

Manufacturing Origin of Perfluorooctanoate (PFOA) in Atlantic and Canadian Arctic Seawater

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Supporting Information



ABSTRACT: The extent to which different manufacturing sources and long-range transport pathways contribute to perfluorooctanoate (PFOA) in the world's oceans, particularly in remote locations, is widely debated. Here, the relative contribution of historic (i.e., electrochemically fluorinated) and contemporary (i.e., telomer) manufacturing sources was assessed for PFOA in various seawater samples by an established isomer profiling technique. The ratios of individual branched PFOA isomers were indistinguishable from those in authentic historic standards in 93% of the samples examined, indicating that marine processes had little influence on isomer profiles, and that isomer profiling is a valid source apportionment tool for seawater. Eastern Atlantic PFOA was largely (83–98%) of historic origin, but this decreased to only 33% close to the Eastern U.S. seaboard. Similarly, PFOA in the Norwegian Sea was near exclusively historic, but the relative contribution decreased to ~50% near the Baltic Sea. Such observations of contemporary PFOA in coastal source regions coincided with elevated concentrations, suggesting that the continued production and use of PFOA is currently adding to the marine burden of this contaminant. In the Arctic, a spatial trend was observed whereby PFOA in seawater originating from the Atlantic was predominantly historic (up to 99%), whereas water in the Archipelago (i.e., from the Pacific) was predominantly of contemporary origin (as little as 17% historic). These data help to explain reported temporal and spatial trends from Arctic wildlife biomonitoring, and suggest that the dominant PFOA source(s) to the Pacific and Canadian Arctic Archipelago are either (a) from direct emissions of contemporary PFOA via manufacturing or use in Asia, or (b) from atmospheric transport and oxidation of contemporary PFOA-precursors.

INTRODUCTION

Perfluorinated acids (PFAs) and their precursors (PFA-precursors) have been manufactured for over 60 years for use in various commercial products and industrial processes. These substances can have considerable long-range transport¹ and bioaccumulation potentials,² and they are now widespread contaminants of the global environment, including in seawater^{3–5} and Arctic wildlife.⁶ Despite increased international concern regarding these chemicals,⁷ their production and use continues,⁸ and concentrations of some PFAs continue to increase in humans⁹ and wildlife¹⁰ in some areas of the world.

Perfluorooctanoate (PFOA, $\text{C}_7\text{F}_{15}\text{COO}^-$) is among the most commonly detected PFAs in the environment. It has been associated with low birth weight in humans¹¹ and is a carcinogen in lab animals.¹² Two large-scale manufacturing techniques have been used to produce PFOA, and these are readily distinguishable by the isomeric composition of the final

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commercial products (reviewed in ref 13). The oldest process, electrochemical fluorination (ECF), results in a mixture of branched and linear isomers. It is estimated that the majority (80–90% in 2000¹⁴) of historic global PFOA manufacturing (1950s until 2002) was by ECF, manufactured by the 3M Co. at plants in Cottage Grove, MN (ECF PFOA pilot production only), Cordova, IL, Decatur, AL, and Antwerp (Belgium).¹⁵ ECF PFOA had a consistent isomer composition of 78% linear (stdev 1.2%) and 22% branched (stdev 1.2%) in 18 production lots over a 20 year period based on analysis by ¹⁹F-nuclear magnetic resonance.¹⁶ The 3M Co. voluntarily phased out ECF perfluorooctyl chemistries in 2002, and while the extent of current global ECF PFOA manufacturing is unknown, it is likely minor today.

Despite the phase-out of ECF PFOA by the 3M Co., large-scale production of PFOA continued after 2002 by telomerization, a process originally developed by DuPont in the 1970s.¹⁷ Telomerization is distinct from ECF in that the isomer composition of products is pure, with typically linear geometry (although isopropyl is also possible¹⁷). This process accounted for only 10–20% of ammonium PFOA produced globally from 1975 to 2004¹⁴ but is currently the dominant manufacturing process in North America for perfluorinated carboxylic acids (PFCAs) and fluorotelomer products (i.e., $\text{CF}_3(\text{CF}_2)_x\text{C}_2\text{H}_4\text{R}$);¹⁸ some of which can degrade to PFCAs in the environment.^{19–21}

Although there is some minor overlap in the historical and contemporary use of ECF and telomerization for PFOA manufacturing, for simplicity we will refer to ECF as the historical manufacturing source, and telomerization as the contemporary manufacturing source. The extent to which ECF or telomer PFOA contribute to environmental concentrations in remote marine food webs today, and in the future, has potential regulatory implications. Environmental models estimate that historical emissions of ECF PFOA, and its subsequent slow long-range transport in oceans, are the dominant source of PFOA to remote regions.^{14,22–24} PFA concentrations in seawater^{3–5} (including North Atlantic, Greenland, and Norwegian Seas) are generally consistent with this notion,²³ but the importance of alternative pathways to specific marine regions of the Arctic have not been ruled out. Alternative transport mechanisms include the long-range atmospheric transport of PFOA-precursors (e.g., fluorotelomer alcohols) and their subsequent oxidation,²⁵ or the partitioning of PFOA (or its conjugate acid) to the atmosphere via marine aerosols.^{26,27}

We hypothesized that if PFOA in remote seawater is predominantly “old PFOA”, and was slowly transported in ocean currents from source regions (as predicted by global transport models), then branched PFOA isomer content in remote seawater should be largely consistent with ECF PFOA produced by the 3M Co. Here we applied an established isomer-profiling technique for seawater²⁸ to assess the relative extent of ECF PFOA in various seawater samples, including in remote samples from the Canadian Arctic Archipelago and North Baffin Bay, for the first time. The relative profile of individual branched isomers was also carefully examined for potential abiotic fractionation, as hypothesized by others.^{26,29} Data are discussed with respect to sources, transport mechanisms, and potential environmental fractionation of PFOA isomers.

■ EXPERIMENTAL METHODS

Nomenclature. The major PFOA isomers are abbreviated as follows: the linear isomer *n*-perfluorooctanoate (*n*-PFOA); perfluoro-6-methylheptanoate (*iso*-PFOA); perfluoro-5-methylheptanoate (*5m*-PFOA); perfluoro-4-methylheptanoate (*4m*-PFOA); perfluoro-3-methylheptanoate (*3m*-PFOA). As discussed, in the context of PFOA manufacturing, the terms “historical” and “contemporary” are used synonymously with ECF and telomer manufacturing processes, respectively.

Standards and Reagents. HPLC-grade methanol was purchased from Fisher Scientific (Ottawa, ON, Canada) and HPLC-grade formic acid (50%) was purchased from Sigma-Aldrich (Oakville, ON, Canada). *n*-PFOA and *n*-perfluoro [^{1,2,3,4-¹³C₄]}octanoate (¹³C-PFOA) were purchased from Wellington Laboratories (Guelph, ON, Canada). An authentic ECF-manufactured PFOA standard (Lot 332) was provided by the 3M Co. (St. Paul, MN). Chemicals and reagents used for extraction and analysis can be found in refs 30–32.

Sample Collection. All samples were provided as extracts that were previously analyzed for total PFAs (i.e., nonisomer-specific analysis) in separate studies. Details on sampling, extraction, and treatment of samples can be found in refs 30–32 and in the Supporting Information (SI). Briefly, sampling aboard the Research Vessel (RV) *Polarstern* was conducted from October 29 to November 22, 2007, in the Eastern Atlantic (Figure 1A, Table S-1 in the SI). Samples in the North and Norwegian Seas (I–VI) were collected from August 14 to 17, 2007, aboard the RV *Maria S. Merian* (Figure 1, SI Table S-2). Surface water samples from the Western Atlantic (Figure 1A, SI Table S-3) were collected in July, 2009 aboard the RV *Endeavor* (cruise EN464). Spatial and depth (8 and 20 m) samples were collected aboard the Icebreaker (IB) *Oden* (Beringia expedition) from Southwest Greenland through the Canadian Archipelago to the Bering Strait in July–August 2005 (Figure 2A, coordinates in Table S-4, SI). Northern Baffin Bay and eastern Lancaster Sound were also sampled aboard the CCGS *Amundsen* in September, 2008 (Figure 2A, Table S-5, SI).

Instrumental Analysis. Seawater extracts were analyzed by liquid chromatography tandem-mass spectrometry, employing a FluoroSep RP Octyl column (3 μm , 100 Å, 15 cm \times 2.1 mm, ES Industries, West Berlin, NJ) and API 5000Q triple-quadrupole mass spectrometer (AB Sciex, Concord, ON, Canada) operating in negative ion mode with multiple reaction monitoring (MRM).^{28,33} Each sample was received as a sealed extract, and no manipulation of these extracts were made prior to isomer analysis. All extracts were provided in 50:50 (v/v) methanol:water and total volumes were estimated visually to determine feasible injection volumes. To achieve accurate sensitivity, in all instances the “whole” sample (~90% of estimated total volume) was injected. Injections were typically 100–275 μL , but in some instances were as low as 50 μL depending on the volume of extract received.

QA/QC. Laboratory and field blanks were examined with sample sets from each cruise, and PFA isomer concentrations/profiles observed in blanks were subtracted from samples in all instances. Details of spike/recovery experiments, assessment of matrix effects, the “% branched dynamic range”, and PFA isomer limits of detection were previously reported and discussed.²⁸

PFOA Quantification and Source Assignment. Our ability to accurately quantify the source apportionment of

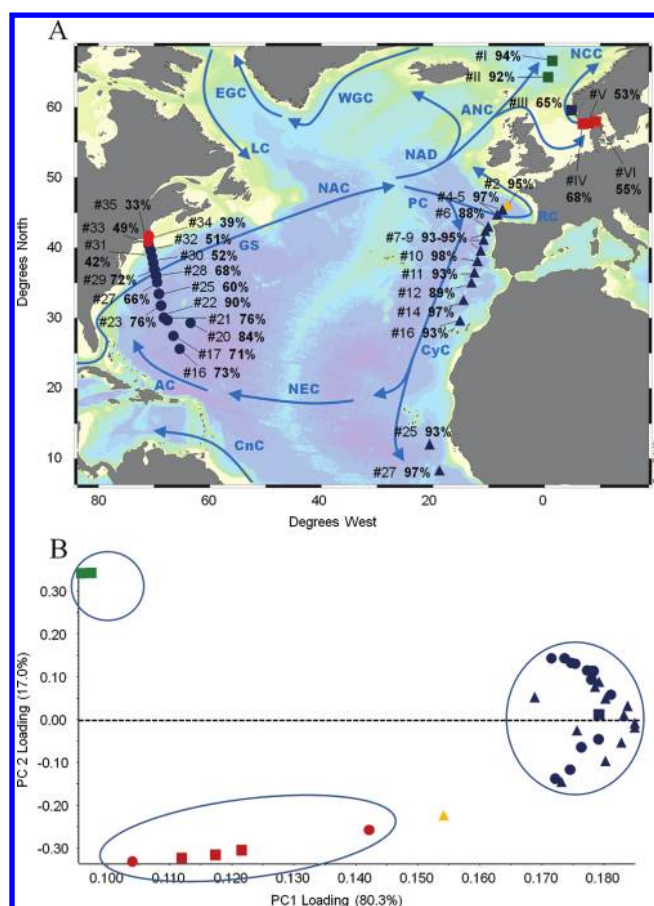


Figure 1. (A) Sampling locations, surface water circulation, and % contribution of ECF PFOA to total PFOA plotted using Ocean Data View,⁵¹ and (B) results of PCA analysis of total PFOA, % ECF, latitude, and longitude, for Western Atlantic (circles), Eastern Atlantic (triangles), and Norwegian/North Sea (squares) sampling campaigns. Samples were colored according to PCA grouping; red: low % ECF/high total PFOA concentration; blue: moderate-high % ECF/moderate total PFOA concentration; Green: high % ECF/low total PFOA concentration. Yellow triangle indicates outlier (high % ECF/high total PFOA). See main text for further detail. PCA scores (%) are shown on the x- and y-axes. Ocean currents are abbreviated as follows: CnC-Caribbean Current, CyC-Canary Current, NEC-North Equatorial Current, AC-Antilles Current, GS-Gulf Stream, NA-North Atlantic Current, NAD-North Atlantic Drift, RC-Rennell Current, PC-Portugal Current, ANC-Atlantic Norwegian Current, NCC-Norwegian Coastal Current, WGC-West Greenland Current, EGC-East Greenland Current, LC-Labrador Current.

PFOA in seawater was previously validated²⁸ and we refer the reader to this reference for specific details of PFOA source assessment. In brief, a linear PFOA standard was used to quantify both total PFOA (i.e., sum of *n*, iso, 5*m*, 4*m*, 3*m*-PFOA peaks in *m/z* 369 product ion) and *n*-PFOA separately, which was previously shown to give isomer compositions within 4% from true weight percentages using ¹⁹F-NMR. This practice is unlikely to influence % ECF determinations, because branched content was measured and compared the same way in both samples and standards (see ref 28 for details). To ensure our results were not affected by abiotic fractionation of the isomer profile, we compared the relative proportions of individual branched isomers in samples to the corresponding proportions in our ECF PFOA standard using one-way analysis of variance (ANOVA, SigmaStat Software Inc., San Jose, CA). Since

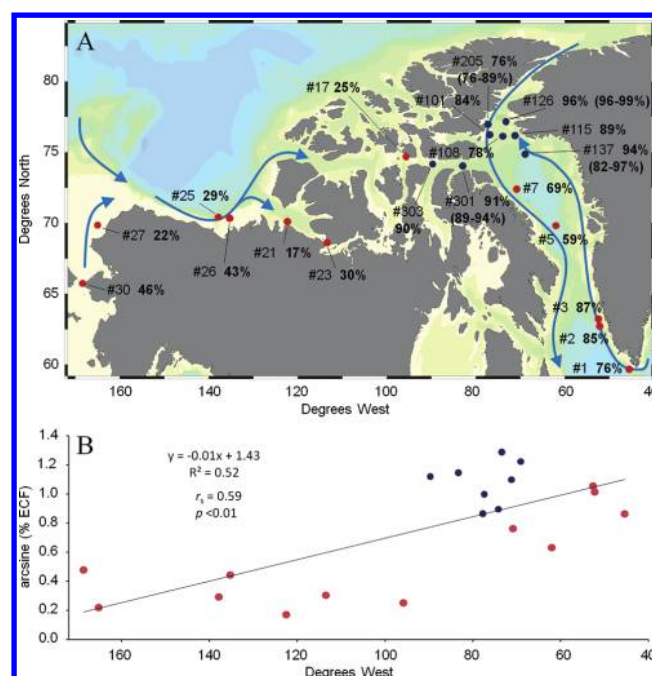


Figure 2. (A) Sampling locations and % ECF for Arctic cruises plotted using Ocean Data View⁵¹ and (B) correlation between arcsine (% ECF PFOA) and longitude for surface samples. In both figures, red markers represent July 2005 West Greenland/Canadian Archipelago/Bering Strait cruise (nos. 1–30), while blue markers represent September 2008 Baffin Bay/Lancaster Sound cruise (nos. 101–301). Arrows represent general flow of West Greenland Current, Baffin Current, and water flowing through Canadian Archipelago.^{52,53} Percentages shown for stations 126, 137, 205, and 301 are values for surface samples, with the range observed over all depths provided in parentheses.

typically only a single sample was analyzed for each sampling site, we assumed the standard deviation of each measurement using the % relative standard deviation of 4 replicate analyses of 3M ECF PFOA at low concentration (<200 pg/L). % ECF was only calculated on samples in which the relative ratio among individual branched isomers were not statistically (i.e., $p < 0.05$) different from those in our 3M ECF PFOA standard. Quantifying the contribution of ECF and telomer PFOA to total PFOA concentrations was accomplished using a calibration curve of % branched (by weight, based on the aforementioned quantification method) versus % ECF prepared with standards containing known quantities of ECF and telomer-manufactured PFOA (see Figure S-1, SI). Calculation of isopropyl telomer source contribution (necessary in only a few cases) is also described elsewhere.²⁸

Principle Component Analysis. Principle component analysis (PCA) was performed on latitude, longitude, % ECF, and total PFOA concentrations in surface samples from East Atlantic, West Atlantic, and North/Norwegian Sea sampling campaigns using Applied Biosystems/MDS Analytical Technologies MarkerView Software (Carlsbad, CA). PCA was processed using autoscale without weighting.

Statistical Analysis of % ECF, Temperature, And Salinity Data. Correlations between % ECF, water temperature, and salinity were examined using Pearson Product Moment or Spearman Rank Order correlation (SigmaStat Software Inc.). Data which were normally distributed ($p > 0.05$, Shapiro-Wilk) following transformation (i.e., arcsin transformation of % ECF and log transformation of temperature

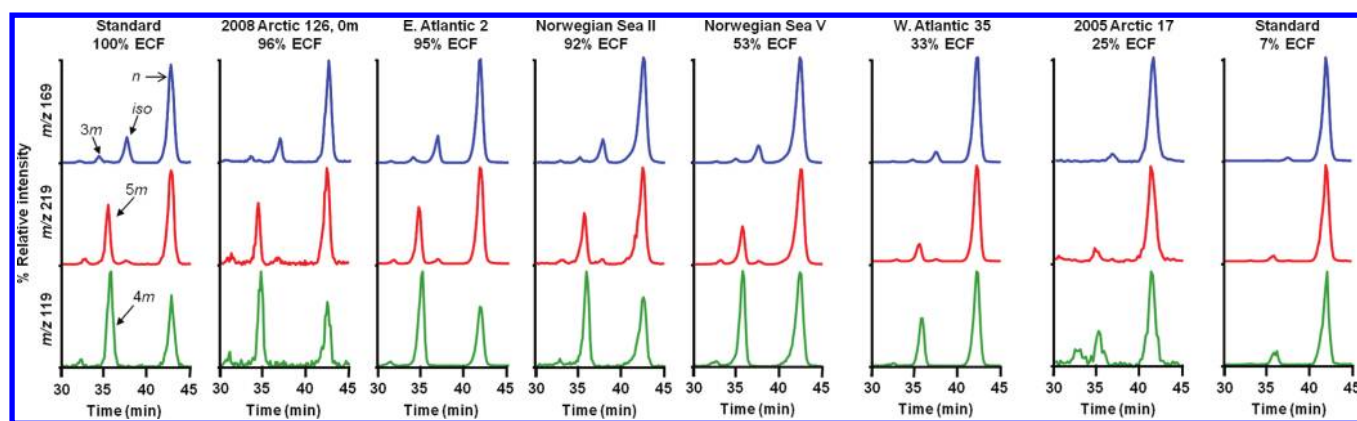


Figure 3. Example PFOA chromatograms from each of the five sampling campaigns examined in the present study and comparison to 100% and 7% ECF standards. Three MRM chromatograms are shown for each sample, blue traces represent m/z 413/169; red represents m/z 413/219, and green represents m/z 413/119.

and salinity data), were examined statistically using Pearson Product Moment. For data which were not normally distributed following transformation, correlations were assessed using Spearman Rank Order.

RESULTS AND DISCUSSION

A detailed discussion on total concentrations of PFOA relative to other PFAs can be found elsewhere.^{30–32} Total and *n*-PFOA concentrations, along with % branched, % ECF, depth, temperature and salinity data are provided in Tables S1–S5 of the SI, whereas isomer ratio data used for statistical analysis are presented in Tables S6–S14 of the SI. Out of the 81 samples analyzed in this study, only 6 showed evidence of abiotic fractionation (as indicated by statistically significant differences between branched isomer ratios in samples versus our reference standard). For those 6 samples, % ECF was not calculated. The fact that 93% of the samples we examined displayed no significant differences in the relative ratio of individual branched isomers compared to a historical reference standard is good evidence that isomer fractionation is minimal in seawater. It is notable that a recent study²⁹ which examined environmental samples near a training facility which utilized aqueous film forming foams (AFFF) observed an average of 25% branched PFOA in groundwater samples (compared to 18–22% branched reported by others in historical PFOA). While these observations may indeed be reflective of minor abiotic fractionation, the processes responsible are likely very different from those occurring in the open oceans (if any). Certainly the role of other surfactants, as well as high PFOA concentration, groundwater pH, and the potential formation of PFOA aggregates^{34,35} (which may enhance isomer fractionation) should be considered before extrapolating results from AFFF sites to more remote environments.

PFOA concentrations in the Atlantic Ocean were typically <100 pg/L in samples collected in the Canary and Antilles currents, increasing to several hundred pg/L in the Bay of Biscay and the eastern seaboard of the United States. Sites near highly populated areas such as Narragansett Bay (Rhode Island) reached as high as ~1200 pg/L, consistent with coastal waters of Asia.^{5,36} Concentrations in the Norwegian Sea were low (~10 pg/L), but this increased moving eastward into the North Sea. In North Baffin Bay and the Canadian Arctic Archipelago, total PFOA concentrations were consistently <100 pg/L. As discussed in ref 28, accurate isomer profiles by our

method can be achieved down to ~2 pg in a given volume of water assuming preconcentration to 300 μ L and injections of up to 275 μ L (i.e., >90% of the extract).

2007 Eastern Atlantic Sampling Campaign. Eastern Atlantic seawater contained PFOA isomer profiles consistent with 3M ECF PFOA (Figures 1, 3, and Figure S-2 in the SI) and no spatial trend in the isomer profiles were observed in these samples. Statistical analysis of water temperature versus % ECF also revealed no correlation (Spearman coefficient (r_s) = 0.01, p = 0.96; Figure S-3, SI). A maximum of 11% of total PFOA was attributable to the telomerization process in any sample from this region. In addition, two samples (6 and 16) contained minor contributions (8 and 6%, respectively) of PFOA from a strictly isopropyl telomer source (Table S-1, SI). The % ECF could not be calculated in four samples (1, 3, 19, 26) due to a small (i.e., 0.7–5.4%), albeit significant (p < 0.05) enrichment in branched isomer content above that in our 3M ECF PFOA standard (Table S-1, SI). Others^{26,37} have suggested that fractionation of PFOA isomers could occur at the surface boundary layer, resulting in enrichment of branched content. For samples 3 and 26, the relative ratio of individual branched isomers was consistent with the ECF PFOA standard (Tables S-6, S-7, S-8, SI), but for samples 1 and 19, the relative ratios among branched isomers were significantly (p < 0.05) different (albeit visually subtle, see chromatogram of sample 1 in SI Figure S-2) from 3M ECF PFOA. It is unclear what might have caused this minor apparent environmental fractionation. Two of the samples (1 and 3) were collected in the Bay of Biscay, an area which contained the highest concentrations of PFOA out of all Eastern Atlantic sampling sites. Nonetheless, other samples (2 and 4) collected in the Bay of Biscay showed no branched isomer enrichment, and the high branched content (18.8–23.4%) in samples 1, 3, 19, and 26, suggests minimal input from a telomer source, consistent with the remaining Atlantic samples.

2007 Norwegian and North Seas. ECF was again the major source of PFOA here, but measurable contributions from a linear-telomer source were observed in all samples from this region, to varying extents. For those collected in the Norwegian Sea (I and II), this contribution was up to 6% telomer PFOA (Figures 1, 3, S-4, Table S-2, SI). These results are consistent with model predictions^{23,24,38} on the marine transport of PFOA to the Arctic, as well as with our observations of high ECF contributions in the Canary Current (Eastern Atlantic Ocean),

which is fed by the same water (i.e., North Atlantic Current) as the Norwegian Strait.

Sampling on a southeast trajectory into the North Sea and eventually into the Skagerrak (between Norway and Denmark), data revealed an increasing contribution from telomer sources and increasing total PFOA concentration. This was confirmed by a statistical analysis of % ECF versus water temperature which showed warmer water (from the Baltic) containing lower % ECF (Pearson coefficient (r_p) = 0.88, p = 0.02, Figure S-3, SI). Telomer PFOA accounted for 32–35% of total PFOA in samples III and IV, and 45–47% in samples V and VI (Figures 1, S-4, Table S-2, SI). The increase of total PFOA concentrations in samples III–VI likely arises from elevated PFOA concentrations in the Baltic Sea, as previously reported (in samples from 2007),³¹ and the concurrent increase in % linear-PFOA suggests that this source region is highly influenced by contemporary emissions of linear-telomer PFOA. Approximately 50% of Atlantic water entering the North Sea is mixed with brackish water from the Baltic before it leaves the North Sea as the Norwegian Coastal Current. This mixing occurs predominantly in the Skagerrak,^{39,40} where samples V and VI were collected. Considering the relative contributions of Atlantic and Baltic water to this area, and the fact that Atlantic water contains a predominantly ECF PFOA signature, it is furthermore reasonable to predict that water in the Baltic contains a predominantly linear-telomer PFOA signature.

According to Möller et al.⁴¹ and Pistocchi et al.,⁴² fluoropolymer industries located near the Scheldt (Netherlands), Elbe (Germany), and Rhine (Germany) river basins are important sources of PFAs directly to the North Sea, while industries located near the Oder river basin (Germany/Poland) are expected to contribute significantly to PFA concentrations in the Baltic Sea. Secondary sources from consumer products entering wastewater streams directly, or from degradation of PFOA-precursor compounds in wastewater treatment plants, may also be significant sources in this area.^{41,42} Further PFOA isomer profiling should be conducted in and around the Baltic Sea to gain a more comprehensive picture of current-use PFOA in this region. Overall, PFOA in the Norwegian Sea is reflective of historic ECF PFOA, similar to the Canary Current (Eastern Atlantic Ocean), while concentrations in the North Sea and its headwaters (e.g., the Baltic Sea) appear to have been recently influenced by manufacturing or use of telomer PFOA and associated precursors.

2009 Western Atlantic Sampling Campaign. A consistent increase in the contribution of telomer PFOA sources and total PFOA concentrations were also observed with increasing proximity to the eastern seaboard of the United States (Figures 1, 3, S-5, SI). The northwesterly flowing water of the Antilles Current contained low concentrations of PFOA (60–89 pg/L) that were predominantly of ECF origin (71–90% ECF). The low concentrations and high ECF contribution in these waters (SI Table S-3) are consistent with what was observed in the East Atlantic (Canary Current); not surprising considering that water from the Canary Current is transported west by the North Equatorial Current and into the Antilles Current. The slightly lower relative ECF contribution in the Western Atlantic may be a result of contributions from the northerly flowing Caribbean Current, although these waters were not examined in the present study. Alternatively, these differences may be a result of sampling the Western Atlantic 2

years after the Eastern Atlantic, thus allowing contemporary PFOA sources to become increasingly important.

Western Atlantic water samples 25, 28, and 29 were most likely influenced from mixing of North Atlantic water with water from both the Antilles Current and Gulf Stream, as these showed higher total PFOA concentrations (78–92 pg/L) as well as a slight decrease in ECF contribution (60–72% ECF in samples 25–29 compared to 71–90% ECF in samples 16–23). Statistical analysis of % ECF, salinity, and water temperature also revealed significant positive associations between % ECF and water temperature (r_p = 0.72, p < 0.01) and salinity (r_p = 0.79, p < 0.01), which is consistent with inputs from the Western Atlantic coastal water (substantially colder and containing lower salinity due to contributions from the Labrador current and freshwater inputs from riverine discharge) for the more northerly sampling locations (Figure S-3, SI). The Western Atlantic coastal water (samples 30–34) likely receives inputs from sources in the Eastern United States and this water showed substantially higher PFOA concentrations (154–635 pg/L) and telomer source contributions (39–52% ECF). Of the samples collected in this transect, the highest concentrations (>1.1 ng/L) and lowest % ECF (33%) were both observed in Narragansett Bay (sample 35).

PCA Analysis of Source Region Data. The results of a PCA analysis on Atlantic and North/Norwegian Sea samples indicated that samples in source regions fell into one of three distinct groups (Figure 1B). The first group (denoted by red markers in Figure 1) consisted of samples with elevated total PFOA concentrations (~250–1200 pg/L), and low to moderate historical PFOA contributions (33–68% ECF). Most samples from the Eastern and Western Atlantic fell into the second group (denoted by blue markers in Figure 1), which was characterized by low to moderate total PFOA concentrations (~30–150 pg/L), and moderate to high historical PFOA contributions (42–98% ECF). Finally, the two most northerly samples collected in the Norwegian Sea, which contained the lowest total PFOA concentrations (10 pg/L), and which were made up of almost entirely historical PFOA (92–94% ECF), comprised the last group (denoted by green markers in Figure 1). The only sample that did not fit into one of these three groups was sample 2 from the Eastern Atlantic sampling campaign (yellow triangle in Figure 1B), which displayed high total PFOA concentrations as well as high ECF contributions (~210 pg/L, 95% ECF). This may suggest a current ECF source contributing to loadings in the Bay of Biscay, but this requires further investigation. Overall, the data provide further evidence of contemporary telomer PFOA sources contributing significantly to coastal water concentrations. It is therefore a concern that contemporary PFOA manufacturing will increase the overall marine burden of PFOA in the future. Continued vigilance of reducing contemporary PFOA emissions is recommended, such as is outlined by the PFOA Global Stewardship Program⁴³ and the Strategic Approach to International Chemicals Management.⁴⁴

2005 and 2008 Greenland, Canadian Archipelago, and Bering Strait sampling campaigns. Samples from the July 2005 cruise of the *Oden*, and the September 2008 cruise of the *Amundsen* contained substantial contributions from both ECF and telomer sources (Figures 2, 3, S-6, S-7, Tables S-4, S-5, SI). Depth profiles from the 2008 cruise indicated that total PFOA concentrations reached a maximum within 100 m and then generally decreased with increasing depth, while % ECF remained fairly constant with depth (Figure S-8, SI). Only

two samples from the 2008 campaign (one collected at 400 m depth from station 301, and the other from the surface of Prince of Wales glacier, station 205) showed relative branched isomer ratios that were statistically different from the ECF standard, and % ECF could not be calculated for these samples (Tables S-10, S-11, S-12, S-13, SI).

PFOA in samples 1–3 collected off the coast of South-Western Greenland were predominantly of ECF origin (76–87% ECF, Figure 2), consistent with ECF contributions observed in the Gulf Stream and Antilles Current (60–90% ECF) but slightly less % ECF than in the Canary Current (88–97% ECF) and Atlantic-Norwegian Current (samples I and II; 92–94% ECF) (Figure 1). Considering that the West Greenland current is fed by the North Atlantic Ocean (in addition to Arctic Ocean), the high % ECF contributions (consistent with Atlantic locations) are not surprising. These results are also fairly consistent with the subsequent September 2008 sampling campaign in North Baffin Bay, where predominantly ECF contributions were observed (76–99% ECF, Figure 2). Water in North Baffin Bay originates from both the Arctic Ocean (i.e., Pacific and Atlantic water) and West Greenland Current (i.e., Atlantic Ocean water). Considering that most PFOA entering the Arctic Ocean is estimated to be from the Atlantic Ocean,³⁸ PFOA profiles consistent with Atlantic water in North Baffin Bay are not surprising. Multiple linear regressions of % ECF versus depth, longitude, latitude, and total PFOA concentration for 2008 North Baffin/Lancaster sound samples revealed no significant correlations ($p > 0.05$).

Interestingly, samples collected in 2005 from South-Western Baffin Bay (Labrador Current, Figure 2, samples 5 and 7) showed remarkably lower ECF contributions (i.e., 59–69%) than those from South-Western Greenland (collected in 2005) and North Baffin Bay (collected in 2008). Samples from South-Western Baffin Bay are likely distinct from those samples collected further east because water flows from west to east through the Canadian Archipelago, with water originating in the Pacific Ocean.⁴⁵ Very low % ECF PFOA contributions in samples from the Bering Strait (22 and 46% ECF for samples 27 and 30, respectively, collected in 2005, Figure 2) confirmed that the Pacific Ocean was influenced to a greater relative extent by telomer sources than ECF sources. The 2005 results from Bering Strait were confirmed in samples collected in the Southern Beaufort Sea (samples 25, 26; 29–43% ECF), the southern Amundsen Gulf (samples 21, 23; 17–30% ECF), and a sample collected southwest of Cornwallis Island (sample 17; 25% ECF) all from the same year.

Samples in Lancaster Sound (301, 303) were anomalous for the Canadian Archipelago, as relatively high ECF contributions were observed here (89–94% ECF; collected 2008). One possibility is that water from North Baffin flowing west into Lancaster Sound (which has been recognized as far as about Prince Regent Inlet (73°00'N, 90°30'W), but not as far as Barrow Strait⁴⁶), may contribute to the high ECF content in these few samples. Another possibility is that differences in ice cover (which was much greater in July 2005 compared to September 2008), or perhaps ice melt influenced the contribution from atmospherically deposited PFAs in the ice to the water in 2005 compared to 2008. While this requires further investigation, overall, a spatial trend of decreasing ECF contributions from east to west across the Canadian Archipelago was observed ($r_s = 0.59$, $p < 0.01$; Figure 2B).

Unlike the Arctic Ocean, which consists of water from both the Atlantic and Pacific Oceans, water in the Canadian Arctic

Archipelago is near exclusively of Pacific origin.⁴⁵ A recent model estimated that PFOA from the Pacific Ocean (originating from point sources in Japan and entering the Arctic via the Bering Strait) contributed only 2–8% (0.6–1.5 t/yr) to PFOA in the Arctic Ocean from 1991–2004.³⁸ This flux is similar to that calculated for atmospheric deposition of PFOA in the Arctic during the 1990s (~1 t/yr, based on emission of 8:2 FTOH).³⁸ Since Archipelago water is exclusively from the Pacific, and PFOA contributions from the Pacific to the Arctic (and by extension, the Archipelago) are of the same order of magnitude as atmospheric deposition, there is reason to believe that atmospheric inputs can contribute significantly to PFOA in the Canadian Arctic Archipelago. The results of our isomer profiling in the Canadian Archipelago indicate a predominantly linear signal, supporting the hypothesis of either (a) atmospheric transport of linear PFOA-precursors,^{1,20} or (b) production and consumer use of linear PFOA or PFOA-precursors in East Asian countries, emitted directly to seawater and slowly transported in marine currents. No data currently exist on the isomer profile of PFOA in Pacific seawater, thus this latter hypothesis remains tentative. However, a recent study estimated that ~53% of total PFOA measured in Tokyo Bay seawater was from a linear-telomer source,²⁸ consistent with manufacturing in this country,¹⁴ and a separate study observed a smaller proportion of branched PFOA isomers in samples with higher total PFOA concentrations, further supporting the importance of linear-telomer sources in this region.⁴⁷ When this Pacific water moves through the Archipelago and mixes with the predominantly ECF PFOA signature originating from the Atlantic, a predominantly ECF-profile is expected, as was observed in samples from west Baffin Bay (i.e., 59–69% ECF).

Statistical analysis of % ECF versus water temperature for Arctic surface samples revealed no significant correlation ($r_s = -0.19$, $p = 0.43$; SI Figure S-3). However, a weak, yet statistically significant positive correlation was observed between % ECF and salinity ($r_s = 0.47$, $p = 0.04$; SI Figure S-3). While this may simply be a function of differences in salinity between water originating from the Pacific (i.e., lower salinity) versus the Atlantic (i.e., higher salinity), it is also possible that water collected in the Archipelago is more influenced by riverine discharges, for example from the Mackenzie River, which would presumably contain PFOA derived from an atmospheric source (i.e., linear FTOH). This latter hypothesis is consistent with a recent study which suggested FTOHs as the dominant source of PFCA in dated sediment cores from two Canadian high alpine lakes, based on temporal trends and isomer analysis.⁴⁸ Taken together, these results further support the hypothesis that PFOA in the Western Arctic is a result of long-range transport and degradation of FTOHs, while water in the Eastern Arctic is resultant from slow oceanic transport of PFOA.

The current findings are also supported by the results of De Silva and Mabury,⁴⁹ in which polar bears from Ittoqqortoormiit/Scoresby Sound (East Greenland) in 1999–2001 showed higher branched PFOA content (up to 10% based on GC-MS peak areas) than bears sampled in 2002 from South-Eastern Hudson Bay, near Sanikiluaq, Nunavut (0% branched). Since East Greenland water is predominantly influenced by both Atlantic and Arctic water (Arctic seawater itself being a mixture of mostly Atlantic and some Pacific water), these bears are exposed, through the foodweb, to PFOA that is largely of ECF origin (i.e., high branched content), consistent with their

observations. The continued increase in PFOA concentrations in these bears¹⁰ is also consistent with the predicted increase in PFOA concentrations in Arctic water from slow-oceanic transport from the midlatitude Atlantic Ocean.²⁴ In contrast, marine contributions to Hudson Bay are predominantly from the Pacific⁴⁵ and riverine discharge, the latter representing an exclusively atmospheric source due to the low population density around Hudson Bay. Accordingly, water in this region would be expected to have a highly linear profile, as observed in the Canadian Archipelago, thus providing a possible explanation for the exclusively linear PFOA profile observed in polar bears in Hudson Bay.

Future Marine Burdens of PFOA. The extent to which historical ECF or contemporary telomer PFOA contributes to concentrations in remote seawater is of increasing importance as phase-outs, manufacturing controls, and alternative replacement chemistries are considered. Isomer profiling in Arctic seawater supports model predictions^{22–24} of slow marine transport of historically manufactured PFAs to the Arctic Ocean, via the North Atlantic Drift. However, contributions from telomer manufacturing predominated in the Canadian Arctic Archipelago, suggesting either direct marine transport of linear PFAs from Asia, or atmospheric transport of linear PFOA or linear PFOA-precursors. If the latter is true, atmospheric transport mechanisms may be the dominant PFOA exposure pathway for marine wildlife in the Canadian Archipelago and Hudson Bay. A similar hypothesis was presented by Armitage et al. for exposure to perfluorooctane sulfonate (PFOS) and PFOS-precursors in this area.⁵⁰

PCA analysis of the Atlantic Ocean, North Sea, and Norwegian Sea (Figure 1B), indicated that the samples with the highest total PFOA also contained higher telomer contributions. The close proximity of these samples to the U.S. Eastern Seaboard and Baltic Sea suggests significant contributions from current PFOA manufacturing and/or use in these regions. Therefore, the total oceanic burden of PFOA is expected to continue to increase, driven by ongoing emissions of telomer PFOA. Continued coastal seawater monitoring of PFOA may be a useful means of tracking the overall effectiveness of the PFOA Global Stewardship program; which aimed to reduce manufacturing facility emissions of PFOA and PFOA-precursors by 95% by 2010, and to eliminate these chemicals from emissions and products by 2015.⁴³

■ ASSOCIATED CONTENT

■ Supporting Information

Further information on sampling, extraction and analysis, along with chromatograms and isomer profiles can be found in the SI. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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