2024

Whale Baleen To Monitor Per- and Polyfluoroalkyl Substances (PFAS) in Marine Environments

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Citation/Publisher Attribution

Savoca, M. S., Robuck, A. R., Cashman, M. A., Cantwell, M. G., Agvent, L. C., Wiley, D. N.,...Lohmann, R. (2024). Whale Baleen To Monitor Per- and Polyfluoroalkyl Substances (PFAS) in Marine Environments. *Environ. Sci. Technol. Lett.* Ahead of print. https://doi.org/10.1021/acs.estlett.4c00409
Available at: https://doi.org/10.1021/acs.estlett.4c00409

Whale baleen as a biomonitor for per- and polyfluoroalkyl substances (PFAS)

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Abstract

Per- and polyfluoroalkyl substances (PFAS) comprise > 10,000 synthetic compounds that are globally distributed and highly persistent but remain challenging to monitor. Here we assess the utility of baleen—an accreting, keratinaceous tissue that baleen whales use for filter-feeding—to track PFAS dynamics in marine food webs. In six species investigated, PFAS were detected in all baleen tested (n = 18 plates, 220 samples, Σ_{10}PFAS range 0.02 - 60.5 ng/g dry weight), higher than other tissue types besides liver. Three of the species in our dataset had not been tested for PFAS-contamination previously and two of those species—blue whale and North Atlantic right whale—are endangered species internationally. Apparent links were observed between PFAS and life-history events by testing successive subsamples along the growth axis of the baleen plates. These results establish baleen as a viable sample matrix for assessing PFAS contamination in marine ecosystems by enabling multiyear time-series analyses through single-tissue sampling with seasonal resolution.

Keywords

PFAS, PFOS, bioaccumulation, ecosystem sentinels, marine mammals, baleen whales

Synopsis

Baleen exhibits high affinity for PFAS, with concentrations varying along the growth axis, enabling time-series PFAS monitoring in baleen whales.

Introduction

Synthetic chemical pollution is a potential driver of planetary change[1,2], necessitating monitoring and mitigation to identify and minimize consequences for species and ecosystems. The rapid introduction of novel substances, in concert with multiple-anthropogenic stressors (e.g., habitat degradation, climate change), can cause profound transformations to the biosphere[3–5]. PFAS have been detected in fish and other aquatic wildlife for decades[6], and some PFAS bioaccumulate and can biomagnify within aquatic trophic pyramids[7–9]. Among marine vertebrates, PFAS have been detected in the feathers of sea eagles [10], and in the liver, muscle, and adipose tissues of fish[11], seabirds[12,13], and marine mammals[14,15]. Cetaceans are relatively well-studied in regards to PFAS pollution[15–20]; however, this research is limited by accessibility and viability of blood-fed or protein-rich tissues to monitor PFAS over time.

Baleen whales (Mysticeti), the largest cetaceans, are sentinels of global change and marine pollution[21–23]. They feed on schooling forage fish or swarming pelagic crustaceans via bulk filtration feeding. In this process, large volumes of prey-laden water are drawn into the buccal cavity and filtered out using baleen plates attached to the upper palate[24]. Baleen is an epidermal tissue made of two morphologically distinct layers of alpha-keratin[25]. As the baleen grows from the gum tissue (i.e., the Zwischensubstanz)[26], it continually erodes on the lingual side, creating a dense fringe mat, which acts as the filter. As the plates grow dorsoventrally, at a rate of ~20 cm per year (range: 12-32 cm per year)[25], the chemical signature acquired when the baleen first emerged is preserved, as in human hair[27–29]. This makes baleen a useful tissue for investigating key physiological and phenological variables over time, including individual movements and diet patterns via stable isotopes[30–32], hormonal changes related to breeding and feeding[33–36], and variation in exposure to trace metal pollution[37]. However, only a limited time window for analysis is available (the most recent 3-13 years)[25] as the plate eventually erodes distally and is replaced by new keratinous tissue.

Despite its utility as a matrix for trace metal analysis[37,38], baleen has been underutilized for organic pollutant monitoring, primarily due to concerns regarding its affinity for lipophilic persistent organic pollutants (POPs). However, PFAS readily associate with specific proteins in biological matrices, with demonstrated affinity for human liver fatty acid binding protein and serum albumin, among others[39,40]. PFAS have also been found in human hair, which is primarily composed of keratin[41]. Here, we test the hypotheses that PFAS 1) are detectable in mysticete baleen, 2) vary within an individual along a baleen plate, and 3) whether PFAS varies between tissue types (baleen as compared to skin, blubber, liver, and gum tissues). We test these hypotheses on samples from six species (Table 1). Unlike wet tissues, baleen can be stored at room temperature without chemicals or fixatives. Thus, if PFAS are consistently detected in baleen, this may facilitate pollutant monitoring at spatial and temporal scales previously unexplored by tapping into the vast stores of baleen currently held by museums, stranding networks, and private or opportunistic collections.

Materials and Methods

Sample collection and storage

U.S. West Coast samples were collected by The Marine Mammal Center (TMMC) under National Oceanic and Atmospheric Administration (NOAA)/National Marine Fisheries Services (NMFS) permit 18786-04 and 24359 (Fig. S1). In the Southern Gulf of Maine, samples were collected by the International Fund for Animal Welfare (IFAW) under a NOAA/NMFS Permit No. 18786-06 (Fig. S1). Samples were collected in the Northern Maine region by the College of the

Atlantic's (COA) Marine Mammal Stranding Response Program (MMSRP) known as Allied Whale under a stranding agreement or Permit No. 22723 NOAA/NMFS (Fig. S1). MMSRP contributed one plate initially collected by Marine Animal Lifeline, a stranding network no longer in existence, and two plates received from IFAW that were archived at COA. All samples were collected during necropsy examinations from deceased whales following existing standard necropsy procedures[42,43]. Carcasses were either fresh dead or in moderate states of decomposition at the time of sample collection (Table S1). Liver, blubber, and skin samples were stored in sterile polypropylene bags at either -20°C or -80°C. Baleen was stored at room temperature or -20°C or -80°C if fresh gum tissue was attached. Species included in this study were humpback whale (*Megaptera novaeangliae*), common minke whale (*Balaenoptera acutorostrata*), North Atlantic right whale (*Eubalaena glacialis*), sei whale (*B. borealis*), fin whale (*B. physalus*), and blue whale (*B. musculus*) (Table S1).

Sampling of baleen plates

The exterior of each baleen plate was rinsed with PFAS-free milliQ water three times and scrubbed as needed to remove dirt and dust. A Kimwipe was then soaked in acetone and used to thoroughly wipe the plate to desorb any superficial organic contaminants; multiple Kimwipes were used dependent on the size of the plate. The plate exterior was then triple-rinsed with LCMS-grade methanol via a squirt bottle and allowed to dry in a fume hood before further manipulation. Baleen plates were and subsampled sequentially and vertically every ~2 cm, beginning at the dorsal buccal edge (Fig. 1), using an electric rotary grinder (Dremel model 4000) with a 1.25 cm sanding band attachment to grind baleen into a fine powder. Sampling equipment was also wiped with Kimwipes soaked in > 99% methanol to prevent cross-contamination. Overall, 221 discrete baleen samples

(~0.25 g powder per sample) were collected from 18 baleen plates from 17 different individuals (Tables S1-S2, Supporting Information). Given the restrictions on collection and use of marine mammal parts based on international and national law, this approach afforded a large sample size unusual in contaminant studies relying on opportunistic samples from large whales.

PFAS Analysis

Liver and other wet tissue samples were spiked with internal standard and solvent-extracted in acetonitrile using sonication, centrifugation, and freezing, paired with graphitized non-porous carbon clean-up via a modified version of the extraction described in Spaan et al.[15]. Dry baleen samples were spiked with 5ng of a mixture of mass-labeled surrogates and extracted twice in series using a basic methanol digestion, sonication, centrifugation, and graphitized carbon clean-up following a modified version of an extraction developed for feathers[10] (for details, see Supporting Information). Measurement and quantification of target PFAS in this proof-of-concept application was achieved using liquid chromatography tandem-mass spectrometry (UPLC-MS/MS) experiments in negative electrospray ionization mode (Supporting Information for details; Tables S3-S9).

Quality assurance and statistical analysis

Procedural blanks were included with the sample set to monitor process recovery and background contamination (Tables S10-S13). Baleen samples displayed an average median recovery of 86% and wet tissue samples displayed an average median recovery of 76% (excluding non-detected FTS, PFBA, PFBS). Method detection limits (MDLs) were defined as procedural blank levels of a given analyte plus three times the standard deviation.

Concentration data were non-normal despite log transformation and therefore treated non-parametrically for statistical analyses; summary statistics and group comparisons were derived using uncensored data analyzed using the cenfit function in the R package NADA version 1.6 - 1.1 to account for artifacts of left-censored data[44,45]. Significant differences in contaminant concentrations between individuals or other ecologically relevant groups were assessed using both uncensored and censored log-transformed data. Left-censored data was also assessed for significant differences by group and compound using Kruskal-Wallis tests followed by post-hoc application of Dunn's test for multiple comparisons. Data is presented as median ± SD.

Results and Discussion

PFAS concentrations in baleen

We found quantifiable levels of PFAS in every baleen sample (n = 220) across 18 plates from six species (Fig. 1, Table S14). Across all tissue types we tested, 16 of 26 targeted PFAS compounds were quantifiable in at least one sample (for more information on these compounds, see the Supplemental Information). In baleen samples, ten PFAS – PFUdA, PFTrDA, PFDA, PFDoA, PFOS, PFOA, PFNA, FOSA, PFHxA, and PFTeDA, referenced as Σ_{10}PFAS hereafter – – were found in > 40% of samples. The median Σ_{10}PFAS for all baleen samples was 10 ± 10 ng/g dry weight (d.w.). Using data from the most recently emerged baleen (i.e., the first ~2 cm segment on each plate that was fully erupted from the gumline) on each plate, the Σ_{10}PFAS ranged from 0.02 ng/g d.w. for a blue whale from the Pacific Coast to 61 ng/g d.w. for a humpback whale from the Atlantic Coast (Fig. 2). The PFAS concentrations we report here represent lower-bound estimates of the total PFAS-burden in these whales, as there are likely additional PFAS compounds that we did not detect with our evaluation of 26 targeted analytes[15]. Of the 26 target analytes, half were below instrumental detection limits in baleen samples (4:2-FTS, 6:2-FTS, 8:2-FTS, EtFOSAA, 7:3 FTCA, HFPODA-GenX, N-MeFOSAA, Nafion BP2, PFBA, PFNS, PFHpS, PFPeA, and PFPeS), but there were quantifiable levels of PFUdA, PFTrDA, PFDA, and PFDoA – all long-chain perfluoroalkyl carboxylic acids (PFCAs) – in > 80% of baleen samples. The abundance of these long-chain PFCAs has been noted in other marine food webs, potentially driven by long-range transport and transformation of PFCA intermediates to remote ocean and polar regions[46–48]. Of the 10 compounds found in > 40% of baleen samples, PFOS – a long-chain perfluoroalkyl sulfonic acid (PFSA) – had the highest median concentration 2 ± 4 ng/g d.w.

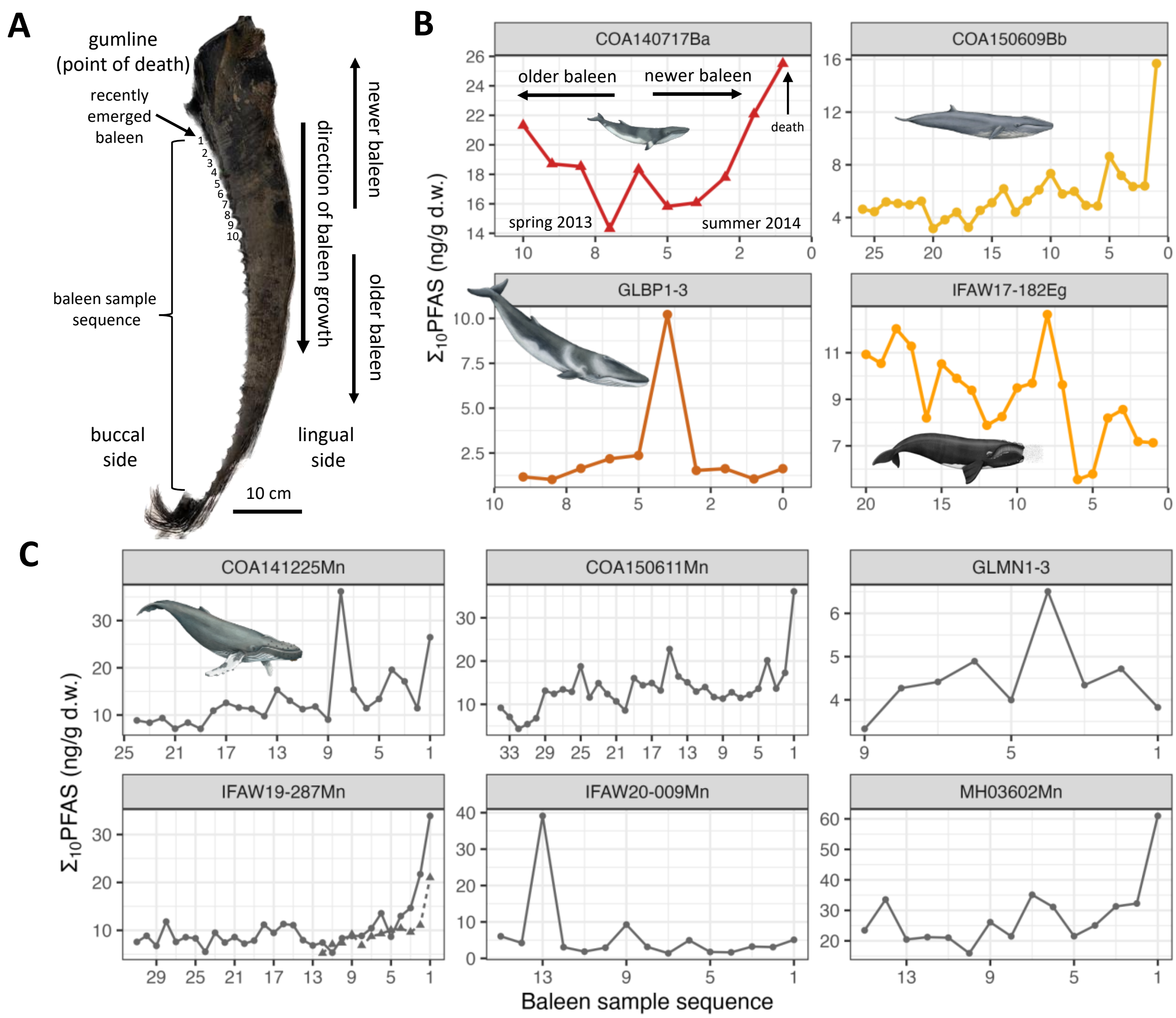

Fig. 1. PFAS load along baleen plates. Data showing sampling points and PFAS data for samples

taken 2-3cm along each plate. Ten PFAS compounds appeared in > 40% of all baleen samples along baleen plates, the Σ_{10}PFAS of these compounds are plotted. Longitudinal data for Common minke, sei, fin, and blue whale not shown. A) Baleen plate sampled from a humpback whale (IFAW19-287Mn) showing sampling locations, direction of growth, and orientation in the oral cavity. B) Common minke (n = 3 total; one shown here), sei, fin, and North Atlantic right whales; blue whale not shown due to short plate available for analysis and thus no time series. C) humpback whales plotted by individual, only individuals with > 3 samples per plate are shown; note that for IFAW19-287 two plates were sampled one represented with circular points and solid line, another with triangular points and dashed line. Whale illustrations by Alex Boersma.

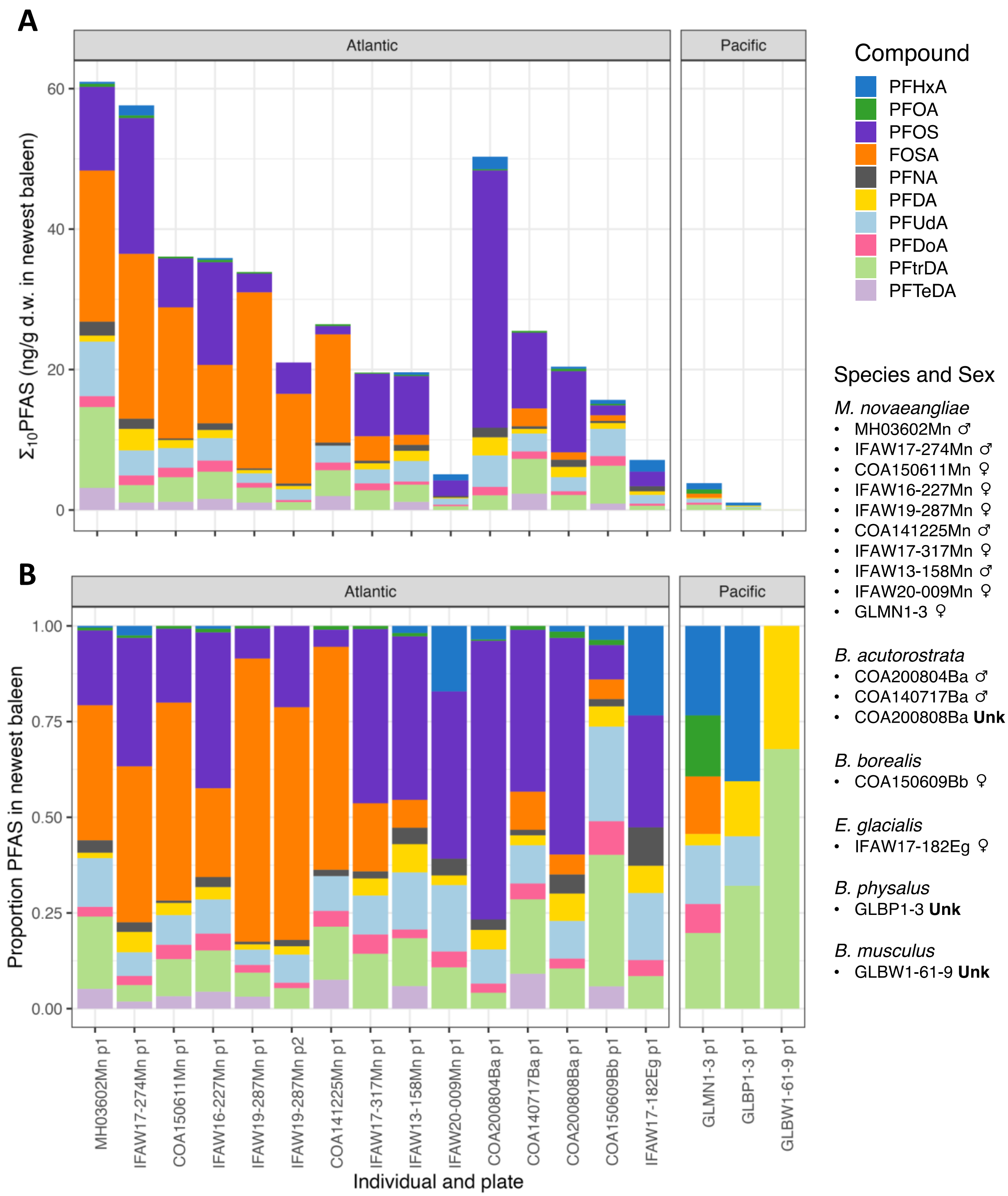

Fig. 2. PFAS in recently emerged baleen. P1 refers to the first plate sampled for each individual, p2 refers to the second plate sampled. Only IFAW19-287Mn had two separate plates sampled. Refer to Table S1 for more information on each individual A) concentration of the Σ_{10}PFAS for the subsample of most recently emerged baleen on each plate studied colored by compound. B) proportion of PFAS compounds for the most recently emerged baleen on each plate studied colored by compound.

Trends along a baleen plate

In addition to the universal detection of PFAS in our baleen samples, there were trends in PFAS contamination along each plate that may be related to life history events. Most commonly, there was a spike in Σ_{10}PFAS in the final 3-4 samples prior to death (Fig. 1). This could be due to changes in habitat use, behavior, feeding, or body condition in the months prior to death. However, the yearling North Atlantic right whale (IFAW17-182Eg; NARW Catalogue #4694) baleen we tested showed the opposite pattern, with a decreasing PFAS-baleen burden over time (Fig. 3A). This may be due to rapid weight gain of the individual as it grew from newborn to yearling; typical NARW birthweight is 1 ton and its final weight, 7.5 tons, was measured at necropsy[49] (Fig. 3A). Baleen whales have determinate growth—growing rapidly in their first two years before somatic growth slows as they approach sexual maturity (5-10 years old in most species)[49,50]. In addition, during their first year, baleen whales transition from feeding on milk at birth to prey as a yearling – NARWs fully wean by 8-17 months[51]. It is likely that mammalian milk is enriched in PFAS as compared to zooplankton. Based on baleen growth rates and the known age of this NARW at its time of death, the steadily decreasing Σ_{10}PFAS in its baleen likely reflects body dilution in the growing calf that occurred as its diet shifted from milk to copepods (Fig 3A). Furthermore, the necropsy report indicated that the cause of death was probable blunt trauma from a vessel strike. An acute cause of death (e.g., vessel strike) reduces the possibility of other factors (e.g., chronic stress, starvation, or a change in habitat use following injury or entanglement in fishing gear) causing long-term changes in body chemistry that can be reflected on a baleen plate[35,36,52].

In contrast, IFAW19-287Mn, "Vector," was a mature female humpback whale that had been studied for 35 years at the time of her death and had a documented calving history. Based on a baleen growth rate of 12 cm/yr for an adult humpback[25] and her time of death, the length of the longer of her two plates we sampled (67 cm, representing ~5 years of growth) contained the gestation, parturition, and nursing periods of her final two calves. Long-chain PFSAs (e.g., PFOS) are known to transfer from mother to offspring in the womb and through milk[53]. The portion of baleen that coincides with these two reproductive periods shows two declines in PFOS levels, which may represent maternal offloading *in utero* and via milk (Fig. 3B). In the future, larger sample sizes of females with known reproductive histories and concurrent hormonal analysis of baleen would provide further opportunities to examine maternal offloading of various PFAS compounds.

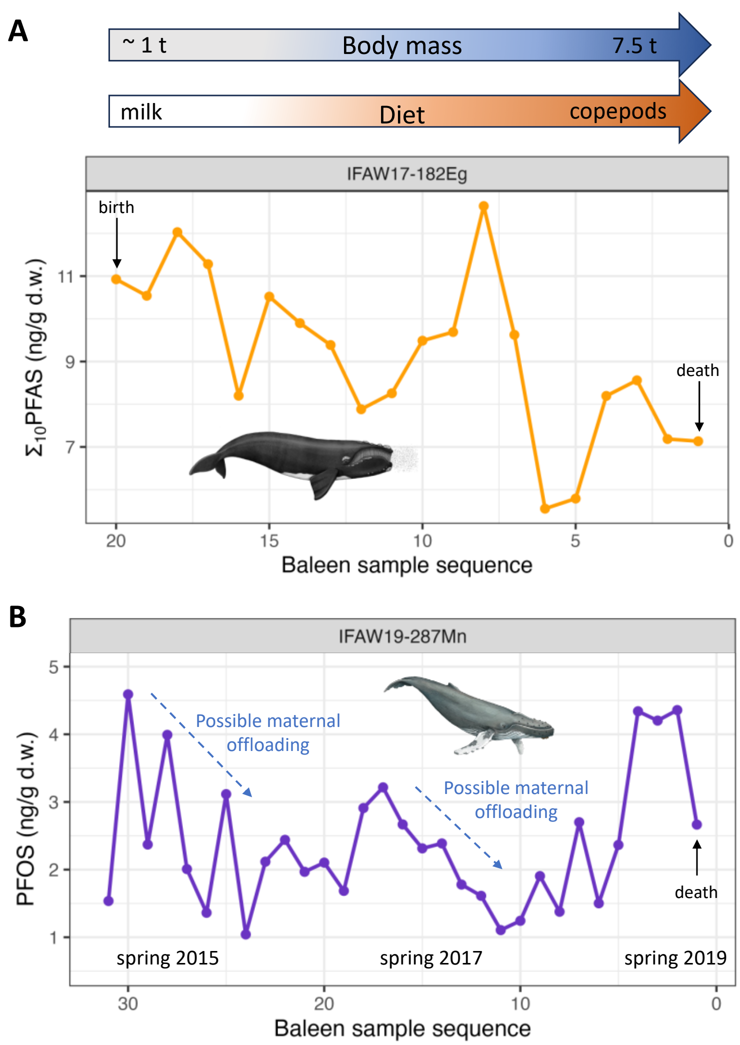

Fig. 3. Baleen-PFAS signature and life-history events. A) Longitudinal record of NARW baleen-PFAS signal with samples every ~3 cm along the plate; the only baleen plate in our study that captured the entire life of the individual. This individual was 15 months old at its time of death (likely via ship strike) and capturing the weaning period. B) The longitudinal PFOS record of the longer of Vector's (IFAW19-287Mn) two plates that were analyzed, showing declining PFOS-levels coinciding with two known calving periods, one in winter-spring 2015 the other in winter-spring 2017. Whale illustrations by Alex Boersma.

Geographic trends

We did not have adequate sample size or geographic coverage to statistically assign differences in PFAS values between whales from the Atlantic vs. Pacific coasts of North America. However, our initial results suggest higher PFAS concentrations in marine food webs in the Gulf of Maine compared to the California Current (Fig. 2A). This is in agreement with available global data and models on PFAS distributions in seawater[47,64]. The median Σ_{10}PFAS for the most recently emerged baleen samples was 26 ± 17 ng/g d.w. for individuals from the Gulf of Maine (n = 15), as compared to 1 ± 3 ng/g d.w. for individuals from the U.S. West Coast (n = 3). Preliminary differences this large suggest the need for further investigation. Globally, it would be useful to compare our findings – across species and compounds – with data from the highly polluted Mediterranean and Western North Pacific regions where data on PFAS and large whales are limited and outdated.

PFAS across whale tissues

Of the five tissues we tested, only liver (n = 5, 4 humpbacks, 1 NARW) had consistently higher PFAS-burdens than baleen. The average PFAS burden in liver samples was fivefold higher than what was found in baleen, but roughly twentyfold higher than that in blubber and skin (Fig. S2, Table S15). PFAS concentrations by tissue type were liver > baleen ≈ gum > skin > blubber (Fig. S2). Skin and blubber are the only tissues that can be reliably sampled from living cetaceans due to restrictions on interactions with marine mammals mandated by global and US law; however, our findings suggest these are the least effective tissues for PFAS monitoring across the five tissue types we tested. This is in contrast with lipophilic POPs that are well represented in blubber[54–56].

While our wet tissues sample size was limited, our findings suggest tissue-specific partitioning of PFAS. For instance, 7:3 FTCA was found in all liver samples (n = 5), 38% of blubber samples (3 out of 8), 25% of skin samples (2 out of 8) but was absent from all gum and baleen samples (n = 228 total). In contrast, median PFOS values in baleen were tenfold higher than PFOS in blubber (2.1 ng/g vs. 0.24 ng/g). Thus, multi-tissue sampling provides a more complete contaminant picture than any single tissue alone, providing rationale for future efforts to assess PFAS in multiple tissues from marine mammals[16,57].

Comparison to other marine mammals

Most studies on PFAS in marine mammals have tested liver tissue. We used our liver samples to compare to other findings for PFAS in marine mammals. In our study, we found eight PFAS that were present in > 40% of wet tissue (liver, skin, blubber) samples that we included in our analyses. Those compounds were PFUdA, PFNA, PFDA, PFOS, FOSA, PFtrDA, 7:3 FTCA, and PFDoA. Our Σ_8PFAS concentrations for liver samples were 75 ± 85 ng/g wet weight (w.w.), which is lower than the majority of pinniped seal and odontocete whale studies[15,16,18,19], but aligns well with other mysticete whale data (Table S16). This was expected as baleen whales tend to have lower trophic positions than pinnipeds or odontocetes[58]. These levels are within range to cause immune suppression in mice (64 - 118 ng/g w.w. serum PFOS)[59] and humans (6 - 21 ng/mL serum PFOS)[60,61]; no comparable toxicological testing has yet been conducted in any marine mammal.

As with other cetacean studies[62,63], we recorded FOSA in all liver samples (16 ± 14 ng/g w.w.) and in most baleen samples (61% of baleen samples; 1 ± 4 ng/g d.w.). Humpback whales had significantly higher concentrations of FOSA than the other species in our dataset, which may be indicative of their nearshore residency and feeding (humpback whale recently emerged baleen

FOSA: 13 ± 10 ng/g d.w.; other species' baleen FOSA: 0 ± 1 ng/g d.w.; Kruskal-Wallis test, P = 0.007). In addition, we found 7:3 FTCA in higher concentrations than previously published mysticete studies (Table S16), though recent work uncovered high levels of 7:3 FTCA in killer whales (*Orcinus orca*) off the North American west coast[19]. It is likely that air-breathing species have higher levels of 7:3 FTCA as compared to fish and aquatic invertebrates due to atmospheric oxidation of fluorotelomer alcohols as the likely origin of environmental 7:3 FTCA.

Implications

We report quantifiable levels of PFAS in all samples (n = 251) across five tissue types in six species of baleen whales from the Atlantic and Pacific coasts of North America with concentrations spanning five orders of magnitude (0.02 ng/g Σ_{10}PFAS in blue whale baleen to > 200 ng/g Σ_{8}PFAS in a humpback whale liver). While PFAS have been found in other keratin-based tissues, including bird feathers and human hair[10,65–67], this is the first report of these contaminants in baleen. Future work should explore whether there are additional PFAS present in baleen. Our initial work focused on a list of common PFAS compounds, while other research has indicated that there might be additional organofluorine present in marine mammals, including baleen whales[15].

The proof-of concept work presented here relied on fairly large baleen samples (~0.25g / sample) to ensure detection of the targeted PFAS present. A more precise temporal resolution in the PFAS chronology could be achieved by using lower masses, and thus increase the temporal resolution. The size, ease of storage, longitudinal growth, and demonstrated PFAS binding affinity makes baleen a valuable resource for monitoring PFAS in the environment. Moreover, museum baleen collections dating back to the 19th-century can provide a window into the global emergence of PFAS in marine ecosystems across space and time.

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Acknowledgments:
The hard work of the stranding and necropsy teams at IFAW were essential to obtain the samples used in this study. On the US West Coast, we thank The Marine Mammal Center, and specifically Barbie Halaska, for assistance with the specimen collection and curation. We thank Thomas Garrow for support with labwork at URI, and Rachel Anderson for editorial assistance.

Supporting information:

Analyte list, QAQC information, sample information.

Additional summary data, additional text describing methods, quality assurance, and additional figures in support of the text.

Funding:

NSF PRFB 1906332 (MSS)

National Geographic Society EC-53352R-18 (MSS)

National Institute of Environmental Health Sciences under Award Number P42ES027706 (ARR, RL)

Author contributions:

Conceptualization: MSS, ARR, JAG

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Investigation: MSS, ARR, MAC, LCA, RR, NEH, JR

Visualization: MSS, ARR

Supervision: MGC, DNW, ST, JAG, RL

Writing—original draft: MSS, ARR

Writing—review & editing: all authors

Competing interests:

Authors declare that they have no competing interests.

Data and materials availability:

All data are available in the main text or the Supporting Information; Code for figures and analyses can be found at: https://github.com/mssavoca/Baleen_PFAS_2020

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