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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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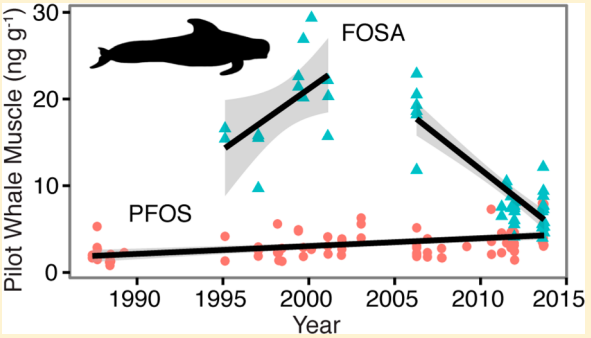
Supporting Information

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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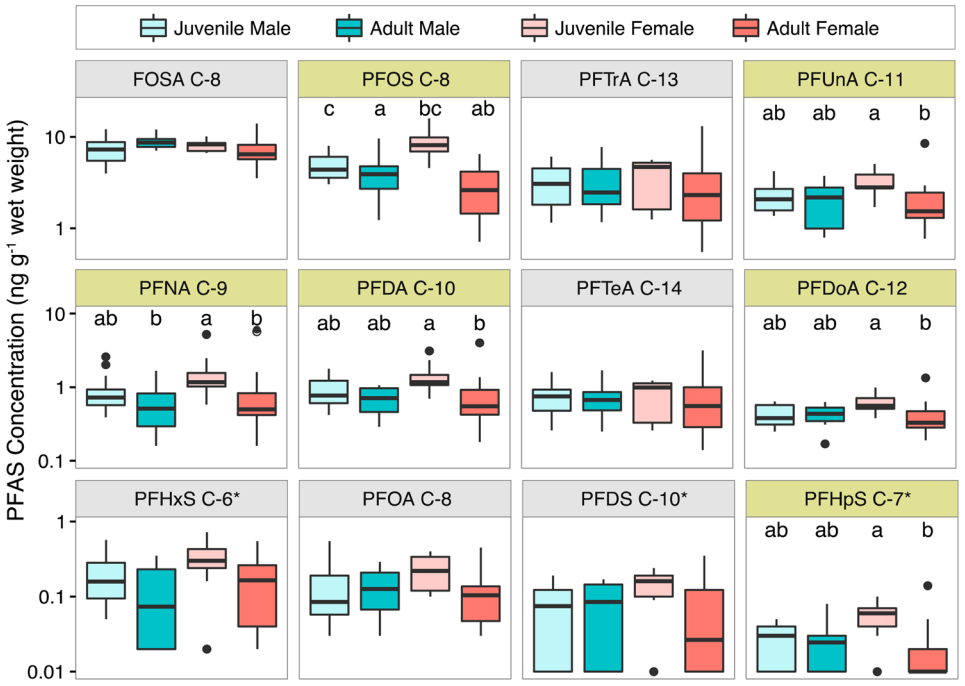

Figure 1. Effects of life stage and gender on measured PFAS concentrations in pilot whale muscle (*Globicephala melas*) sampled in 2013. Median concentrations for each group are represented by the horizontal black line in box/whisker plots. Notches represent 25th and 75th percentile concentrations, whiskers 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

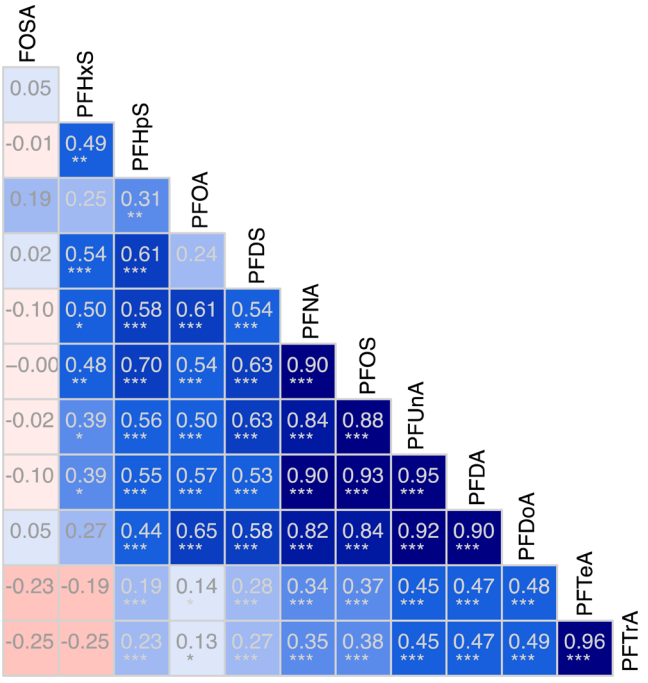

Figure 2. Correlation matrix for PFASs measured in pilot whale muscle tissue (*Globicephala melas*) in 2013. Numbers indicate Spearman correlation coefficients for a two-sided statistical test. The intensities of blue and red show the strength of positive and negative correlations, respectively. Significant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

of precursors such as FOSA (50−80 days for FTOHs and even less for water-soluble FASAs).[12,67,68]

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

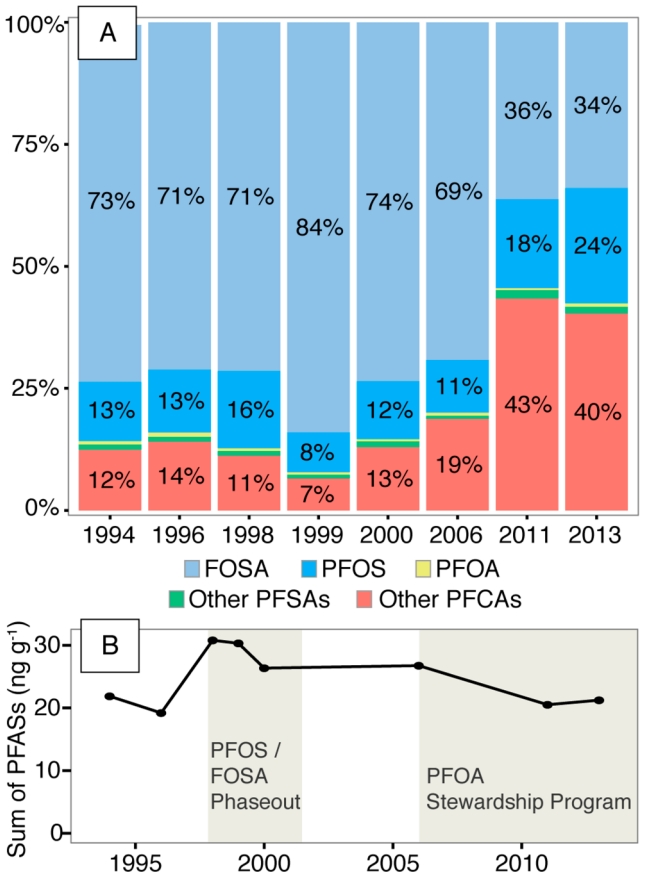

Figure 3. Temporal patterns in PFAS concentrations in juvenile male pilot whale muscle tissue (*Globicephala melas*) between 1994 and 2013. Compounds are grouped into categories reflecting one or more compound: perfluorooctane sulfonamide: FOSA, the neutral atmospheric precursor to perfluorooctanesulfonate (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.

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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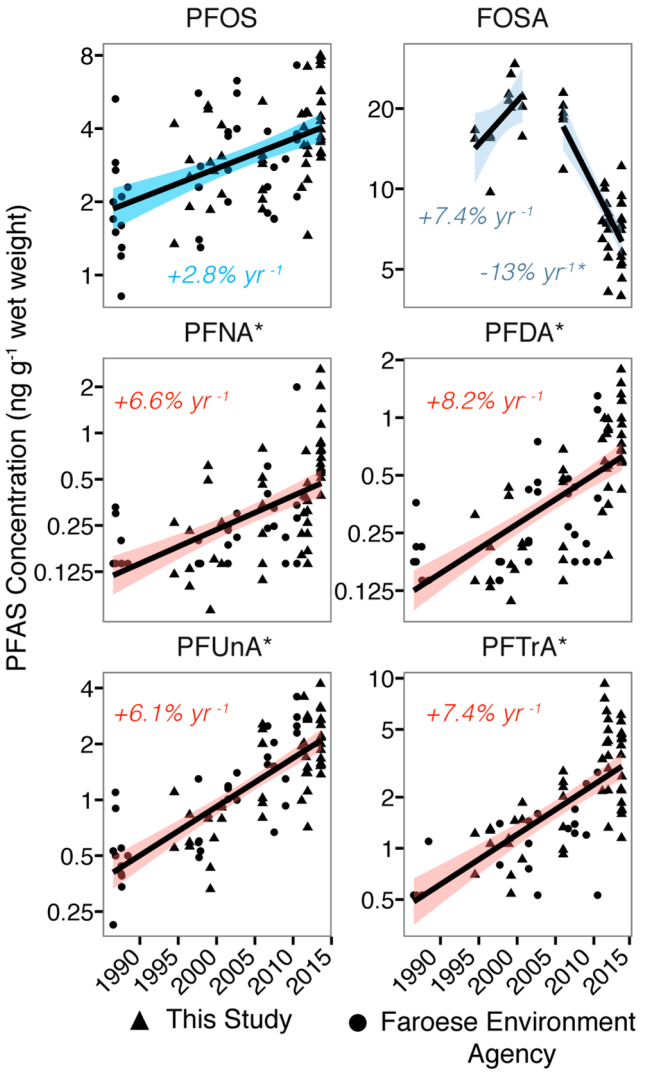

Figure 4. Temporal trends in concentrations of selected PFASs in juvenile male North Atlantic pilot whale muscle tissue (*Globicephala melas*) between 1986 and 2013. All trends (shown as percent annual changes) are significant at the $p < 0.05$ level based on linear regression of log-transformed concentrations. 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]

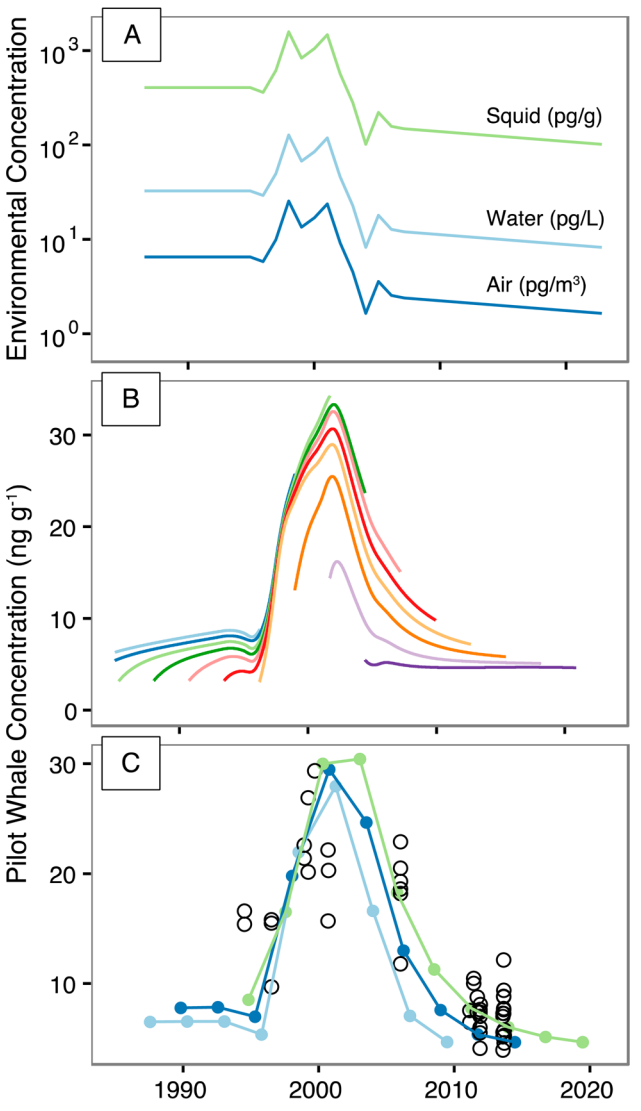

Figure 5. Modeled concentrations of perfluorooctane sulfonamide (FOSA) in air, water, squid (*Todarodes sagitatus*), and pilot whales (*Globicephala melas*) compared to temporal measurements collected in this study. Panel A shows reconstructed concentrations in air based on historic ice core data,[26,50] 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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Notes

The authors declare no competing financial interest.

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