospheric FOSA concentrations are driven by shifts in chemical production over time, but are poorly constrained based on emissions inventories and direct measurements.[3,12] Three cruises between 2007 and 2008 measured FOSA in the North Atlantic marine boundary layer.[49] We estimated temporal shifts in atmospheric FOSA levels at northern latitudes by linearly scaling the average concentrations from these cruises by changes in FOSA deposition in the Devon Ice cap, Devon Island, Nunavut, Canada[50] between 1994 and 2007 (Table S5). Temporal changes in seawater FOSA concentrations were estimated from a measured air−water partition coefficient (log K_{aw} = −3.7).[51] We compared these values to open ocean measurements from the migratory territory of North Atlantic pilot whales indicated by satellite telemetry data (Figure S2).[40]

Pilot whale stomach contents suggest their diet consists mainly of European flying squid (*Todarodes sagittatus*).[39] We modeled squid FOSA concentrations assuming simple equilibrium partitioning with the ocean surface mixed layer (Table S6). Partitioning of FOSA from seawater to squid is based on an octanol−water partition coefficient (log K_{ow} = 5.8),[52] measured lipid content (1.4%), and protein content (16%).[53]

We parametrized the time-dependent bioaccumulation model for neutral organic pollutants developed by Arnot and Gobas[54] for FOSA in the North Atlantic pilot whale food web (Tables S7 and S8). This model has previously been applied to a wide-range of food-webs, including marine mammals.[54−57] The model quantifies chemical uptake and elimination in biota based on dietary uptake, respiration, fecal egestion, urination, and growth dilution. We assumed metabolism of FOSA by pilot whales is negligible based on prior work.[33−35] Ingestion rates for pilot whales were based on a cetacean specific allometric equation.[58,59] Respiration rates were quantified from breathing frequency and tidal lung volume derived from allometric equations for marine mammals.[60,61] We assumed a 100% uptake efficiency in the lungs, following previous exposure analyses for FOSA.[19,62] Growth rates and body composition were based on data from over 3400 pilot whales from the Faroe Islands.[42,59] A complete description of the bioaccumulation model is provided in the SI (Tables S7 and S8).

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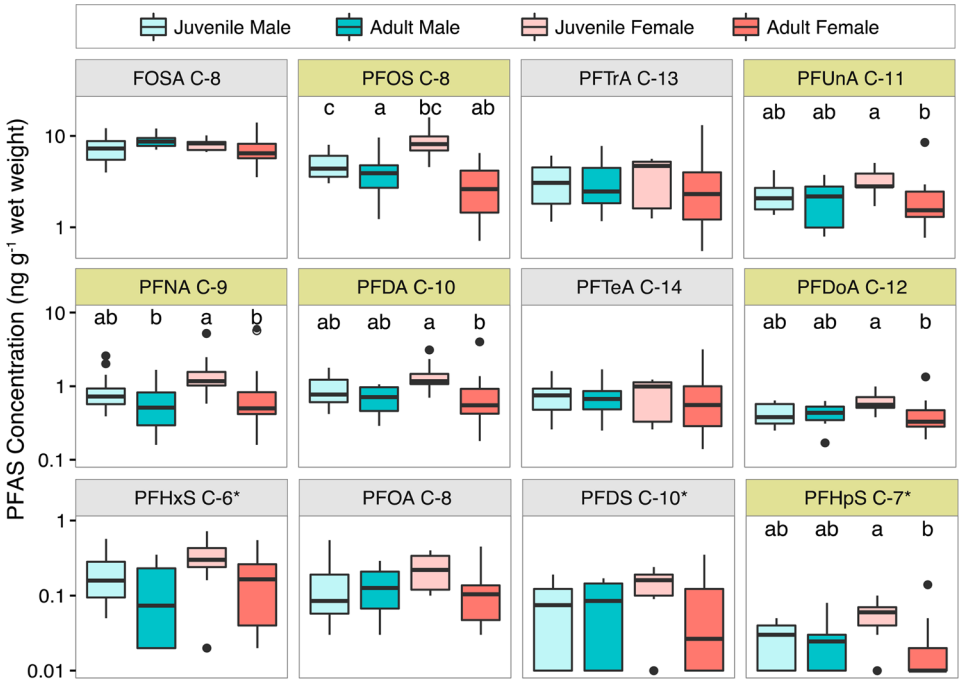

Figure 1. Effects of life stage and gender on measured PFAS concentrations in pilot whale muscle (*Globicephala melas*) sampled in 2013. Median concentrations for each group are represented by the horizontal black line in box/whisker plots. Notches represent 25th and 75th percentile concentrations, whiskers extend to 1.5 times the interquartile range and outliers are shown as circles. Compounds that differ significantly between groups based on one-way ANOVA ($p < 0.05$) are shaded yellow, and common letters above each box indicate groups with no significant difference in between group comparisons in post hoc analysis using Tukey's test. Compounds from Table 1 that are not shown here were infrequently detected. For compounds denoted by "*" nondetects are shown as the detection limit multiplied by $1/\sqrt{2}$.[46]

Temporal changes in FOSA reported here are for juvenile males between the ages of 5 to 14 years (mean 6–9 years) (Figure S1).[18] To reproduce these measurements with the bioaccumulation model, we simulated birth cohorts born between 1980 and 2025 and FOSA exposure across the lifetime of each pilot whale individual given changes in environmental concentrations. We sampled the expected FOSA concentrations in whales at ages 5, 10, and 15 years from each simulation to reproduce cross-sectional body burden-age trends (CBATs).[18] We evaluated the simulation by comparing modeled means and changes over time to measured FOSA concentrations and slopes of the regression model for temporal changes in observations.

RESULTS AND DISCUSSION

Contemporary PFAS Levels in Pilot Whale Muscle. Concentrations of different PFASs in pilot whale muscle in 2013 were highest for FOSA, PFOS, and the PFCAs with chain lengths between 9 and 14 carbons (Figure 1, Table 1). The largest fractions of total measured PFASs consist of PFOS (23%) and its neutral precursor FOSA (34%). Prior cetacean studies report concentrations of FOSA to be as high or greater than PFOS,[5,63−65] but underlying mechanisms for accumulation have not been explored.

The lack of statistical correlation between FOSA and other PFASs in Figure 2 highlights its contrasting origin and time scales for environmental cycling.[66] Most PFASs were correlated with each other, indicating similarity in production sources and/or cycling in the ocean (Figure 2). Their lifetimes in surface seawater, where biological exposures occur, are thought to be long (decades)[12,67,68] relative to the atmospheric half-lives of precursors such as FOSA (50–80 days for FTOHs and even less for water-soluble FASAs).[12,67,68]

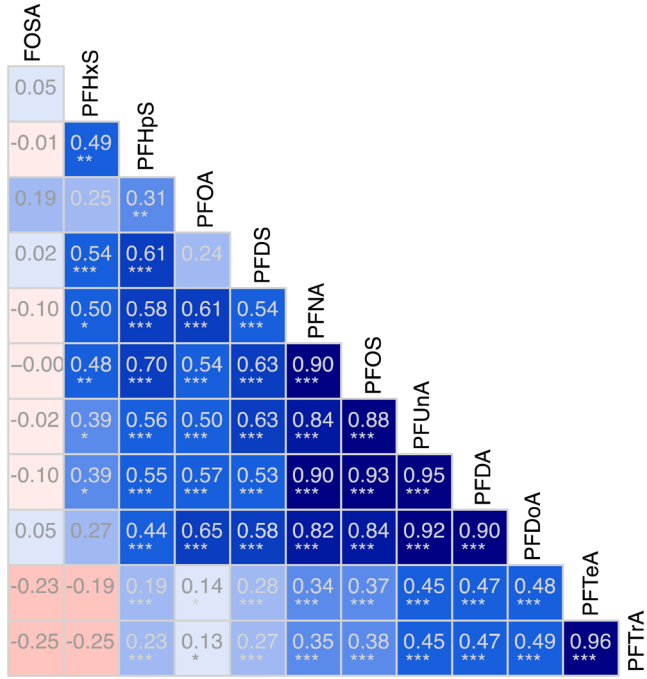

Figure 2. Correlation matrix for PFASs measured in pilot whale muscle tissue (*Globicephala melas*) in 2013. Numbers indicate Spearman correlation coefficients for a two-sided statistical test. The intensities of blue and red show the strength of positive and negative correlations, respectively. Significant correlations are denoted by asterisks (* = $p < 0.05$; **=$p < 0.005$, ***=$p < 0.0005$).

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For whales sampled in 2013, odd numbered long-chain PFCAs (PFTrA, PFUnA, and PFNA) were comparable in magnitude to PFOS and FOSA, but other compounds (PFHxS, PFOA, PFDS, and PFHpS) were all at least an order of magnitude lower (Figure 1). The enhanced propensity for PFOS and other long-chained PFASs to bioaccumulate in aquatic food-webs has been demonstrated in many other studies.[69,70] Sturm and Ahrens[14] suggest enrichment of the odd numbered PFCAs in many marine mammals is consistent with atmospheric fluorotelomer alcohol (FTOH) degradation as an important exposure source. Greater bioaccumulation of the longer chain (odd numbered) compounds is expected when there is equal production of odd and even PFASs during degradation of precursors such as 8:2 FTOH and 10:2 FTOH.[14]

We found significant differences (one-way ANOVA, $p < 0.05$) across life stage and gender for PFOS, PFUnA, PFNA, PFDA, PFDoA, and PFHpS in pilot whales sampled in 2013 (Figure 1). For all compounds except FOSA, median concentrations were highest in nulliparous juvenile females (Figure 1). Juvenile females were significantly higher than adult females for PFNA, PFDA, PFUnA, PFDoA, and PFHpS (one-way ANOVA, $p < 0.05$ and posthoc Tukey test). Juvenile males were statistically elevated ($p < 0.05$) compared to adult males and females for PFOS, but not statistically different for other compounds.

Observed differences between PFAS concentrations in juvenile and adult females are consistent with prior work showing that birth and lactation are large elimination pathways for PFASs in mammals.[71−75] FOSA is the only neutral compound and is known to partition differently than the other PFASs across tissues.[21] In pilot whales, female calves nurse longer than males and juvenile females are also known to consume a wider range of prey.[39] For these reasons, juvenile males were selected for temporal trends analysis in this study to minimize impacts of life stage and gender related variability.

Temporal Patterns in Juvenile Male Pilot Whales. Between 1994 and 2013, FOSA accounted for a large but declining fraction of the 15 PFASs (ΣPFASs) measured in juvenile male whale muscle tissue (Figure 3A). The fraction of ΣPFASs consisting of FOSA peaked in 1999 at 84% and declined after the phase out in chemical production of PFOS and its precursors around the year 2000 to a low of 34% in 2013 (Figure 3A). By contrast, long chain PFCAs (C9−C14) have continued to increase in relative importance over this same period from between 7 and 14% for 1994 to 2000, up to 40% of the ΣPFASs in 2013 (Figure 3A). All reported changes in composition were statistically significant based on Aitchison compositional regression. Declining concentrations of FOSA between 1994 and 2013 were offset by increases in other compounds over the same time-period, resulting in no significant change in ΣPFASs between 1994 and 2013 (Figure 3B). Peak ΣPFAS concentrations occur in 1998 (31 ng g^{-1} wet weight: ww) and levels in 1994 are comparable to 2013 (21 ng g^{-1} ww).

Figure 4 shows statistically significant temporal trends for six PFASs (PFOS, FOSA, PFNA, PFDA, PFUnA, and PFTrA) between 1986 and 2013 inferred from log−linear regression models. All compounds show increases for the entire period except FOSA, which declined by 13% yr^{-1} after 2006. Increases since 1986 observed for the other five compounds range from 2.8% yr^{-1} (PFOS) to 8.2% yr^{-1} (PFDA) (Figure 4). We calculated crude trends as well as trends adjusted for pilot whale

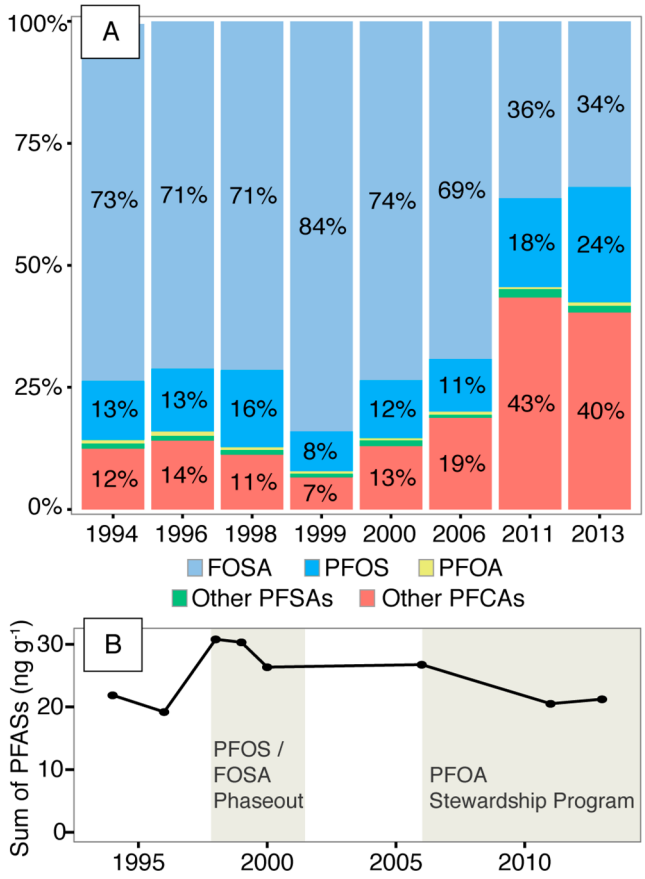

Figure 3. Temporal patterns in PFAS concentrations in juvenile male pilot whale muscle tissue (*Globicephala melas*) between 1994 and 2013. Compounds are grouped into categories reflecting one or more compound: perfluorooctane sulfonamide: FOSA, the neutral atmospheric precursor to perfluorooctanesulfonate (PFOS); perfluorooctanoic acid: PFOA; perfluorosulfonic acids: PFSAs; perfluorinated carboxylic acids: PFCAs. Panel (A) shows the changing composition of PFASs over time. Panel (B) shows the sum of the 15 detectable PFASs measured in this study.

length as a proxy for age. Length was only statistically significant for PFOS, but the effect size was minimal as shown in Table S9.

Increases in long-chained PFCAs in juvenile male pilot whale muscle reported here fall within ranges previously reported for other marine mammals. Swedish sea otters (6−11% yr^{-1}) and Alaskan beluga whales (9−14% yr^{-1}) show greater increases and Norwegian ringed seals are comparable (5−9%) to pilot whale changes observed here. However, increases in polar bears from east Greenland through 2006 (2−3% yr^{-1}) and decreases since 2006 are lower than pilot whale trends.[16,17,66] Varying rates of change likely reflect species-specific differences in metabolism and environmental exposures, as discussed in other work.[14]

We find that increases in PFOS concentrations in pilot whales are smaller than those for long-chained PFCAs, consistent with shifting emissions away from PFOS. This has been confirmed by results across several wildlife species.[16,17,66] We speculate that relatively rapid decreases in PFOS reported in other studies such as for harbor seals from the German Bight (2002−2008),[76] ringed seal from the Canadian Arctic (2000−2005),[77] and ringed seals and polar bears from Greenland (2006−2010)[16] may reflect decreases in FOSA exposure that

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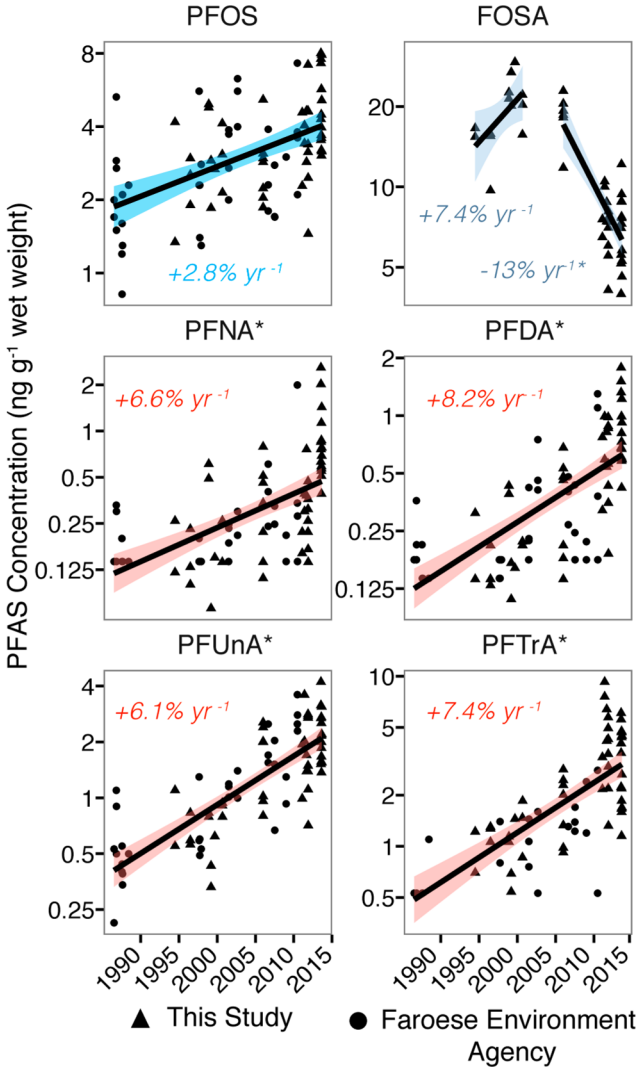

Figure 4. Temporal trends in concentrations of selected PFASs in juvenile male North Atlantic pilot whale muscle tissue (*Globicephala melas*) between 1986 and 2013. All trends (shown as percent annual changes) are significant at the $p < 0.05$ level based on linear regression of log-transformed concentrations. Shaded areas represent 95% confidence intervals of the mean. Triangles are pilot whale analyzed for this study and circles are analyzed by the Faroese Environment Agency.[41] For compounds denoted by "*" nondetects are represented in plots as the detection limit multiplied by $1/\sqrt{2}$,[46] but slopes are based on maximum likelihood estimates for nondetect values.[45]

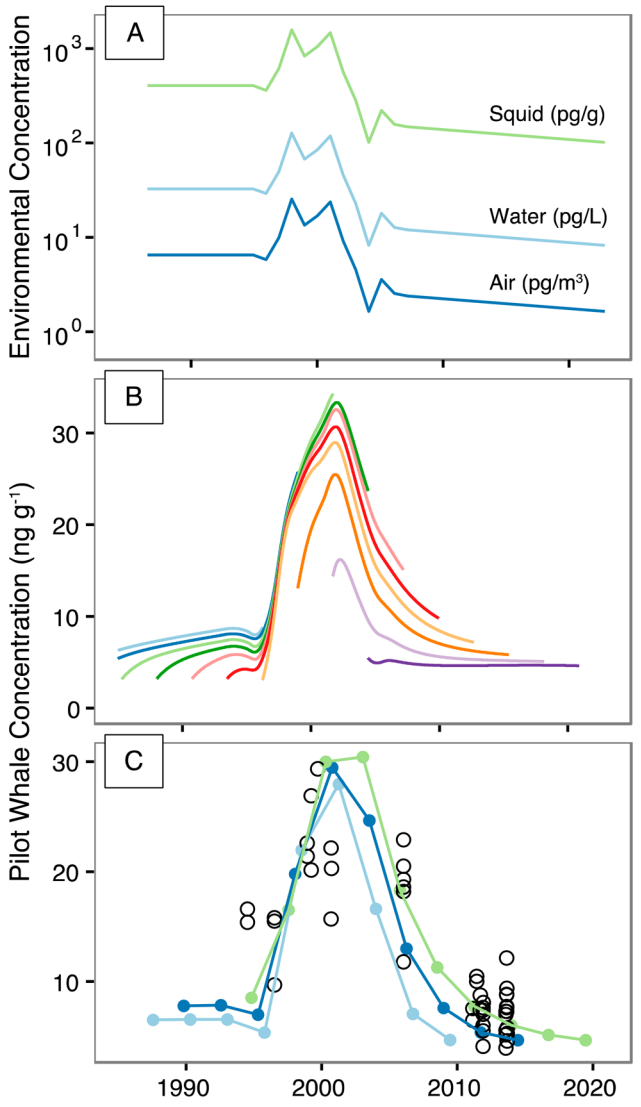

Figure 5. Modeled concentrations of perfluorooctane sulfonamide (FOSA) in air, water, squid (*Todarodes sagitatus*), and pilot whales (*Globicephala melas*) compared to temporal measurements collected in this study. Panel A shows reconstructed concentrations in air based on historic ice core data,[26,50] and corresponding concentrations in surface seawater and squid based on equilibrium partitioning. Panel (B) shows modeled concentrations of FOSA in different pilot whale birth cohorts based on environmental levels (Panel A). Panel (C) shows average concentrations of FOSA in juvenile male pilot whales for ages ranging between 5 to 15 years to match the bounds of observations. Measured values from this study shown as black circles in Panel (C).

has been biotransformed into PFOS. Previous studies have alluded to a potential role for precursors affecting biological trends,[6,12] but did not specifically identify FOSA as a major intermediate compound.

Temporal Patterns of FOSA Exposure in Pilot Whales. Figure 5a shows reconstructed atmospheric trends in FOSA from ice core measurements and ship cruise data (Table S5), and corresponding concentrations in seawater and squid based on simple equilibrium partitioning calculations. Results suggest FOSA levels peaked between 1997 to 2001 at ~22 pg m^{-3} in the atmosphere, ~110 pg L^{-1} in seawater, and ~1355 pg g^{-1} wet weight in European flying squid. By 2010, modeled levels suggest declines to ~2.2 pg m^{-3} in the atmosphere, ~11 pg L^{-1} in seawater, and ~138 pg g^{-1} in squid.

By comparison, a mean atmospheric FOSA concentration of 1.2 pg m^{-3} was measured at a remote high elevation site in Switzerland in 2010.[78] A variety of studies report seawater FOSA concentrations from the North Atlantic and Arctic between 2005 and 2009 but results varied widely (1−300 pg L^{-1}) depending on sampling methods, reported detection limits, and proximity to the coast (and thus point sources).[27,79−85] Measurements from the offshore North Atlantic Ocean in 2005 were all <17 pg L^{-1} and in the Norwegian Sea in 2007 were all <60 pg L^{-1}.[80,81] For squid (n = 5) collected for this study in 2010, measured FOSA concentrations ranged between 177 and 386 pg g^{-1} (Table S10).

Given the simplicity of our partitioning modeling approach, approximations based on atmospheric FOSA appear to reasonably capture the magnitude of concentrations and

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differences across media. We slightly underestimate available observations in recent years (post-2005), but are generally within a factor of 2 difference, which is acceptable given spatial variability in measurements. Reported ranges from prior modeling studies on PFOS and its precursors are within a factor of 5 of observations.[12]

Reasonable agreement between observed and modeled FOSA concentrations suggests that changes in atmospheric FOSA levels and equilibration with the surface mixed layer ocean on time scales of less than one year are driving changes in biological concentrations. Such a response is more rapid than predicted for PFOS and PFOA in the ocean by prior work due to lag times introduced by penetration into subsurface waters and accumulation of legacy releases.[12,67]

Modeling results for pilot whales further confirm that the relatively rapid atmospheric decline in FOSA accounts for the observed changes in pilot whales between 1986 and 2013 (Figure 5b,c). To correct for the confounding influence of age on temporal trends, we modeled FOSA in pilot whale cohorts born between 1980 and 2020 (Figure 5B). To capture the distribution of measured values, we modeled low, moderate, and high scenarios (Figure 5C) that correspond to birth cohort simulations between 5 and 15 years. Modeled mean values (3−8 ng g^{-1}) agree well with average measured FOSA between 2011 and 2013 of 7.3 ± 1.9 ng g^{-1}. Modeled FOSA prior to 1998 (6−10 ng g^{-1}) falls slightly below observed concentrations (mean: 14.6 ± 2.8 ng g^{-1}) but is generally within a factor of 2 of measurements.

Modeling results suggest a 9%−10% yr^{-1} increase in FOSA concentrations in pilot whales between 1994 and 2002 (Figure 5C), which is slightly greater than the observed increase of 7.4% yr^{-1} (Figure 2). Modeled declines in FOSA after 2006 range from approximately 6% to 10% yr^{-1} while observations suggest an average of 13% yr^{-1} (Figure 2). These differences are consistent with the underestimate in seawater and squid data based on partitioning calculations (Figure 5). Increasing whale age from 5 to 15 years results in up to a doubling of FOSA tissue burdens, depending on the timing of exposure. The greatest difference is during the period of declining environmental concentrations because the oldest whales had high exposures during their early life. In summary, we find that FOSA declines in pilot whale muscle can be generally reproduced by accounting for changing atmospheric concentrations, and simple equilibrium partitioning between the atmosphere, surface ocean and prey items. This implies that changing atmospheric burdens of FOSA exerted a major influence on biological exposures in the Arctic and Subarctic regions.

The average FOSA:PFOS ratios in juvenile male pilot whales peaked at 7.5 in 1998−2002 and declined to 1.6 by 2013 (Table 1). This implies that for species that biotransform FOSA to PFOS, observed decreases in PFOS may refelect a decline in exposure to precursors even if direct exposure to PFOS remained unchanged. This would help to explain inconsistent trends across species from different remote locations. Biological PFOS concentrations are expected to decline more rapidly in locations where precursors historically represented a larger exposure source (i.e., high latitude locations). An example of this can be seen in two distinct populations of beluga whales (*Delphinapterus leucas*) harvested off the northern and southern Alaskan coasts. FOSA:PFOS ratios in beluga whales from northern Alaska were higher and decreased more rapidly compared to those from southern Alaska.[66] The authors suggest that these patterns could reflect greater direct exposures to PFOS in southern Alaska from Anchorage and potentially higher precursor contributions in the northern Alaskan Arctic.

Implications for Future Exposures. We find that shifts in PFASs released to the environment have led to large changes in the composition of PFAS exposures in pilot whales, but not necessarily to overall decreases in concentrations. Declines in FOSA, the most prevalent PFAS around the year 2000, has been offset by increasing levels of long-chained PFCAs. Despite the phase-out of both PFOS and FOSA before 2002, PFOS concentrations have continued to increase, highlighting the relatively longer time scales of removal through ocean transport. If current trends continue, then long-chained PFCAs will likely become the dominant compounds in pilot whales and total PFAS exposures may also increase. Production of long chain PFCAs (>C7) by eight major global manufacturers was phased-out in 2015 as part of the U.S. Environmental Protection Agency's PFOA Stewardship Program.[11] However, new manufactures in Asia have continued production of these compounds.[11] The slow response of PFOS to its phase out prior to 2002 suggests declines in long-chained PFCAs may lag production by decades, depending on the ages, sizes, and foraging depths of biota.

FOSA levels in pilot whale muscle reported here indicate that precursors are important exposure sources for marine food webs. While we know that whales cannot biotransform FOSA to PFOS, we do not know their metabolic capacity for the other precursor compounds.[21] For this reason, FOSA levels in samples described here could represent an integrated signal of overall precursor concentration, a subset of precursors that degrade to FOSA, or FOSA itself. Measuring total organic fluorine (TOF) and identifying novel precursors would provide much needed insights on the contribution of fluorinated precursors to ongoing biological exposurs.[23] Rapid observed declines in FOSA suggest atmospherically derived PFAS exposures in remote locations will be more responsive to changes in emissions than those originating from coastal discharges and ocean circulation.

While results from this study apply primarily to the marine environment, they may also point to a potential pathway for declining human exposures. Rapid decreases in measured concentrations of PFOS observed in humans globally[86−89] since 2000 may be due in part to the large decrease in atmospheric precursors.[90,91] Furthermore, increases in PFOS and other long-chained PFCAs in whales, which are consumed by the population of the Faroe Islands, implies a continued source of exposure to these contaminants from marine food consumption.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00293.

Details on samples, analytical methods, and supporting figures and tables (PDF)

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The authors declare no competing financial interest.

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■ REFERENCES

(1) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40* (1), 32−44.
(2) Yamashita, N.; Taniyasu, S.; Petrick, G.; Wei, S.; Gamo, T.; Lam, P. K.; Kannan, K. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. *Chemosphere* **2008**, *70* (7), 1247−55.
(3) Paul, A. G.; Jones, K. C.; Sweetman, A. J. A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate. *Environ. Sci. Technol.* **2009**, *43* (2), 386−392.
(4) Tomy, G.; 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.
(5) Tomy, G.; Pleskach, K.; Hare, J.; Ferguson, S. H.; Hare, J.; Stern, G. A.; 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.
(6) Butt, C. M.; Berger, U.; Bossi, R.; Tomy, G. T. Levels and trends of poly- and perfluorinated compounds in the arctic environment. *Sci. Total Environ.* **2010**, *408* (15), 2936−65.
(7) Dietz, R.; Bossi, R.; Riget, F. F.; Sonne, C.; Born, E. W. Increasing perfluoroalkyl contaminants in east Greenland polar bears (Ursus maritimus): a new toxic threat to the Arctic bears. *Environ. Sci. Technol.* **2008**, *42* (7), 2701−2702.
(8) Houde, M.; De Silva, A. O.; Muir, D. C.; Letcher, R. J. Monitoring of perfluorinated compounds in aquatic biota: an updated review. *Environ. Sci. Technol.* **2011**, *45* (19), 7962−73.
(9) Lindstrom, A. B.; Strynar, M. J.; Libelo, E. L. Polyfluorinated compounds: past, present, and future. *Environ. Sci. Technol.* **2011**, *45* (19), 7954−61.
(10) Grandjean, P.; Andersen, E. W.; Budtz-Jorgensen, E.; Nielsen, F.; Molbak, K.; Weihe, P.; Heilmann, C. Serum vaccine antibody concentrations in children exposed to perfluorinated comopunds. *Jama* **2012**, *307* (4), 391−397.
(11) Wang, Z.; Cousins, I. T.; Scheringer, M.; Buck, R. C.; Hungerbuhler, K. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ. Int.* **2014**, *70*, 62−75.
(12) Armitage, J. M.; Schenker, U.; Scheringer, M.; Martin, J. W.; Macleod, M.; Cousins, I. T. Modeling the Global Fate and Transport of Perfluorooctane Sulfonate (PFOS) and Precursor Compounds in Relation to Temporal Trends in Wildlife Exposure. *Environ. Sci. Technol.* **2009**, *43*, 9274−9280.
(13) Wang, Z.; Cousins, I. T.; Scheringer, M.; Buck, R. C.; Hungerbuhler, K. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part II: the remaining pieces of the puzzle. *Environ. Int.* **2014**, *69*, 166−76.
(14) Sturm, R.; Ahrens, L. Trends of polyfluoroalkyl compounds in marine biota and in humans. *Environmental Chemistry* **2010**, *7* (6), 457.
(15) Rotander, A.; Karrman, A.; van Bavel, B.; Polder, A.; Riget, F.; Audhunsson, G. A.; Vikingsson, G.; Gabrielsen, G. W.; Bloch, D.; Dam, M. Increasing levels of long-chain perfluorocarboxylic acids (PFCAs) in Arctic and North Atlantic marine mammals, 1984−2009. *Chemosphere* **2012**, *86* (3), 278−285.
(16) Riget, F.; Bossi, R.; Sonne, C.; Vorkamp, K.; Dietz, R. Trends of perfluorochemicals in Greenland ringed seals and polar bears: indications of shifts to decreasing trends. *Chemosphere* **2013**, *93* (8), 1607−14.
(17) Roos, A.; Berger, U.; Järnberg, U.; van Dijk, J.; Bignert, A. Increasing Concentrations of Perfluoroalkyl Acids in Scandinavian Otters (Lutra lutra) between 1972 and 2011: A New Threat to the Otter Population? *Environ. Sci. Technol.* **2013**, *47* (20), 11757−11765.
(18) Binnington, M. J.; Wania, F. Clarifying relationships between persistent organic pollutant concentrations and age in wildlife biomonitoring: individuals, cross-sections, and the roles of lifespan and sex. *Environ. Toxicol. Chem.* **2014**, *33* (6), 1415−26.
(19) Gebbink, W. A.; Berger, U.; Cousins, I. T. Estimating human exposure to PFOS isomers and PFCA homologues: the relative importance of direct and indirect (precursor) exposure. *Environ. Int.* **2015**, *74*, 160−9.
(20) Gebbink, W. A.; Bignert, A.; Berger, U. Perfluoroalkyl Acids (PFAAs) and Selected Precursors in the Baltic Sea Environment: Do Precursors Play a Role in Food Web Accumulation of PFAAs? *Environ. Sci. Technol.* **2016**, *50* (12), 6354−62.
(21) Martin, J. W.; Asher, B. J.; Beesoon, S.; Benskin, J. P.; Ross, M. S. PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? *J. Environ. Monit.* **2010**, *12* (11), 1979−2004.
(22) Yeung, L. W.; De Silva, A. O.; Loi, E. I.; Marvin, C. H.; Taniyasu, S.; Yamashita, N.; Mabury, S. A.; Muir, D. C.; Lam, P. K. Perfluoroalkyl substances and extractable organic fluorine in surface sediments and cores from Lake Ontario. *Environ. Int.* **2013**, *59*, 389−97.
(23) Loi, E. I.; Yeung, L. W.; Taniyasu, S.; Lam, P. K.; Kannan, K.; Yamashita, N. Trophic magnification of poly- and perfluorinated compounds in a subtropical food web. *Environ. Sci. Technol.* **2011**, *45* (13), 5506−13.
(24) Miyake, Y.; Yamashita, N.; Rostkowski, P.; So, M. K.; Taniyasu, S.; Lam, P. K.; 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.
(25) Stock, N. L.; Furdui, V. I.; Muir, D. C.; Mabury, S. A. Perfluoroalkyl Contaminants in the Canadian Arctic: Evidence of Atmospheric Transport and Local Contamination. *Environ. Sci. Technol.* **2007**, *41*, 3529−3536.
(26) Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C.; Mabury, S. A. Perfluorinated Acids in Arctic Snow: New Evidence for Atmospheric Formation. *Environ. Sci. Technol.* **2007**, *41*, 3455−3461.
(27) Benskin, J. P.; Muir, D. C.; Scott, B. F.; Spencer, C.; De Silva, A. O.; Kylin, H.; Martin, J. W.; Morris, A.; Lohmann, R.; Tomy, G.; Rosenberg, B.; Taniyasu, S.; Yamashita, N. Perfluoroalkyl acids in the Atlantic and Canadian Arctic Oceans. *Environ. Sci. Technol.* **2012**, *46* (11), 5815−23.
(28) Kwok, K. Y.; Yamazaki, E.; Yamashita, N.; Taniyasu, S.; Murphy, M. B.; Horii, Y.; Petrick, G.; Kallerborn, R.; Kannan, K.; Murano, K.; Lam, P. K. Transport of perfluoroalkyl substances (PFAS) from an arctic glacier to downstream locations: implications for sources. *Sci. Total Environ.* **2013**, *447*, 46−55.

DOI: 10.1021/acs.est.7b00293
Environ. Sci. Technol. 2017, 51, 4512−4521

(29) Bossi, R.; Dam, M.; Riget, F. F. Perfluorinated alkyl substances (PFAS) in terrestrial environments in Greenland and Faroe Islands. *Chemosphere* **2015**, *129*, 164−9.
(30) Vestergren, R.; Berger, U.; Glynn, A.; Cousins, I. T. Dietary exposure to perfluoroalkyl acids for the Swedish population in 1999, 2005 and 2010. *Environ. Int.* **2012**, *49*, 120−7.
(31) Ullah, S.; Huber, S.; Bignert, A.; Berger, U. Temporal trends of perfluoroalkane sulfonic acids and their sulfonamide-based precursors in herring from the Swedish west coast 1991−2011 including isomer-specific considerations. *Environ. Int.* **2014**, *65*, 63−72.
(32) D'eon, J. C.; Mabury, S. A. Is indirect exposure a significant contributor to the burden of perfluorinated acids observed in humans? *Environ. Sci. Technol.* **2011**, *45* (19), 7974−7984.
(33) Letcher, R. J.; Chu, S.; McKinney, M. A.; Tomy, G. T.; Sonne, C.; Dietz, R. Comparative hepatic in vitro depletion and metabolite formation of major perfluorooctane sulfonate precursors in Arctic polar bear, beluga whale, and ringed seal. *Chemosphere* **2014**, *112*, 225−31.
(34) Galatius, A.; Bossi, R.; Sonne, C.; Riget, F. F.; Kinze, C. C.; Lockyer, C.; Teilmann, J.; Dietz, R. PFAS profiles in three North Sea top predators: metabolic differences among species? *Environ. Sci. Pollut. Res.* **2013**, *20* (11), 8013−20.
(35) Gebbink, W. A.; Bossi, R.; Riget, F. F.; Rosing-Asvid, A.; Sonne, C.; Dietz, R. Observation of emerging per- and polyfluoroalkyl substances (PFASs) in Greenland marine mammals. *Chemosphere* **2016**, *144*, 2384−91.
(36) Xu, L.; Krenitsky, D. M.; Seacat, A. M.; Butenhoff, J. L.; Anders, M. W. Biotransformation of N-Ethyl-N-(2-hydroxyethyl)-perfluorooctanesulfonamide by Rat Liver Microsomes, Cytosol, and Slices and by Expressed Rat and Human Cytochromes P450. *Chem. Res. Toxicol.* **2004**, *17*, 767−775.
(37) Fu, Z.; Wang, Y.; Wang, Z.; Xie, H.; Chen, J. Transformation pathways of isomeric perfluorooctanesulfonate precursors catalyzed by the active species of P450 enzymes: in silico investigation. *Chem. Res. Toxicol.* **2015**, *28* (3), 482−9.
(38) Gannon, D. P. Stomach contents of long-finned pilot whales (*Globicephala melas*) stranded on the U.S. mid-atlantic coast. *Mar. Mammal Sci.* **1997**, *13* (3), 405−418.
(39) Desportes, G.; Mouritsen, R. Preliminary Results on the Diet of Long-Finned Pilot Whales off the Faroe Islands. *Rep. Int. Whal Commn* **1993**, No. 14, 305−324.
(40) Bloch, D.; Heide-Jorgense, M. P.; Stefansson, E.; Mikkelsen, B.; Ofstad, L. H.; Dietz, R.; Andersen, L. W. Short-term movements of long-finned pilot whales Globicephala melas around the Faroe Islands. *Wildlife Biology* **2003**, *9* (1), 47−58.
(41) Dam, M.; van Bavel, B.; Rigét, F.; Rotander, A.; Polder, A.; Audunsson, G. A.; Bloch, D.; Víkingsson, G.; Mikkelsen, B.; Gabrielsen, G. W.; Sagerup, K. *"New" POPs in Marine Mammals in Nordic Arctic and NE Atlantic Areas during Three Decades*; Nordic Council of Ministers: Copenhagen, Denmark, 2011.
(42) Bloch, D.; Lockyer, C.; Zachariassen, M. Age and growth parameters of the long-finned pilot whale off the Faroe Islands. *Report of the International Whaling Commission* **1993**, No. 14, 163−207.
(43) Ahrens, L.; Siebert, U.; Ebinghaus, R. Total body burden and tissue distribution of polyfluorinated compounds in harbor seals (Phoca vitulina) from the German Bight. *Mar. Pollut. Bull.* **2009**, *58* (4), 520−5.
(44) Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr A* **2005**, *1093* (1−2), 89−97.
(45) NADA: *Nondetects And Data Analysis for Environmental Data. R Package*, Version 1.5−6; 2013.
(46) Hewett, P.; Ganser, G. H. A comparison of several methods for analyzing censored data. *Ann. Occup. Hyg.* **2007**, *51* (7), 611−32.
(47) Aitchison, J. *The Statistical Analysis of Compositional Data*; Chapman and Hall: London, 1986.
(48) Van den Boogaart, K. G.; Tolosana-Delgado, R. *Analyzing Compositional Data with R*; Springer: Berlin, 2013.
(49) Dreyer, A.; Ebinghaus, R. Polyfluorinated compounds in ambient air from ship- and land-based measurements in northern Germany. *Atmos. Environ.* **2009**, *43* (8), 1527−1535.
(50) MacInnis, J. J.; French, K.; Muir, D. C. G.; Spencer, C.; Criscitiello, A. S.; DeSilva, A. O.; Young, C. Emerging investigator series: A 14-year depositional ice record of perfluoroalkyl substances in the High Arctic. *Environ. Sci.: Processes Impacts* **2017**, *19*, 22−30.
(51) Vierke, L.; Ahrens, L.; Shoeib, M.; Palm, W. U.; Webster, E. M.; Ellis, D. A.; Ebinghaus, R.; Harner, T. In situ air-water and particle-water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant. *Chemosphere* **2013**, *92* (8), 941−8.
(52) EPA, U. *Estimation Programs Interface Suite for Microsoft Windows, v 4.11*; United States Environmental Protection Agency: Washington, DC, USA, 2012.
(53) Atayeter, S.; Ercoskun, H. Chemical composition of European squid and effects of different frozen storage temperatures on oxidative stability and fatty acid composition. *J. Food Sci. Technol.* **2011**, *48* (1), 83−9.
(54) Arnot, J. A.; Gobas, F. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environ. Toxicol. Chem.* **2004**, *23* (10), 2343−2355.
(55) Kelly, B. C.; Gobas, F. A. P. C. An Arctic Terrestrial Food-Chain Bioaccumulation Model for Persistent Organic Pollutants. *Environ. Sci. Technol.* **2003**, *37* (13), 2966−2974.
(56) Gobas, F. A. P. C.; Arnot, J. A. Food web bioaccumulation model for polychlorinated biphenyls in San Francisco Bay, California, USA. *Environ. Toxicol. Chem.* **2010**, *29* (6), 1385−1395.
(57) Armitage, J. M.; Arnot, J. A.; Wania, F.; Mackay, D. Development and evaluation of a mechanistic bioconcentration model for ionogenic organic chemicals in fish. *Environ. Toxicol. Chem.* **2013**, *32* (1), 115−28.
(58) Innes, S.; Lavigne, D. M.; Earle, W. M.; Kovacs, K. M. Feeding rates of seals and whales. *J. Anim. Ecol.* **1987**, *56*, 115−130.
(59) Lockyer, C. Seasonal changes in body fat condition of northeast Atlantic pilot whales, and their biological significance. *IWC Special Issue 14: Biology of the Northern Hemisphere Pilot Whales* **1993**, 205−324.
(60) Mortola, J. P.; Limoges, M. J. Resting breathing frequency in aquatic mammals: a comparative analysis with terrestrial species. *Respir. Physiol. Neurobiol.* **2006**, *154* (3), 500−14.
(61) Lafortuna, C. L.; Jahoda, M.; Azzellino, A.; Saibene, F.; Colombini, A. Locomotor behaviours and respiratory pattern of the Mediterranean fin whale (Balaenoptera physalus). *Eur. J. Appl. Physiol.* **2003**, *90* (3−4), 387−95.
(62) Vestergren, R.; Cousins, I. T.; Trudel, D.; Wormuth, M.; Scheringer, M. Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA. *Chemosphere* **2008**, *73* (10), 1617−24.
(63) Bossi, R.; Riget, F. F.; Dietz, R.; Sonne, C.; Fauser, P.; Dam, M.; Vorkamp, K. Preliminary screening of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, birds and marine mammals from Greenland and the Faroe Islands. *Environ. Pollut.* **2005**, *136* (2), 323−9.
(64) Kannan, K.; Corsolini, S.; Falandysz, J.; Oehme, G.; Focardi, S.; Giesy, J. P. Perfluorooctanesulfonate and related fluorinated hydrocarbons in marine mammals, fishes, and birds from coasts of the Baltic and the Mediterranean Seas. *Environ. Sci. Technol.* **2002**, *36* (15), 3210−3216.
(65) Hart, K.; Kannan, K.; Isobe, T.; Takahashi, S.; Yamada, T. K.; Miyazaki, N.; Tanabe, S. Time Trends and Transplacental Transfer of Perfluorinated Compounds in Melon-Headed Whales Stranded Along the Japanese Coast in 1982, 2001/2002, and 2006. *Environ. Sci. Technol.* **2008**, *42*, 7132−7137.
(66) Reiner, J. L.; O'Connell, S. G.; Moors, A. J.; Kucklick, J. R.; Becker, P. R.; Keller, J. M. Spatial and temporal trends of perfluorinated compounds in Beluga Whales (Delphinapterus leucas) from Alaska. *Environ. Sci. Technol.* **2011**, *45* (19), 8129−36.

DOI: 10.1021/acs.est.7b00293
Environ. Sci. Technol. 2017, 51, 4512−4521

(67) Armitage, J. M.; Macleod, M.; Cousins, I. T. Modeling the Global Fate and Transport of Perfluorooctanoic Acid (PFOA) and Perfluorooctanoate (PFO) Emitted from Direct Sources Using a Multispecies Mass Balance Model. *Environ. Sci. Technol.* **2009**, *43* (4), 1134−1140.
(68) Armitage, J. M.; Macleod, M.; Cousins, I. T. Comparative Assessment of the Global Fate and Transport Pathways of Long-Chain Perfluorocarboxylic Acids (PFCAs) and Perfluorocarboxylates (PFCs) Emitted from Direct Sources. *Environ. Sci. Technol.* **2009**, *43*, 1134−1140.
(69) Conder, J. M.; Hoke, R. A.; Wolf, W. D.; Russell, M. H.; Buck, R. C. Are PFCAs Bioaccumulative? A Critical Review and Comparison with Regulatory Criteria and Persistent Lipophilic Compounds. *Environ. Sci. Technol.* **2008**, *42* (4), 995−1003.
(70) 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.
(71) Karrman, A.; Ericson, I.; van Bavel, B.; Darnerud, P. O.; Aune, M.; Glynn, A.; Lignell, S.; Lindstrom, G. Exposure of perfluorinated chemicals through lactation: levels of matched human milk and serum and a temporal trend, 1996−2004, in Sweden. *Environ. Health Perspect* **2006**, *115* (2), 226−230.
(72) Loccisano, A. E.; Longnecker, M. P.; Campbell, J. L., Jr.; Andersen, M. E.; Clewell, H. J., 3rd Development of PBPK models for PFOA and PFOS for human pregnancy and lactation life stages. *J. Toxicol. Environ. Health, Part A* **2013**, *76* (1), 25−57.
(73) Needham, L. L.; Grandjean, P.; Heinzow, B.; Jørgensen, P. J.; Nielsen, F.; Patterson, D. G.; Sjödin, A.; Turner, W. E.; Weihe, P. Partition of environmental chemicals between maternal and fetal blood and tissues. *Environ. Sci. Technol.* **2011**, *45* (3), 1121−1126.
(74) Mogensen, U. B.; Grandjean, P.; Nielsen, F.; Weihe, P.; Budtz-Jorgensen, E. Breastfeeding as an Exposure Pathway for Perfluorinated Alkylates. *Environ. Sci. Technol.* **2015**, *49* (17), 10466−73.
(75) Gronnestad, R.; Villanger, G. D.; Polder, A.; Kovacs, K. M.; Lydersen, C.; Jenssen, B. M.; Borga, K. Maternal transfer of perfluoroalkyl substances in hooded seals. *Environ. Toxicol. Chem.* **2017**, *36* (3), 763−770.
(76) Ahrens, L.; Siebert, U.; Ebinghaus, R. Temporal trends of polyfluoroalkyl compounds in harbor seals (Phoca vitulina) from the German Bight, 1999−2008. *Chemosphere* **2009**, *76* (2), 151−8.
(77) Butt, C. M.; Muir, D.; Stirling, I.; Kwan, M.; Mabury, S. A. Rapid Response of Arctic Ringed Seals to Changes in Perfluoroalkyl Production. *Environ. Sci. Technol.* **2007**, *41* (1), 42−49.
(78) Muller, C. E.; Gerecke, A. C.; Bogdal, C.; Wang, Z.; Scheringer, M.; Hungerbuhler, K. Atmospheric fate of poly- and perfluorinated alkyl substances (PFASs): I. Day-night patterns of air concentrations in summer in Zurich, Switzerland. *Environ. Pollut.* **2012**, *169*, 196−203.
(79) Ahrens, L.; Felizeter, S.; Ebinghaus, R. Spatial distribution of polyfluoroalkyl compounds in seawater of the German Bight. *Chemosphere* **2009**, *76* (2), 179−184.
(80) Ahrens, L.; Barber, J. L.; Xie, Z.; Ebinghaus, R. Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean. *Environ. Sci. Technol.* **2009**, *43* (9), 3122−3127.
(81) Ahrens, L.; Taniyasu, S.; Yeung, L. W.; Yamashita, N.; Lam, P. K.; Ebinghaus, R. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. *Chemosphere* **2010**, *79* (3), 266−72.
(82) Busch, J.; Ahrens, L.; Xie, Z.; Sturm, R.; Ebinghaus, R. Polyfluoroalkyl compounds in the East Greenland Arctic Ocean. *J. Environ. Monit.* **2010**, *12* (6), 1242−6.
(83) Gonzalez-Gaya, B.; Dachs, J.; Roscales, J. L.; Caballero, G.; Jimenez, B. Perfluoroalkylated substances in the global tropical and subtropical surface oceans. *Environ. Sci. Technol.* **2014**, *48* (22), 13076−84.
(84) Cai, M.; Zhao, Z.; Yin, Z.; Ahrens, L.; Huang, P.; Cai, M.; Yang, H.; He, J.; Sturm, R.; Ebinghaus, R.; Xie, Z. Occurrence of perfluoroalkyl compounds in surface waters from the North Pacific to the Arctic Ocean. *Environ. Sci. Technol.* **2012**, *46* (2), 661−8.
(85) Theobald, N.; Caliebe, C.; Gerwinski, W.; Huhnerfuss, H.; Lepom, P. Occurrence of perfluorinated organic acids in the North and Baltic seas. Part 1: distribution in sea water. *Environ. Sci. Pollut. Res.* **2011**, *18* (7), 1057−69.
(86) Bjerregaard-Olesen, C.; Bach, C. C.; Long, M.; Ghisari, M.; Bossi, R.; Bech, B. H.; Nohr, E. A.; Henriksen, T. B.; Olsen, J.; Bonefeld-Jorgensen, E. C. Time trends of perfluorinated alkyl acids in serum from Danish pregnant women 2008−2013. *Environ. Int.* **2016**, *91*, 14−21.
(87) Toms, L. M.; Thompson, J.; Rotander, A.; Hobson, P.; Calafat, A. M.; Kato, K.; Ye, X.; Broomhall, S.; Harden, F.; Mueller, J. F. Decline in perfluorooctane sulfonate and perfluorooctanoate serum concentrations in an Australian population from 2002 to 2011. *Environ. Int.* **2014**, *71*, 74−80.
(88) Okada, E.; Kashino, I.; Matsuura, H.; Sasaki, S.; Miyashita, C.; Yamamoto, J.; Ikeno, T.; Ito, Y. M.; Matsumura, T.; Tamakoshi, A.; Kishi, R. Temporal trends of perfluoroalkyl acids in plasma samples of pregnant women in Hokkaido, Japan, 2003−2011. *Environ. Int.* **2013**, *60*, 89−96.
(89) Olsen, G. W.; Lange, C. C.; Ellefson, M. E.; Mair, D. C.; Church, T. R.; Goldberg, C. L.; Herron, R. M.; Medhdizadehkashi, Z.; Nobiletti, J. B.; Rios, J. A.; Reagen, W. K.; Zobel, L. R. Temporal trends of perfluoroalkyl concentrations in American Red Cross adult blood donors, 2000−2010. *Environ. Sci. Technol.* **2012**, *46* (11), 6330−8.
(90) Yeung, L. W.; Robinson, S. J.; Koschorreck, J.; Mabury, S. A. Part II. A temporal study of PFOS and its precursors in human plasma from two German cities in 1982−2009. *Environ. Sci. Technol.* **2013**, *47* (8), 3875−82.
(91) Liu, Y.; Pereira, A. S.; Beesoon, S.; Vestergren, R.; Berger, U.; Olsen, G. W.; Glynn, A.; Martin, J. W. Temporal trends of perfluorooctanesulfonate isomer and enantiomer patterns in archived Swedish and American serum samples. *Environ. Int.* **2015**, *75*, 215−22.

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Supporting Information for:

Temporal shifts in poly- and perfluoroalkyl substances (PFASs) in North Atlantic pilot whales indicate large contribution of atmospheric precursors

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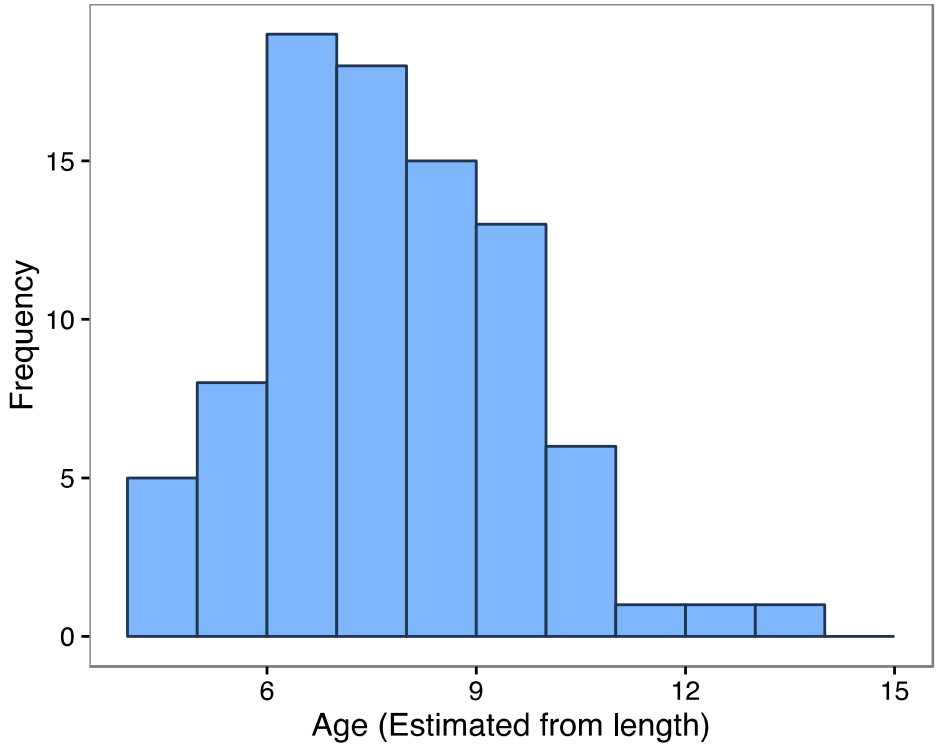

Figure S1. Age distribution of juvenile male pilot whales collected as part of this study and from the Faroese Environment Agency[1] between 1987 and 2013.

Table S1a. Ancillary data on pilot whales harvested in the Faroe Islands with tissues archived by the Faroese Natural History Museum and analyzed for PFASs in this study.

Sample ID	Sampling Date	Gender	Length (cm)	Age Category[a]
19940630-01	6/30/94	M	445	Juvenile
19940630-02	6/30/94	M	435	Juvenile
19960628-03	6/28/96	M	385	Juvenile
19960628-04	6/28/96	M	407	Juvenile
19960628-05	6/28/96	M	380	Juvenile
19981125-06	11/25/98	M	395	Juvenile
19981125-07	11/25/98	M	370	Juvenile
19990314-08	3/14/99	M	400	Juvenile
19990314-09	3/14/99	M	400	Juvenile
19990908-010	9/8/99	M	430	Juvenile
20000831-011	8/31/00	M	390	Juvenile
20000831-012	8/31/00	M	435	Juvenile
20000909-013	9/9/00	M	415	Juvenile
20060101-014	1/1/06	M	470	Juvenile
20060101-015	1/1/06	M	430	Juvenile
20060101-016	1/1/06	M	366	Juvenile
20060101-017	1/1/06	M	450	Juvenile
20060101-018	1/1/06	M	455	Juvenile
20060101-019	1/1/06	M	458	Juvenile
20060101-020	1/1/06	M	411	Juvenile
20110209-021	2/9/11	M	369	Juvenile
20110209-022	2/9/11	M	437	Juvenile
20110528-023	5/28/11	M	423	Juvenile
20110528-024	5/28/11	M	459	Juvenile
20110902-025	9/2/11	M	414	Juvenile
20110902-026	9/2/11	M	450	Juvenile
20111113-027	11/13/11	M	433	Juvenile
20111113-028	11/13/11	M	343	Juvenile
20111113-029	11/13/11	M	436	Juvenile
20111113-030	11/13/11	M	453	Juvenile
20111113-031	11/13/11	M	338	Juvenile
20111118-032	11/18/11	M	415	Juvenile
20111122-033	11/22/11	M	446	Juvenile
20111122-034	11/22/11	M	508	Adult
20130721-035	7/21/13	M	400	Juvenile
20130721-036	7/21/13	M	578	Adult
20130721-037	7/21/13	M	515	Adult
20130721-038	7/21/13	F	424	Adult

Table S1b. Ancillary data on pilot whales harvested in the Faroe Islands with tissues archived by the Faroese Natural History Museum and analyzed for PFASs in this study.

Sample ID	Sampling Date	Gender	Length (cm)	Age Category[a]
20130721-039	7/21/13	M	406	Juvenile
20130721-040	7/21/13	F	442	Adult
20130721-041	7/21/13	F	320	Juvenile
20130721-042	7/21/13	F	324	Juvenile
20130721-043	7/21/13	M	376	Juvenile
20130721-044	7/21/13	F	424	Adult
20130721-045	7/21/13	M	526	Adult
20130721-046	7/21/13	F	454	Adult
20130721-047	7/21/13	F	431	Adult
20130721-048	7/21/13	F	443	Adult
20130721-049	7/21/13	M	459	Juvenile
20130721-050	7/21/13	F	339	Juvenile
20130721-051	7/21/13	M	431	Juvenile
20130730-052	7/30/13	F	429	Adult
20130730-053	7/30/13	F	431	Adult
20130808-054	8/8/13	M	532	Adult
20130808-055	8/8/13	F	452	Adult
20130808-056	8/8/13	F	408	Adult
20130808-057	8/8/13	M	421	Juvenile
20130808-058	8/8/13	M	425	Juvenile
20130808-059	8/8/13	F	324	Juvenile
20130808-060	8/8/13	M	545	Adult
20130808-061	8/8/13	F	425	Adult
20130811-062	8/11/13	M	440	Juvenile
20130811-063	8/11/13	F	338	Juvenile
20130811-064	8/11/13	F	309	Juvenile
20130811-065	8/11/13	F	438	Adult
20130811-066	8/11/13	M	482	Juvenile
20130811-067	8/11/13	F	402	Adult
20130811-068	8/11/13	F	430	Adult
20130811-069	8/11/13	M	564	Adult
20130811-070	8/11/13	M	415	Juvenile
20130811-071	8/11/13	M	340	Juvenile
20130811-072	8/11/13	M	414	Juvenile
20130811-073	8/11/13	F	346	Juvenile
20130811-074	8/11/13	M	542	Adult
20130814-075	8/14/13	F	431	Adult
20130814-076	8/14/13	F	298	Juvenile
20130814-077	8/14/13	F	443	Adult

Table S1c. Ancillary data on pilot whales harvested in the Faroe Islands with tissues archived by the Faroese Natural History Museum and analyzed for PFASs in this study.

Sample ID	Sampling Date	Gender	Length (cm)	Age Category[a]
20130814-078	8/14/13	F	426	Adult
20130814-079	8/14/13	F	434	Adult
20130814-080	8/14/13	M	502	Adult
20130814-081	8/14/13	F	427	Adult
20130814-082	8/14/13	M	430	Juvenile
20130827-083	8/27/13	F	454	Adult
20130827-084	8/27/13	M	493	Juvenile
20130827-085	8/27/13	M	426	Juvenile
20130827-086	8/27/13	M	394	Juvenile
20130827-087	8/27/13	F	303	Juvenile

[a]Age was determined by size following Bloch et al.[4] with adults defined by lengths >500 cm for males and >378 cm for females.

Table S2. Supporting data on pilot whale muscle tissue collected and analyzed by the Faroese Environment Agency.[1]

Sample ID	Sampling Date	Gender	Length (cm)	Age Category[a]
19860712-088	7/12/86	M	385	Juvenile
19860712-089	7/12/86	M	422	Juvenile
19861026-090	10/26/86	M	452	Juvenile
19861026-091	10/26/86	M	360	Juvenile
19861101-092	11/1/86	M	391	Juvenile
19861101-093	11/1/86	M	400	Juvenile
19870722-094	7/22/87	M	380	Juvenile
19870802-095	8/2/87	M	398	Juvenile
19870802-096	8/2/87	M	408	Juvenile
19870819-097	8/19/87	M	410	Juvenile
19870819-098	8/19/87	M	380	Juvenile
19880610-099	6/10/88	M	379	Juvenile
19880610-0100	6/10/88	M	415	Juvenile
19970826-0101	8/26/97	M	390	Juvenile
19970826-0102	8/26/97	M	420	Juvenile
19970924-0103	9/24/97	M	360	Juvenile
19970924-0104	9/24/97	M	430	Juvenile
19971202-0105	12/2/97	M	381	Juvenile
19971202-0106	12/2/97	M	419	Juvenile
20010627-0107	6/27/01	M	440	Juvenile
2001076-0108	7/6/01	M	450	Juvenile
2001076-0109	7/6/01	M	354	Juvenile
2001076-0110	7/6/01	M	418	Juvenile
20020903-0111	9/3/02	M	350	Juvenile
20020903-0112	9/3/02	M	390	Juvenile
20020903-0113	9/3/02	M	440	Juvenile
20060828-0114	8/28/06	M	385	Juvenile
20060828-0115	8/28/06	M	390	Juvenile
20060828-0116	8/28/06	M	430	Juvenile
20070703-0117	7/3/07	M	405	Juvenile
20070703-0118	7/3/07	M	380	Juvenile
20070713-0119	7/13/07	M	370	Juvenile
20090105-0120	1/5/09	M	380	Juvenile
20090105-0121	1/5/09	M	405	Juvenile
20100624-0122	6/24/10	M	370	Juvenile
20100624-0123	6/24/10	M	416	Juvenile
20100702-0124	7/2/10	M	387	Juvenile
20100702-0125	7/2/10	M	440	Juvenile

Table S3. Analytical parameters for target analytes and isotopically labeled compounds.

Analytes	Precursor ion (*m/z*)	Product ions (*m/z*)	Collision energy (V)
PFBS	299	80	-56
		99	-38
PFHxS	399	99	-50
		80	-80
$^{13}C_4$-PFHxS	403	103	-80
PFHxA	313	269	-12
		119	-30
$^{13}C_4$-PFHxA	315	270	-12
PFHpA	363	169	-26
		319	-16
PFOS	499	80	-104
		99	-100
$^{13}C_4$-PFOS	503	99	-100
PFOSA	498	169	-50
		78	-62
$^{13}C_8$-PFOSA	506	78	-62
PFNA	463	419	-22
$^{13}C_5$-PFNA	468	423	-22
PFOA	413	369	-20
		169	-22
$^{13}C_4$-PFOA	417	372	-20
PFHpS	449	80	-92
		99	-84
PFDS	599	99	-104
		80	-104
PFDA	513	219	-30
		469	-22
$^{13}C_2$-PFDA	515	470	-20
PFUnA	563	519	-22
		169	-44
$^{13}C_2$-PFUnA	565	520	-22
PFDoA	613	569	-18
		169	-34
$^{13}C_2$-PFDoA	615	570	-34
PFTrA	663	619	-28
		169	-38
PFTeA	713	669	-24
		169	-38

Table S4. Method recoveries based on duplicate analysis of six calf-liver samples spiked with 1 to 20 ng g^{-1} of each PFAS.

Compound	Average Recovery %	Standard Deviation	RSD%
PFBS	74.7	5.29	7.08
PFHxS	97.3	6.20	6.37
PFHpS	126	15.1	12.0
PFOS	102	7.10	6.97
PFDS	81.2	19.4	23.9
FOSA	104	8.44	8.11
PFHxA	104	5.74	5.52
PFHpA	129	8.16	6.35
PFOA	102	6.01	5.88
PFNA	104	6.58	6.34
PFDA	101	5.40	5.35
PFUnA	99.7	5.27	5.29
PFDoA	103	6.10	5.92
PFTrA	84.4	37.5	44.4*
PFTeA	79.4	36.9	46.5*

*RSDs for PFTeA and PFTrA were higher (44%-47%) because of the tendency of longer-chained PFASs to sorb to surfaces during sample preparation and analysis. Such variability will bias trend analysis toward non-significant findings.[5] So, we include these compounds in all statistical analysis but results may underestimate potential changes.

Table S5. Flux of FOSA derived from the Devon ice cap, Devon Island, Nunavut, Canada[2] and corresponding air concentrations (C_A).

Year	Flux (ng m^{-2} yr^{-1})	Back-calculated C_A (pg m^{-3})
2007	2.07	2.4
2006	2.19	2.5
2005	3.09	3.6
2004	1.42	1.6
2003	2.45	2.8
2002	5.99	6.9
2001	15.74	18.2
2000	13.27	15.4
1999	14.37	16.7
1998	13.94	16.2
1997	18.86	21.9
1996	8.06	9.3
1995	1.51	1.8
1994	2.45	2.8
1993	3.19	3.7

[a] We used mean atmospheric FOSA concentrations from three cruise transects (North Sea: 2.66 pg m^{-3}; Canary Islands to Nfld., Canada: 2.03 pg m^{-3}; Norwegian Sea: 2.48 pg m^{-3}) to estimate atmospheric concentrations between August 2007 and January 2008 (2.39 pg m^{-3}). We use this average atmospheric value and the measurements from ice core data in 2007 of 2.07 ng m^{-2} to calculate: $C_{Air} = \alpha \cdot F$, where: $\alpha = 1.15$. For modelled values between 2007 and 2020 (Figure 5A), we assumed concentrations linearly declined to the minimum value of 1.6 pg m^{-3} in 2004, which is similar to average observations from remote high-mountain top in Zurich[6] in 2010 of 1.7 pg m^{-3}.

Figure S2. Map of satellite telemetry data from three pilot whales tagged off the coast of the Faroe Islands (show in blue) in the summer 2000. Adapted from Bloch et al.[3]

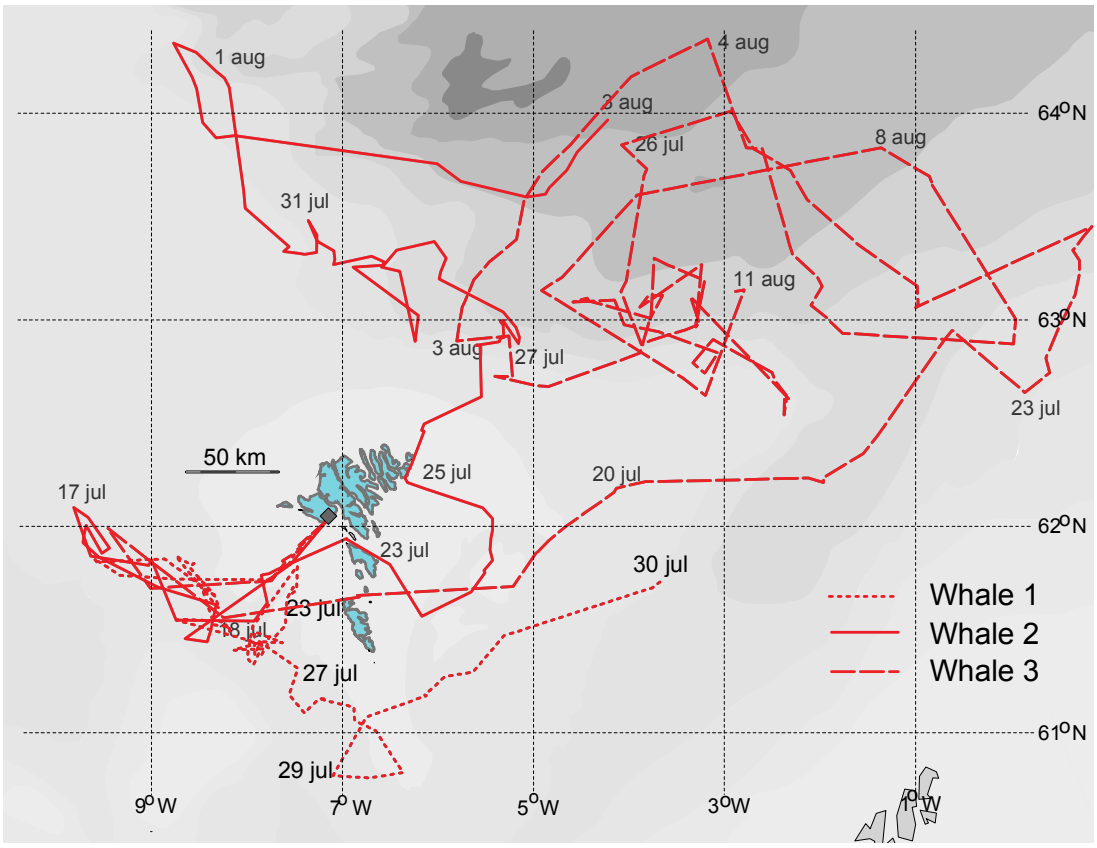

Table S6. Partitioning model for FOSA in seawater and squid.

Parameter	Description	Equation/Value	Reference
Seawater			
C_W	Seawater FOSA (pg L^{-1}),	$C_A K_{AW}$	
C_A	FOSA in air (pg m^{-3})	Table S5	
K_{AW}[a]	Air-water partitioning coefficient (unitless)	-3.6	Vierke et al.[7]
Squid			
C_S	FOSA in Squid (pg g-1 wet weight)	$v_{LD}K_{OW} + v_{ND}\beta K_{OW} + v_{WD}$	
v_{LD}	Lipid fraction (unitless)	0.014	Bloch et al.[4]
v_{ND}	Non-lipid organic matter (NLOM) content (unitless)	0.16	Bloch et al.[4]
$_{vWD}$	Moisture content (unitless)	1- v_{ND} - v_{LD}	
$_{logKOW}$	Octanol-water partition coefficient (unitless)	5.8	U.S. EPA[8]
$\boldsymbol{\beta}$	Sorptive capacity of NLOM relative to octanol	0.035	Arnot and Gobas[9]

[a] K_{AW} for FOSA from an experimental study[7] assuming a pKa value of 6.24.

Table S7a. Bioaccumulation model for pilot whales.

Parameter	Description	Equation	Reference
$\frac{dM_B}{dt}$	Change in mass of FOSA over time	$W_B \cdot \left(k_A C_A + k_D \sum \left(P_i C_{D,i}\right)\right) - (k_O + k_E + k_U + + k_M) \cdot M_B$	
Growth			
W_B	Weight of pilot whale (kg)	$189.68 e^{\frac{0.2802}{0.120}(1-e^{-0.12t})}$	Bloch et al.[4]
L	Length of whale (cm)	$228.92 e^{0.1209/0.13(1-e^{-0.13t})}$	Bloch et al.[4]
Respiration			
k_A	Rate constant for inhalation (L/kg/day)	$\frac{E_A G_A}{W_B}$	
G_A	Inhalation rate (L/day)	$f V_T$	
f	Breaths/day	$33\ {W_B}^{-0.42}$	Limoges et al.[10]
V_T	L	$0.074 {W_B}^{0.9}$	Lafortuna and Jahoda[11]
k_O	Rate constant for exhalation (1/day)	$\frac{k_A}{K_{BA}}$	
K_{BA}	Whale-Air partition coefficient (L/kg)	$(\nu_{LB}/\rho_L + \nu_{NB}\beta/\rho_{NLOM}) K_{OA} + \frac{\nu_{WB}}{K_{AW}\rho_w}$	
K_{OA}	Octanol-air partition coefficient (L/kg)	$\frac{K_{OW}}{K_{AW}}$	

Table S7b. Bioaccumulation model for pilot whales cont'd.

Ingestion			
k_D	Rate constant for ingestion (1/day)	$\frac{E_D G_D}{W_B}$	
G_D	Ingestion Rate (kg/day)	$G_D = 0.123\ {W_B}^{0.8}$	Innes et al.[12]
E_D	Assimilation efficiency (%)	$(10^{-9} K_{OW} + 1.025)^{-1}$	Gobas and Arnot[13]
kE	Rate constant for fecal egestion (1/day)	$\frac{E_D G_F K_{GB}}{W_B}$	
GF	Fecal egestion rate (kg/day)	$\{(1-\varepsilon_L)\nu_{LD} + (1-\varepsilon_N)\nu_{ND} + (1-\varepsilon_W)\nu_{WD}\}G_D$	
KGB	Gut-whale partition coefficient	$(\nu_{LG} K_{OW} + \nu_{NG} K_{OW}\beta + \nu_{WG})/K_{BW}$	
$\boldsymbol{\nu_{LG}}$	Lipid fraction in gut	$(1-\varepsilon_L)\nu_{LD} / \{(1-\varepsilon_L)\nu_{LD} + (1-\varepsilon_N)\nu_{ND} + (1-\varepsilon_W)\nu_{WD}\}$	
$\boldsymbol{\nu_{NG}}$	NLOM fraction in gut	$(1-\varepsilon_N)\nu_{ND} / \{(1-\varepsilon_L)\nu_{LD} + (1-\varepsilon_N)\nu_{ND} + (1-\varepsilon_W)\nu_{WD}\}$	
$\boldsymbol{\nu_{WG}}$	Water fraction in gut	$(1-\varepsilon_W)\nu_{WD} / \{(1-\varepsilon_L)\nu_{LD} + (1-\varepsilon_N)\nu_{ND} + (1-\varepsilon_W)\nu_{WD}\}$	
$\boldsymbol{K_{BW}}$	Whale-water partition coefficient	$(\nu_{LB} + \nu_{NB}\beta)K_{OW} + \nu_{WB}$	
Urination			
kU	Rate constant for urination (1/day)	$\frac{G_U}{W_B K_{BU}}$	
KBU	Whale-urine partition coefficient	$(\nu_{LB}/\rho_L + \nu_{NB}\beta/\rho_{NLOM})K_{OW} + \nu_{WB}/\rho_W$	

Table S8. List of bioaccumulation model parameters

Parameter	Description	Value	Reference
Partition Coefficients			
$logK_{OW}$	Octanol-water partition coefficient (unitless)	5.8	U.S. EPA[8]
$logK_{AW}$	Air-water partition coefficient (unitless)	-3.7	Vierke et al.[7a]
Squid			
v_{LD}	Lipid fraction (unitless)	0.14	Bloch et al.[4]
v_{ND}	Non-lipid organic matter (NLOM) content (unitless)	0.16	Bloch et al.[4]
v_{WD}	Moisture content (unitless)	0.826	
Pilot Whale			
v_{LB}	Lipid fraction in whale (unitless)	0.21	Innes et al.[12]
v_{NB}	NLOM fraction in whale (unitless)	0.373	Innes et al.[12]
v_{WB}	Water fraction in whale (unitless)	0.417	
β	Relative sorption capacity of NLOM to that of octanol (unitless)	0.035	Arnot and Gobas[9]
E_A	Uptake efficiency in lungs (unitless)	1	Vestergren[14]; Gebbink[15]
f	Breathing rate frequency (Breaths/day)	$33 \times W_B(t)^{-0.42}$	Mortola and Limoges[10]
V_T	Volume of breath (L)	$0.074 \times W_B(t)^{0.9}$	Lafortuna and Jahoda[11]
E_D	Uptake efficiency in GIT (unitless)	$(A_{ED}K_{OW}+B_{ED})^{-1}$	Gobas and Arnot[13]
A_{ED}	Constant for E_D eq. (unitless)	1.0×10^{-9}	Gobas and Arnot[13]
B_{ED}	Constant for E_D eq. (unitless)	1.025	Gobas and Arnot[13]
ε_L	Lipid assimilation efficiency (unitless)	0.9	Gobas and Arnot[13]
ε_N	NLOM assimilation efficiency (unitless)	0.5	Gobas and Arnot[13]
ε_W	Water assimilation efficiency (unitless)	0.55	Gobas and Arnot[13]
G_U	Urinary excretion rate (L/day)	300 at full size. Proportional to W_B	Binnington et al.[16]

[a]Measured value at a waste-water treatment plant assuming pKa = 6.24.

Table S9. Results of temporal regressions for each compound adjusted and unadjusted for length of pilot whale using traditional regression for PFOS and FOSA and maximum likelihood estimation (MLE) for the remaining compounds containing non-detects. PFBS, PFHpS, PFDS, and PFHpA were infrequently detected and so were excluded from analysis.

	Unadjusted Model		Adjusted Model			
Compound	Slope (yr^{-1})	p-value	Slope	p-value	Length (cm^{-1})	p-value
PFBS	-	-	-	-	-	-
PFHxS	-0.54	0.89	-0.87	0.82	-0.2%	0.49
PFHpS	-	-	-	-	-	-
PFOS	2.8%	<0.0001	3.0%	<0.0001	-0.3%	0.03
PFDS	-	-	-	-	-	-
FOSA (Before 2003)	7.4%	0.04	7.4%	0.06	0.3%	0.97
FOSA (After 2003)	-13.0%	<0.0001	-12.6%	<0.0001	0.2%	0.08
PFHxA	-	-	-	-	-	-
PFHpA	-	-	-	-	-	-
PFOA	-3.3%	0.052	-3.1%	0.07	-0.3%	0.30
PFNA	6.6%	<0.0001	7.0%	<0.0001	-0.4%	0.06
PFDA	8.2%	<0.0001	8.3%	<0.0001	-0.2%	0.28
PFUnA	6.1%	<0.0001	6.2%	<0.0001	-0.06%	0.66
PFDoA	4.4%	<0.0001	4.4%	<0.0001	-0.009%	0.95
PFTrA	7.4%	0.0003	7.5%	0.004	0.05%	0.93
PFTeA	9.8%	0.67	9.8%	0.67	-0.07%	0.96

Table S10. Measured concentrations (pg g^{-1} wet weight) of FOSA in five European flying squid (*Todarodes sagittatus*) caught off the coast of the Faroe Islands in 2010.

ID	FOSA
S1	232
S2	260
S3	177
S4	386
S5	363
Mean	**284**

References

1. Dam, M.; van Bavel, B.; Rigét, F.; Rotander, A.; Polder, A.; Auðunsson, G. A.; Bloch, D.; Víkingsson, G.; Mikkelsen, B.; Gabrielsen, G. W.; Sagerup, K. *"New" POPs in marine mammals in Nordic Arctic and NE Atlantic areas during three decades*; Nordic Council of Ministers: Copenhagen 2011.
2. Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C.; Mabury, S. A., Perfluorinated Acids in Arctic Snow: New Evidence for Atmospheric Formation. *Environ Sci Technol* **2007,** *41*, 3455-3461.
3. Bloch, D.; Heide-Jorgense, M. P.; Stefansson, E.; Mikkelsen, B.; Ofstad, L. H.; Dietz, R.; Andersen, L. W., Short-term movements of long-finned pilot whales Globicephala melas around the Faroe Islands. *Wildlife Biology* **2003,** *9* (1), 47-58.
4. Bloch, D.; Lockyer, C.; Zachariassen, M., Age and growth parameters of the long-finned pilot whale off the Faroe Islands. *Report of the International Whaling Commission* **1993,** (Special Issue 14), 163-207.
5. Grandjean, P.; Budtz-Jorgensen, E., Total imprecision of exposure biomarkers: implications for calculating exposure limits. *Am J Ind Med* **2007,** *50* (10), 712-9.
6. Muller, C. E.; Gerecke, A. C.; Bogdal, C.; Wang, Z.; Scheringer, M.; Hungerbuhler, K., Atmospheric fate of poly- and perfluorinated alkyl substances (PFASs): I. Day-night patterns of air concentrations in summer in Zurich, Switzerland. *Environ Pollut* **2012,** *169*, 196-203.
7. Vierke, L.; Ahrens, L.; Shoeib, M.; Palm, W. U.; Webster, E. M.; Ellis, D. A.; Ebinghaus, R.; Harner, T., In situ air-water and particle-water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant. *Chemosphere* **2013,** *92* (8), 941-8.
8. EPA, U. *Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11*, United States Environmental Protection Agency: Washington, DC, USA, 2012.
9. Arnot, J. A.; Gobas, F., A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environmental Toxicology and Chemistry* **2004,** *23* (10), 2343-2355.
10. Mortola, J. P.; Limoges, M. J., Resting breathing frequency in aquatic mammals: a comparative analysis with terrestrial species. *Respir Physiol Neurobiol* **2006,** *154* (3), 500-14.
11. Lafortuna, C. L.; Jahoda, M.; Azzellino, A.; Saibene, F.; Colombini, A., Locomotor behaviours and respiratory pattern of the Mediterranean fin whale (Balaenoptera physalus). *Eur J Appl Physiol* **2003,** *90* (3-4), 387-95.
12. Innes, S.; Lavigne, D. M.; Earle, W. M.; Kovacs, K. M., Feeding rates of seals and whales. *Journal of Animal Ecology* **1987,** *56*, 115-130.
13. Gobas, F. A. P. C.; Arnot, J. A., Food web bioaccumulation model for polychlorinated biphenyls in San Francisco Bay, California, USA. *Environmental Toxicology and Chemistry* **2010**, n/a-n/a.
14. Vestergren, R.; Cousins, I. T.; Trudel, D.; Wormuth, M.; Scheringer, M., Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA. *Chemosphere* **2008,** *73* (10), 1617-24.
15. Gebbink, W. A.; Berger, U.; Cousins, I. T., Estimating human exposure to PFOS isomers and PFCA homologues: the relative importance of direct and indirect (precursor) exposure. *Environ Int* **2015,** *74*, 160-9.

16. Binnington, M. J.; Wania, F., Clarifying relationships between persistent organic pollutant concentrations and age in wildlife biomonitoring: individuals, cross-sections, and the roles of lifespan and sex. *Environ Toxicol Chem* **2014,** *33* (6), 1415-26.