We thank Dr. Franklin for his constructive comments on our manuscript. Please find our responses below in yellow, with changes to the manuscript indicated in **bold**.

General comments

This manuscript reports on a study of the levels of perfluoroalkyl acids (PFAAs) in a Canadian Arctic ice cap. The overall aim is to establish a temporal record of the annual deposition fluxes of PFAAs in this area, roughly locate the source regions of the incoming air masses, and determine whether the PFAAs have been transported over long distances "as such" or formed in the atmosphere by transformation of precursor compounds.

Although two previous studies on these questions have been performed and reported by teams including scientists belonging to the present group of authors, this latest study represents considerable progress since (a) it covers a time-span of 38 years of deposition, compared to 10-14 years for the earlier observations; (b) the sampling approach has been improved, by drilling an ice core, rather than by horizontal collection from the sidewall of a snow pit; (c) the analytical methods were upgraded, both in terms of instrument detection limits and accuracy; (d) analysis of major anions and cations in the ice confirmed that marine aerosol inputs, hypothesized by others, are unimportant to the long-range transport mechanisms of the compounds studied. On the basis of these procedural improvements and new conclusions, I recommend publication of this multi-decadal study, after suggested minor changes as detailed below.

Specific comments on the main text

1) P1, L10: Replace "bioaccumulative" by "in some cases bioaccumulative".

Response: We have added "in some cases" before the word "bioaccumulative". Now it reads: "Perfluoroalkyl acids (PFAAs) are persistent, **in some cases** bioaccumulative compounds found ubiquitously within the environment." (P1, L10-L11)

2) P1, L12: After "transport" insert "(LRT)" since this acronym is used later in the text and should therefore be defined here, after the first occurrence of "long-range transport".

Response: We have added the acronym "(LRT)" after the first occurrence of the word "longrange transport". (P1, L12)

3) P1, L13: After "PFAAs" insert "in polar or mountainous regions" or some such phrase, since their usefulness is not globally ubiquitous.

Response: We have added "in polar or mountainous regions" after the word "PFAAs". Now it reads:

"Ice caps preserve a temporal record of PFAA deposition making them useful in studying the atmospheric trends in LRT of PFAAs **in polar or mountainous regions**, as well as understanding major pollutant sources and production changes over time." (P1, L12-L14)

4) P1, L18: Typo – "perfluorooctane"

Response: We have fixed the typo and changed the word from "perflurooctane" to "perfluorooctane". (P1, L19)

5) P1, L19: I feel that it is important to bear in mind here that the regulations and agreements were not only North American in their extent and that deposition on the

Devon Ice Cap would not be expected to be affected solely by emissions from North America, as explained later in the manuscript. The 2006 PFOA Stewardship Program, concluded by US EPA with eight leading companies in the PFAS industry, targeted the global activities of these companies pertaining to PFOA, its precursors and their longerchain homologues. Furthermore: (a) PFOS was added in 2009 to the global Stockholm Convention on Persistent Organic Pollutants; (b) PFOA is now restricted under the European Union's REACH Regulation as a Substance of Very High Concern; (c) PFOS is a Priority Substance under the E.U. Water Framework Directive; etc.

Response: We thank Dr. Franklin for making this point. It is true that we explain this later in the manuscript, but we should make it clearer in this sentence in the abstract. We have changed the sentence to include the word "international" and not just "North American". Now it reads: "Our results demonstrate that the PFCAs and perfluorooctane sulfonate (PFOS) have continuous and increasing deposition on Devon Ice Cap, despite recent North American **and international**

regulations and phase-outs." (P1, L18-L20)

6) P1, L20: I would replace "emission and use" by "manufacture, use and emission". Response: We have replaced "emission and use" with "manufacture, use and emissions". Now it reads:

"We propose that this is the result of on-going **manufacture, use and emissions** of these compounds, their precursors and other newly unidentified compounds in regions outside of North America." (P1, L20-L22)

7) P2, L3: After "(PFAAs)" insert ", a sub-group of PFASs," Response: We have inserted ", a sub-group of PFASs" after "(PFAAs)". Now it reads: "Perfluoroalkyl acids (PFAAs), **a sub-group of PFASs**, are persistent contaminants that are ubiquitous in the environment." (P2, L3-L4)

8) P2, L9: It would be preferable to say "This can occur through the atmosphere, in the gaseous or particle phase (including with marine aerosols), or via oceanic water currents". I believe that the marine aerosol hypothesis was first postulated in the peer reviewed literature in the paper by Prevedouros et al (2006) cited in this manuscript, although – to my knowledge – it first originated in Poster ENV016 by Robert L. Waterland et al. at the 2005 FLUOROS Symposium in Toronto, so perhaps some credit is due here.

Response: We thank Dr. Franklin for his suggestion for reformatting this sentence and who to properly cite for this fact. We have now cited Prevedouros et al (2006) and the sentence now reads:

"This can occur through the atmosphere, in the gaseous or particle phase (including with marine aerosols), or via oceanic water currents (Prevedouros et al., 2006). " (P2, L9-L10)

9) P2, L11: Replace "These compounds" by "These PFAAs", to avoid any confusion with the last-mentioned nouns, i.e. the PFAA precursors.

Response: We have changed the word "compounds" to the word "PFAAs". Now it reads:

"These **PFAAs** are environmentally persistent and longer chain acids (>6 carbons) have a tendency to bioaccumulate and biomagnify in food webs." (P2, L12-L13)

10) P2, L14: It would be preferable to use acronyms inspired by those recommended by Buck et al. (2011), namely (N-alkyl) FASAs and FASEs, since (for example) elsewhere in this manuscript perfluorooctane sulfonamide is abbreviated to FOSA (P4, L27 and other occurrences).

Response: We have changed the acronyms from "NAFSAs/NAFSEs" to (N-Alkyl) FASAs/FASEs, to avoid any confusion with acronyms throughout the paper.

11) P2, L14: To avoid any confusion with fluids used for transferring heat without any change of phase (which never constituted an important market sector for CFCs), I would refer here to "fluids used for refrigeration or air conditioning" : : : if it is necessary to refer to them at all. Indeed, some CFC replacements (hydrochlorofluorocarbons and hydrofluorocarbons) used in such applications (as well as for polymeric foam blowing or as solvents) have been shown by laboratory studies to degrade in the atmosphere to give trifluoroacetic acid or, more rarely, pentafluoropropionic acid, but these shortest chain PFCAs, although present in the ice samples, are not discussed in the present manuscript anyway. So it is probably sufficient to restrict the discussion on precursors to FTOHs, FASAs and FASEs.

Response: We thank Dr. Franklin for this great comment. Since these CFC-replacements will be discussed in a separate paper, we have decided to remove any reference to the "CFC-replacements" or "heat-transfer fluids" from this discussion. This sentence now reads: "In the atmosphere, volatile and semi-volatile precursors such as fluorotelomer alcohols (FTOHs) and N-alkyl perfluoroalkane sulfonamides/sulfonamidoethanols ((N-Alkyl) FASAs/FASEs) undergo oxidation in the gas phase to form PFAAs (D'eon et al., 2006; Ellis et al., 2004; Young and Mabury, 2010)." (P2, L14-L16)

12) P2, L20: See comment above on marine aerosols.

Response: Since the main focus of this paper is on atmospheric inputs of PFAAs and not oceanic inputs, we have decided to remove the short paragraph on marine aerosols, for better clarity. The paragraph and associated references we removed from the introduction reads as follows: "Further transport can occur via ocean currents (Armitage et al., 2006, 2009a, 2009b) and marine aerosols (McMurdo et al., 2008). PFAAs are highly acidic, surface-active compounds, usually present as anions in the aqueous phase under environmental conditions (Cheng et al., 2009). These surface-active compounds will concentrate at the air-water interface and are therefore expected to be in the sea surface microlayer (SSML) and to be present in marine aerosols (Lewis and Schwartz, 2004)." (P2, L20)

13) P3, L9-10: The 15.5-meter ice core corresponded to 38 years of deposition, representing on average about 0.4 m per year. But the core was first separated into 1-meter sections, representing therefore some 2.5 years each. It would be useful to give a brief description of how these lengths were sectioned into discrete samples corresponding to individual years, without loss of critical fragments.

Response: We thank Dr. Franklin for bringing this up and we have added a paragraph into Section S1 of the SI, describing how the ice core was sectioned and bottled into individual years, with minimal loss and contamination. The paragraph reads as follows:

"The 15.5-meter ice core was separated and packaged into 1-meter sections for transport. Extensive care was taken in handling the ice core to avoid any introduction of

contamination that could compromise the trace analysis. During collection process, handling, and sample preparation, no products containing fluoropolymer coatings came into contact with the ice cores. Additionally, care was taken to scrape the potentially contaminated outer "rind" of the core sections, using only the inner uncontaminated ice for analysis. Depths corresponding to calendar years were determined as described above. Using this data, the dates for each 1-meter section were determined. For sectioning the 1meter ice cores into the equivalent years, we removed each 1-meter section from the packaging, and placed the firn and ice pieces onto aluminum foil, cleaned with methanol. We cut the firn or ice pieces at the depth that corresponded to each year with a pre-cleaned saw and then added the sectioned firn and ice for one year into a labeled pre-cleaned polypropylene bottle. Using the aluminum foil underneath the firn and ice pieces, we were able to easily pick up the foil and pour the firn and ice pieces into the labeled bottle, with minimal loss." (P4-P5)

14) P4, L27 and 29: To avoid any confusion, the use of the terms "long-chain" and "shortchain" when referring to PFAAs here and elsewhere (e.g. Supplementary Information, P10) should comply with OECD recommendations. See the Buck et al (2011) citation, page 517.

Response: We thank Dr. Franklin for bringing up the use of these terms in this comment. It is difficult for our approach in this paper to use the terms "long-chain" and "short-chain" in accordance with the OECD described in Buck et al (2011), as we are defining these terms in this paper in terms of source/mechanism of formation. However, to try and avoid confusion, we have reworded sentences where we either avoid using the term "short or long" altogether, or define the PFAA chain-lengths that we are referring to for that individual sentence. In this first instance (P4, L29-L31) we replaced "long-chain PFAA analysis" and "short-chain PFAA analysis" with "**first** PFAA analysis" and "**second** PFAA analysis" and defined the chain-lengths we analyzed in brackets.

15) P6, L23: Typo – Longyearbyen (also in Table S12). Response: We have corrected "Longyearbreen" to "Longyearbyen". (P6, L27 and Table S12)

16) P6, L24: What is meant here by "short-chain PFCAs"? Response: We have removed this sentence. (P6, L28)

17) P7, L14: What was "unusual"? The PFAA concentrations, fluxes, or homologue profiles? Response: We thank Dr. Franklin for asking about this point, as using the word "unusual" is not clear in this sentence. We are referring to the high PFOS flux that was observed in 2013. To make the sentence clearer, it now reads:

"Because of **the high PFOS flux observed** in 2013, we also examined this year to identify any transport anomalies, but found both years (1994 and 2013) to be comparable." (P7, L11-L13)

18) P8, L3: Replace "more than" by "at least".

Response: We have replaced the words "more than" with "at least". Now it reads: "Temporal trends of shorter-chain PFCAs (C2 – C4) will be discussed separately, so this section will focus solely on PFCAs with **at least** five carbons." (P8, L2-L3) 19) P8, L13-14: Although Plassmann et al. (2011) did indeed state that "During melt, the timing of a chemical's release from the snowpack depends on its water solubility and its sorption to the surface of snow crystals or particles present in the bulk snow", for the PFAAs they discussed elution during melting more in terms of chain length and affinity for snow-grain surfaces or particles than of solubility.

Response: We thank Dr. Franklin for this comment. It is true that Plassmann et al. (2011) mention not just water solubility but also chain length in their PFAA elution discussion. We have changed this sentence to include these other factors of PFAA elution. The sentence now reads: "One study has examined elution behaviour of PFAAs from a melting snowpack and found that elution of PFAAs is driven by a number of factors including water solubility in the snowpack, **PFAA chain length, and sorptive capacity of the snow grain surface** (Plassmann et al., 2011)." (P8, L12-L14)

20) P9, L7-8: The references cited refer to animal biota. It would be useful to add one or more references for human blood, e.g. from the NHANES studies (Calafat and coworkers).

Response: We thank Dr. Franklin for making this good point and for offering a reference suggestion. We have added Calafat et al. (2007) and Olsen et al. (2003) as references to human serum and changed the words "human blood" to "human serum". The sentence now reads: "This is evident in temporal trend analysis in Canada and the U.S. such as in human serum, freshwater fish, and non-migratory birds, which do not show much of a decline in PFCAs from 1990s to 2012 (Braune and Letcher, 2013; Calafat et al., 2007; Gewurtz et al., 2016; Olsen et al., 2003)." (P9, L12-L14)

21) P9, Figure 2: It does not seem reasonable to label the right-hand ordinate axes "emissions". The figures refer to production tonnages of polymer products, which may never be exposed to the environment in such a manner that any non-polymeric trace components may leach out or exude.

Response: In response to comment 22, we have removed the production data, which means there is no right-hand axis now. (P10, Figure 2)

22) P9, Figure 2 and ensuing paragraph: However, just comparing ice-cap deposition fluxes of PFOA or PFNA to production volumes of various fluoropolymers makes no sense when one takes into account the following facts: (a) much PTFE and PFNA (and no doubt also FEP and PFA) is manufactured by the suspension polymerization process, which does not require the use of fluorinated surfactants as processing aids, unlike the emulsion (or dispersion) process; (b) PFOA and PFNA were phased out and replaced by alternative processing aids by all the major manufacturers in the developed countries long before 2015, in order to meet the objectives of US EPA's 2006 PFOA Stewardship Program. Useful quantitative information on production volumes for different fluoropolymer types could no doubt be found, if required, in IHS Markit's 2016 Economics Handbook Chemical report on Fluoropolymers (https://www.ihs.com/products/fluoropolymerschemical-economics-handbook.html); (c) fluoropolymer manufacturers have taken steps to drastically reduce the levels of fluorinated processing aids in their final products, for those fluoropolymers made by the dispersion process; (d) as discussed in this manuscript, environmental emissions of PFOA

and PFNA are not related solely to the manufacture and use of (certain) fluoropolymers, but also arise from the degradation of precursors, such as FTOHs and derivatives thereof. I would therefore strongly recommend deleting the misleading fluoropolymer production curves from Figure 2.

Response: We thank Dr. Franklin for this significant comment regarding Figure 2. We understand how plotting production volumes of fluoropolymers might not be the best representation of what we were trying to explain, and so we have removed this data from Figure 2. What we were trying to do was compare production volumes from Wang et al. (2014) (which we could openly access) to PFOA and PFNA to just get an idea of how production volume is increasing in China, but not in the other previous production countries (Europe, Japan, USA). And to add to our discussion about how the ongoing deposition of these PFAAs is likely also coming from China and not just the other countries historically known for manufacturing these fluoropolymers. But again, as Dr. Franklin notes, this fluoropolymer data is not the best representation. Ideally, it would be very beneficial to compare quantitative data on production volumes for different fluoropolymer types to our PFAAs, but information such as this is not open access, including the IHS Markit's 2016 Chemical Economics Handbook report on Fluoropolymers that Dr. Franklin recommends, which is unfortunately very expensive to purchase. To avoid misrepresentation, we have removed this information from Figure 2. (P10)

23) P10, L1 and 2: Use "PFASs" as the plural of "PFAS".

Response: We have corrected this so that when we refer to the plural of "PFAS", it is now written as "PFASs". (P10, L5-L6)

24) P10, L18-19: The anomalous value of 80 ng m-2 yr-1 is indeed plotted for the year 2012 in Figure 3, but it is listed in Table S11 for 2013.

Response: We thank Dr. Franklin for pointing this error out. That was an error on our part in plotting the data in terms of both depth and year. We have fixed this in figure 3, which now shows the high PFOS flux for the year 2013, and have made sure that we refer to 2013 throughout the paper when discussing the 80 ng m-2 yr-1 anomalies. (P11, L12) (P12, Figure 3)

25) P10, L22-23: "This suggests FOSA is not the primary source of PFOS to the Devon Ice Cap". I do not feel that the lack of correlation is very significant. If there are several distinct spatial pathways for transport of air masses from sources regions to the Devon Ice Cap, the degree of atmospheric transformation of FOSA along the trajectory (for which the lifetime is not discussed in this manuscript) may vary with the individual pathway, so that the FOSA/PFOS ratio on arrival may depend not only on the corresponding ratio in the source region, but also on the pathway followed. In any case, it is reasonable to assume that there are sources of PFOS ("as such") that are quite independent of FOSA or other sulfonamido derivatives.

Response: We thank Dr. Franklin for this insightful and important comment. We have removed the phrase "This suggests FOSA is not the primary source of PFOS to the Devon Ice Cap" and replaced it with:

"Therefore, it is reasonable to assume that there are sources of PFOS that are independent of FOSA or other sulfonamido derivatives." (P11, L15-L17)

26) P11, L8-9: If POSF-based products were replaced by PBSF-based ones after 2002, is it not surprising that PFBS was detected in the ice samples only in two recent years? Does this not warrant a comment?

Response: We thank Dr. Franklin for making an excellent point here. We have added a comment about PFBS detection in this paragraph, as well as a short statement about how our understanding of the LRT mechanisms of these PFASs is incomplete and needs further study. This sentence reads:

"This is interesting because we actually detected quantifiable levels of PFBS in the ice core in two recent years, and so our understanding of LRT of these PFASs is incomplete and warrants further research." (P13, L1-L3)

27) P12, L8: "The decline of the production of the precursor FOSA by 3M". Should this be interpreted as meaning the "decline of precursor POSF production, and hence of all C8 sulfonamido derivatives, including FOSA"?

Response: We thank Dr. Franklin for suggesting clearer phrasing. The sentence has been reworded:

"The decline of precursor POSF production, and hence of all C8 sulfonamido derivatives, including FOSA, by 3M..." (P13, L7-L8)

28) P12, L28, 29, 30 and 31: "2013" or "2012"?

Response: We thank Dr. Franklin for pointing out this error. The high PFOS flux was in 2013, which is correctly specified in this paragraph. We have fixed this error elsewhere, in Figure 3 and P11, L12 where it stated and showed 2012.

29) P13, L6: Change acronyms for NAFSEs and NAFSEs.

Response: We have changed the acronyms from "NAFSAs and NAFSEs", to "(N-Alkyl) FASAs/FASEs". (P14, L6)

30) P13, L17: Typo – Longyearbyen

Response: We have corrected "Longyearbreen glacier" to "Longyearbyen, Svalbard". (P14, L17)

31) P13, L31: Replace "compound" by "homologue".

Response: We disagree with Dr. Franklin here. In this paragraph we are referring to the pairs of PFCAs as "homologues" and the n:2 fluorotelomers as "compounds". Therefore, on P14, L31, we are referring to the 8:2 FTOH "compound", not "homologue".

32) P14, L13: I do not feel that it has been demonstrated that direct transport of PFOS and other PFSAs to the ice cap is unlikely.

Response: We thank Dr. Franklin for making this important point. We have changed the language of this sentence to indicate that direct transport may act as a minor source of PFAAs to the ice cap. The sentence now reads:

"Thus far, evidence **supports** indirect formation of PFAAs in the atmosphere from volatile precursor compounds **as the major source**, indicating that direct transport is **likely a minor** source of PFAAs to the ice cap." (P15, L12-L13)

33) P14, L14: What is meant by "and to the atmosphere into the ocean", since deposition from the atmosphere to any oceanic system has already been mentioned in the same sentence?

Response: We thank Dr. Franklin for bringing this up. We have removed "and to the atmosphere into the ocean" from the sentence as it is a repetitive. Now it reads: "Atmospherically formed PFAAs can deposit to any terrestrial or oceanic system. **Those PFAAs deposited to oceans can** re-enter the atmosphere **in the form of** marine aerosols (McMurdo et al., 2008)." (P15, L13-L15)

34) P14, L14-15: "and then re-enter the atmosphere from oceanic currents and marine aerosols". Are the fully ionized PFAAs likely to partition from the ocean to the atmospheric compartment other than in marine aerosol particles?

Response: We thank Dr. Franklin for noting this error. We have rephrased the sentence as described above in the response to comment 33 to indicate that only marine aerosols are reentering the atmosphere and have included the reference McMurdo et al. (2008). The sentence now reads:

"Atmospherically formed PFAAs can deposit to any terrestrial or oceanic system. Those PFAAs deposited to oceans can re-enter the atmosphere in the form of marine aerosols (McMurdo et al., 2008)." (P15, L13-L15)

35) P14, L16-17: Insert "PFAAs" between "and" and "may" (i.e. when on aerosols, they are no longer "gas-phase").

Response: We have added the word "PFAAs" between "and" and "may" for further clarity. The sentence now reads: "Gas-phase PFAAs will deposit through wet or dry deposition and **PFAAs** may also be transported on aerosols (Thackray and Selin, 2016)." (P15, L17)

36) P15, L11: Typo – Arctic

Response: We have corrected "Artic" to "Arctic". (P16, L13)

37) P15, L13 and 14: Change "concentrations" to "fractions" or "proportions"?

Response: We have changed "concentrations" to either "concentration fractions" or just "fractions". The sentence now reads:

"Molar concentration **fractions** of PFAAs on the ice cap differed from ocean PFAA **fractions**, with higher molar concentration **fractions** of PFBA and PFNA, and lower molar concentration **fractions** of PFSAs found on Devon Ice Cap." (P16, L15-L17)

38) P15, L15: I do not understand the claim that "indirect sources are of importance for Arctic deposition" since PFHxS was not found on the ice cap. Does "indirect sources" refer to ocean transport?

Response: We thank Dr. Franklin for this comment. We have clarified these couple sentences to explain why PFHxS is an important marker, and how it adds to our discussion that marine aerosols are not a major source of PFAA deposition to the Arctic environment. We also added MacInnis et al., (2017) as a reference, as they provide a more detailed explanation on the significance of PFHxS. These sentences now read:

"As described by MacInnis et al. (2017), PFHxS can act as a marker for direct transport. The absence of PFHxS on the ice cap is further confirmation that marine aerosols are not a significant source for PFAA deposition to the Arctic environment." (P16, L18-L20) 39) P15, Figure 5: Are the Devon Ice Cap values taken solely from the present study, or are previous measurements included (for 2005, at least)?

Response: The Devon Ice Cap values in Figure 5 are from the present study. We have now indicated this in the description for Figure 5, to avoid confusion. The description now reads: "Molar concentration fraction of sum of PFAAs on the Devon Ice Cap (from the current 2015 ice core collection) compared to levels in the Canadian Arctic Archipelago (Benskin et al., 2012), Arctic Ocean (Benskin et al., 2012; Cai et al., 2012b), North Atlantic Ocean (Zhao et al., 2012), and North Pacific Ocean (Cai et al., 2012b) in 2005 and 2010." (P17, L2)

40) P16, L8: See previous comment on "heat transfer fluids". Response: We have removed the words "heat transfer fluids". The sentence now reads: "The degradation of many PFCA precursors forms both PFCA and HF." (P17, L10)

41) P17, L10-11: This sentence needs some rephrasing. What seems obvious is that there are ongoing emissions of many PFAAs and/or their precursors and that they arrive through the atmosphere as far as the Devon Ice Cap. The "use" of PFAAs is not so evident. Long-chain ones and their precursors are probably still used in the less-developed countries, while the short-chain homologues have largely replaced them in the developed world. What is intended by "likely new unidentified compounds" if they are not included in "PFAA precursors"?

Response: We thank Dr. Franklin for this important comment. We understand how this sentence can be confusing. We've rephrased this sentence to read:

"Continuous and increasing deposition of many PFAAs on Devon Ice Cap was observed, suggesting on-going emission and use of these **PFAAs and their precursors in areas such as North America and Eurasia.**" (P18, L27-L28)

42) P17, L16: After "PFAAs" insert "in the atmosphere".

Response: We added "in the atmosphere" after "PFAAs". The sentence now reads:

"Use of major ion tracers provided new information regarding the transport of PFAAs **in the atmosphere**, confirming that marine aerosol inputs are unimportant and suggest a relationship with mineral dust." (P18, L30-L32)

43) P20, L16: Perhaps "ECCC" should be spelled out for those readers not familiar with the acronym. Also, it would be useful to provide a web-link, as in the Supplementary Information.

Response: We have changed "ECCC" to "Environment and Climate Change Canada" in the reference and provided a web-link. We also corrected this in the SI. (P22, L2-L3)

44) P21, L28: Typo – Kallenborn Response: We have corrected "Kallerborn" to "Kallenborn". (P23, L8)

45) P24, L5-6: This paper has now been published in Atmospheric Chemistry and Physics, so the citation should be replaced by that of the final published version.

Response: We have updated this citation: "Thackray, C. P. and Selin, N. E.: Uncertainty and variability in atmospheric formation of PFCAs from fluorotelomer precursors, Atmos. Chem.

Phys., 17(7), 4585–4597, doi:10.5194/acp-17-4585-2017, 2017." (P25, L20-L21)

46) P24, L7: It would be useful to provide a web-link, as in the Supplementary Information. Response: This citation has been updated with a web-link. (P25, L23-L24)

Specific comments on the Supplementary Information:

47) P8, Table S4: The concentration units should be indicated. Response: We have added the concentration units of ng/L to Table S5. (P9)

48) P12, first line of text: Since FOSA is neither a PFCA nor a PFSA, "including" should be replaced by "as well as" or "together with".

Response: We have replaced the word "including", with "as well as". Now it reads: "A number of PFCAs and PFSAs, **as well as** FOSA were detected on the Devon Ice Cap." (P13)

49) P17, penultimate line: "albeit with some subtle differences".

Response: We have corrected the sentence. It now reads:

"The data sets generally agree albeit **with** some subtle differences (i.e. the mean +/- uncertainty overlap between the three studies), the exception being PFOS." (P18)

50) P19: On this right-hand page, the figure does not extend until the year 2015 and data for some PFCAs (e.g. PFNA) appear to be missing even for 2014. Similarly, on the left-hand panel (P18) some data (PFOA, PFHxA) listed in Table S10 for 2015 are not plotted on the chart.

Response: We have corrected these two plots in figure S2. (P19-P20) Both plots now include the year 2015 and the correct data presented in Table S11.

51) P21, Table S12: Would not this table be more readable if the concentrations were expressed in pg/L, as in Tables S8 and S9?

Response: The Reviewer makes a good point. We have changed the concentrations in Table S13 to pg/L instead of ng/L. (P22)

52) P23, Table S13 and P24, Table S14: Does N/A mean "not available" or "not applicable"? Response: The N/A means "not available". We have added this to the footnotes in Tables S14 and S15. (P24-P25)

53) In Table S14, does "non-US" include Canada?

Response: Non-US operations in Table S15 refer to the companies located in Europe and Asia. Canada is included in Table S14. We have added "Non-U.S. and Non-Canadian operations" to the heading for Table S15 to make it clearer. (P25)

54) P25, Table S15: The title should explicitly include FOSA, which is not a PFAA homologue.

Response: We have included "and FOSA" to the title of Table S16. (P26) We have also added "as well as FOSA" to Tables S20 and S21. (P33-P34)

55) P33, 2nd Kwok reference: Typo – Kallenborn Response: We have corrected the typo "Kallerborn" to "Kallenborn". (P37)

References

Armitage, J., Cousins, I. T., Buck, R. C., Prevedouros, K., Russell, M. H., Macleod, M. and Korzeniowski, S. H.: Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources, Environ. Sci. Technol., 40(22), 6969–6975, 2006.

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We thank the reviewer for their thoughtful comments on our manuscript. Please find our responses below in yellow, with changes to the manuscript indicated in **bold**.

This is an interesting effort to measure and discuss the PFAS concentrations and fluxes at a multidecadal scale from an ice core in the high arctic. The topic is of great importance, and the data set may be unique. I disagree with an important fraction of the discussion (see below). Briefly, important issues are, i) a better assessment of discussion of blanks, ii) a complete description of the data set, iii) a different discussion of air mass back trajectories, iv) a re-evaluation of the processes responsible to transfer PFAS from the air to snow, including the post depositional processes and the assessment of the role of sea-salt aerosol. Therefore, I think that this manuscript needs major revision before it can be accepted.

1. Page 4, line 5. The assessment of blanks is weak. Blanks were performed for the cartridges, but this only covers the potential contamination during analysis in the laboratory. There is no assessment of field blanks, as samples could be contaminated during sampling, handling, transport, and sectioning. This needs some comments.

Response: We thank the Reviewer for their comment concerning the assessment of blanks. We agree with the Reviewer that an ideal field blank would be able to provide background contamination contributed by the ice core extrusion and sectioning. However, the unique procedure of extruding an ice core does not provide a straightforward approach to capturing blank contamination caused by such sampling. A literature search of other ice core sampling studies confirms that field sampling blanks to encompass the sampling acquisition and handling are not typical (Table 1).

Location	Ice Core Sampling	Blanks	Analytes	Reference
Southeast	90 m core	No field blanks;	$CH_3SO_3^-, Cl^-, SO_4^{2-},$	(Iizuka et al.,
Greenland		only reagent lab blanks.	NO_3^- , Na^+ , Ca^{2+} , NH_4^+ , Mg^{2+} , and K^+	2018)
Svalbard,Norway	5 m core using a	No field blanks;	Amino acids and	(Barbaro et al.,
	Kovacs drill	only reagent lab	chlorophyll A	2017)
		blanks.		
Siberian Altai	139 m core	No field blanks;	Mercury	(Eyrikh et al.,
		only reagent lab		2017)
		blanks		
Svalbard,	125 m core using	No field blanks;	Elemental carbon	(Ruppel et al.,
Norway	a PICO drill	only reagent lab		2017)
		blanks		
Akademii Nauk	129 m	No field blanks;	Aromatic acids	(Grieman et
ice core (Siberia)		only reagent lab	(vanillic and para-	al., 2017)
		blanks	hydroxybenzoic	
			acids)	
Greenland	87 m and 213 m	No field blanks;	Methanesulfonate,	(Maselli et al.,
		only reagent lab	Br, Cl, Na, Ca, S,	2017)
		blanks	Ce, and Pb	
European Alps	10 m	No field blanks;	Polybrominated	(Kirchgeorg et

Table 1. Literature Survey	on Use of Blanks in Recent Ice Core Sampling

		only reagent lab	diphenyl ethers,	al., 2016)
		blanks for	perfluorinated	
		sample	acids, polyaromatic	
		extraction	hydrocarbons	
East Antarctica	1196 m core	No field blanks;	Organochlorine	(Bigot et al.,
		only reagent lab	pesticides	2016)
		blanks		
Eastern	101 m using	No field blanks;	Polychlorinated	(Pavlova et al.,
Switzerland	electromechanical-	only instrument	biphenyls	2015)
	thermal drill	blanks		
Tibetan Plateau	22 m	No field blanks;	Perfluorinated	(Wang et al.,
		only reagent	acids	2014)
		blanks for		
		sample		
		extraction		

We have amassed an annual data set on field blanks (HPLC grade water) transported and exposed to the atmosphere in the Arctic location Resolute Bay, Nunavut since 2010. These samples are shipped back to the lab, extracted and analyzed with methods analogous to the ice samples and compared to the same HPLC grade water stored in the lab. These results indicate that the environmental exposure and shipping do not contribute to PFAS background contamination. We have included tables of this data in the SI (Table S4a-S4b) and added to the main text:

"Previous results from field blanks (HPLC grade water) transported and exposed to the atmosphere in the Canadian Arctic (Resolute Bay, Nunavut) have indicated that the environmental exposure and shipping do not contribute to background PFAS contamination. We have amassed an annual data set on these field blanks (Table S4a-S4b)." (P4, L4-L6, Tables S4a-S4b).

We also have some key observations that suggest PFAS background contamination is not compromising our results in this study. We have added text to the manuscript to highlight the measures taken to avoid PFAS contamination such as outfitting the sampling team in PFAS-free apparel, not using polytetrafluoroethene or any other fluorinated polymers during sampling, shipping and handling, rinsing and cleaning all sampling and sample handling equipment with methanol. We've also specified that the Kovacs ice coring drill bit is stainless steel for those unfamiliar with ice coring. For PFAS analysis, the most commonly reported blank contaminant is PFOA arising from polytetrafluoroethene (PFTE) polymers. Our analysis of PFOA in the samples have concentration that are much lower than other ice core analyses suggesting that background contamination was minimal. Any systematic bias encountered through background contamination would not impact the temporal trends.

The text we added to the manuscript now reads:

"Extensive measures were taken to avoid PFAS contamination during both sample collection and sectioning (i.e. PFAS-free apparel and equipment, methanol-rinsed sampling tools and equipment)." (P3, L4-L6) 2. Page 5, line 13. As I understand the back trajectories provided by Hysplit, there is an increasing uncertainty for longer time periods. While the 48 hours back trajectories are reliable, there is a huge uncertainty for 10 day back trajectories. I suggest to shorten the back trajectories and discuss the uncertainties.

Response: We thank the Reviewer for this important comment regarding back trajectory analysis uncertainty. It is standard to run 10-day back trajectories when subsequently running a residence time analysis, which greatly reduces the uncertainty in any one pathway (see (Criscitiello et al., 2016) and references therein). If the back trajectory run-time is shortened prior to residence time analysis, this often disregards the atmospheric residence time of the species of interest, resulting in erroneous (incomplete) scaled air mass transport densities that cluster around the trajectory endpoint (ice core site, in this case). In numerous earth science applications, 10-day back trajectories are the standard. For example; (Harris and Kahl, 1994; Huang et al., 2009; Kulshrestha and Kumar, 2014).

In addition to current peer-review literature, we base our methods on discussions contained in the following two books: (1) "Lagrangian Modeling of the Atmosphere" (Lin et al., 2013), which describes in detail why a back trajectory length of 10 days is ideal for such applications, and (2) "Intercontinental Transport of Air Pollution" (Stohl, 2004), which discusses specifically why 10-day back trajectories are used when investigating long-range transport of pollutants to the Arctic.

3. Page 6, line 5. Report and discuss the method for dating the subsamples from the ice core and determining the annual snow accumulation.

Response: We thank the Reviewer for this suggestion. We have indicated in this paragraph where more detail can be found on the ice core dating and have provided a sentence explaining how annual snow accumulation was determined. These sentences read:

"The dating of the ice core itself is discussed in more detail in the SI (section S1). Annual snow accumulation was determined by measuring the length of the annual ice core sections. Annual snow accumulation was calculated as $0.15 - 0.64 \text{ m yr}^{-1}...$ " (P6, L7-L9)

4. Page 6, line 15. "The most: : :." This sentence needs a reference or justification. Response: We thank the Reviewer for pointing this out. The most straightforward identification of seasonal maxima is in ice cores from the summit of the ice cap. We have added in the reference, (Legrand and Mayewski, 1997). Legrand and Mayewski say that accurate ice dating is based on visual stratigraphy, oxygen isotopic ratios of the ice, and electrical conductivity measurements in areas of high accumulation. The sentence now reads:

"The most **straightforward** temporal record of atmospheric deposition is obtained at the summit of an ice cap **(Legrand and Mayewski, 1997)**;" (P6, L22-23)

5. Page 6, line 21: : :. Compare as well with concentrations and fluxes from maritime Antarctica (Casal et al. EST 2017). Response: As per the Reviewer's suggestion, we have added PFAA concentrations from Casal et al. (2017) to Table S13 in the SI (P22) and have referenced Casal et al. (2017) in this paragraph (P6, L27-L28).

6. Section 3.1 I suggest to include one or two figures with the patterns, concentrations or fluxes, and extend the discussion. There are some differences in the patterns reported for snow (fresh and/or accumulated) and it is not clear how the results shown here fit with

previous results. For me, the major contribution of this manuscript is the data set of the measurements, much more important than the modelling, however, the paper does not reflect this.

Response: We thank the Reviewer for this comment. Section 3.1 is meant to just be a short discussion on the PFAA concentrations detected on Devon Ice Cap for this study, whilst comparing these measurements to previous studies, particularly the previous two Devon Ice Cap studies. We believe it is important to include a section discussing what has previously been done/measured and how our current results compare. To respond to this Reviewer's comment, the rest of the sections in the paper (sections 3.3 to 3.7) do indeed discuss our measurement data set, where we include multiple figures illustrating fluxes and patterns, among other topics.

7. Page 7, line 10. Provide information for the other years.

Response: As described above and in Section 3.2, we calculated back trajectories for only 2 years to determine whether the unusual PFAA observations of 2013 were caused by a transport anomaly. Preliminary back trajectory analyses that we conducted showed minimal variation from year to year. The year 1994, modeled in Figure 1, was our typical year for comparison, which we used as our baseline, compared to the Meyer et al., 2012 paper. The back trajectory analyses between both their study and our study showed very similar results. We have added in text to section 3.2 to explicitly say this. It now reads:

"The year 1994 was selected to compare to previous trajectory analyses conducted by Meyer et al, and showed similar results." (P7, L10-L11)

8. Figure 1 and page 7. I don't agree with the discussion and conclusions for the results shown in figure 1. There is a very weak evidence for source regions in part of Asia, first, due to the uncertainty of the analysis, and secondly, because the signaled regions have a very low population. Figure 1 shows that the Arctic ocean (ice covered or not) may be the main source regions. I wonder if specific ice-influenced photochemistry may affect the formation of the targeted compounds.

Response: It is not clear what type of ice-mediated photochemistry the Reviewer is referring to. Perhaps the Reviewer is referring to enhanced PFAA formation from precursors? There is currently no evidence in literature for ice-mediated PFAS formation to warrant speculative discussions. However, the most thoroughly studied mechanisms for producing PFAA from atmospheric precursors, are presented in the discussion with supporting data to postulate sources of PFAAs in this remote ice cap including the measured temporal deposition profiles, known production inventories, air mass transport density analysis, PFAA molar flux ratios of homologue pairs, major ion tracers, and previous modeling studies on air mass transport (see response to comment 2). We have added a sentence to section 3.7 to warrant a focus on this subject for future work:

"The role of ice in the formation of PFAAs from precursors is currently unknown and future work should focus on ice-mediated PFAA formation." (P18, L3-L4)

9. I would suggest to try to correlate the concentrations and fluxes with the extension of the arctic ice cap.

We thank the Reviewer for this innovative suggestion. We have correlated the annual PFAS deposition fluxes with minimum Arctic sea ice extent and sea ice area. The results of the correlations are now mentioned in the text and reported in the SI:

"Additionally, correlations between annual PFAS deposition and Arctic sea ice minimum were calculated (NSIDC, 2017) (Table S22). If marine aerosols were a major source of PFAS to the ice cap, then a negative correlation between annual sea ice extent and deposition would be expected, but the majority (12 of 14) showed a positive correlation." (P16, L22-L25)

Table S22. Coefficients of determination (R²) and statistical significance (p) between PFAS
deposition and Arctic sea ice extent and area. Sea ice time series are based on
SMMR/SMM/I satellite observations. The slope sign is indicated as either positive (+) or
negative (-) for each PFAA compound. Correlations are ranked in terms of significance by
purple>blue>orange.

	Sea Ice Extent	Sea Ice Area	Slope Sign (+/-)
	$R^2 = 0.047$	$R^2 = 0.050$	
PFPeA	p=0.2088	p=0.1959	+
	$R^2 = 0.217$	$R^2 = 0.215$	
PFHxA	p=0.0048	p=0.0050	+
	$R^2 = 0.295$	$R^2 = 0.295$	
PFHpA	p=0.0007	p=0.0007	+
	$R^2 = 0.106$	$R^2 = 0.114$	
PFOA	p=0.0559	p=0.0470	+
	$R^2 = 0.183$	$R^2 = 0.199$	
PFNA	p=0.0104	p=0.0073	+
	$R^2 = 0.129$	$R^2 = 0.142$	
PFDA	p=0.0339	p=0.0258	+
	$R^2 = 0.161$	$R^2 = 0.169$	
PFUnDA	p=0.0168	p=0.0140	+
	$R^2 = 0.058$	$R^2 = 0.067$	
PFDoDA	p=0.1648	p=0.1334	+
	$R^2 = 0.030$	$R^2 = 0.033$	
PFTrDA	p=0.3172	p=0.2938	+
	$R^2 = 0.007$	$R^2 = 0.017$	
PFOcDA	p=0.6437	p=0.4618	-
	$R^2 = 0.113$	$R^2 = 0.116$	
PFBS	p=0.0485	p=0.0451	+
	$R^2 = 0.055$	$R^2 = 0.049$	
PFHpS	p=0.1735	p=0.2000	+
	$R^2 = 0.099$	$R^2 = 0.085$	
PFOS	p=0.0659	p=0.0887	+
	$R^2 = 0.266$	$R^2 = 0.261$	
FOSA	p=0.0015	p=0.0017	-

10. Page 13, lines 4-5. I don't understand this sentence.

Response: We thank the Reviewer for mentioning this. We have clarified this sentence, which now reads:

"Indirect sources of PFAAs are contributors to the global presence of these compounds, particularly in locations such as the Canadian Archipelago (Benskin et al., 2012a)." (P14, L4-L5)

11. An implicit assumption in this work is that the observed pattern and concentrations are a direct consequence of atmospheric snow deposition, thus snow scavenging of atmospheric PFAS. No discussion is made of post-depositional processes affecting the concentrations and patterns of PFAS.

Response: In regards to the post-depositional processes, we do discuss this in some detail in section 3.3 (P8, L4-L24). Melting events can occur in the ice core, which can cause PFAAs to elute into the snowpack and refreeze at ice layer interfaces. MacInnis et al. (2017) discuss these post-depositional processes in more detail. To make this discussion more implicit, we have added more detail on these post-depositional processes to this paragraph, which now reads: "One study has examined elution behaviour of PFAAs from a melting snowpack and found that elution of PFAAs is driven by a number of factors including water solubility in the snowpack, PFAA chain length, and sorptive capacity of the snow grain surface (Plassmann et al., 2011). Due to melting at the surface, concentrations of PFAAs measured near the surface layer can result in inaccurate estimations whereby one year might be overestimated and another year underestimated. Melting events on the ice cap have likely happened periodically over the last 15 – 20 years, thereby blurring to some extent, the vertical profile. However, we expect any melting that occurred to have primarily affected the seasonal trends, as Koerner, 2005 states that the percolation of meltwater in a snowpack will refreeze within an annual layer, and so seasonal cycles of PFAA deposition will be biased, but annual interpretations should not be affected (Koerner, 2005)." (P8, L12-L20)

12. Even If I was convinced that most PFAS in the studied arctic region come from atmospheric oxidation of neutral precursors, no discussion is made on the processes responsible for the transport of ionizable PFAS from the gas phase (I guess oxidation occurs in the gas phase) to deposited snow. Once a ionizable PFAS is formed, it may attach rapidly to aerosols. Which are the dominant aerosol types in this region? A reference is needed to support the response to this question. Furthermore, it could be that neutral precursors are the main contributors to ionizable PFAS in the surface Arctic ocean, and then these are transferred to Devon Cap by sea-salt aerosol formation and deposition.

Response: It is not clear what the Reviewer is referring to by "aerosol type" – size, inorganic composition, organic composition, nucleating ability, optical depth, water content? We feel the scope of identifying aerosol types in the Devon Ice Cap atmosphere is beyond the scope of this study. However, what is directly relevant to this paper is the differences in physical properties of the precursors (neutral and volatile) and the acids (ionic and sorptive). As we mention in the introduction, after PFAAs are formed in the gas phase, they can be deposited to the surface through both wet and dry deposition due to their physicochemical properties. We have clarified our introductory sentence and added references to a few modelling studies: "Once these PFAAs are formed in the **gas phase**, they undergo wet or dry deposition **to the surface. The specifics of these processes have been considered in several modelling studies**

<mark>in the literature (Armitage et al., 2009a, 2009b; Schenker et al., 2008; Wallington et al., 2006; Yarwood et al., 2007)." (P2, L18-L21)</mark>

13. Page 15, line 5. I don't know any study on the occurrence of PFAS in the marine surface microlayer, but for other POPs, there is a huge variability on the enrichment factors, thus a lack of correlation does not contradict the potential role of marine aerosols.

Furthermore, Na can be forced to move out from the snow/ice after deposition.

Response: The mechanisms for sea surface microlayer enrichment of PFAS are not analogous to other POPs due to the unique properties imparted by the combination of the hydrophobic and lipophobic perfluoroalkyl chain and the hydrophilic carboxylate or sulfonate moiety. A preliminary study of enrichment of PFAS in the freshwater surface microlayer has been described (Reth et al., 2011), with enrichment increasing with chain length. As discussed in a previous paper from our team (and briefly mentioned in this work), surfactant strength does not describe the differences between PFAS levels in the ice cap and ocean. To clarify this, we have added a reference to that paper at the beginning of the discussion of ice cap/ocean comparisons to make clear we are using a previously described data analysis technique:

"Another technique used to assess the influence of marine aerosol deposition of PFAAs to the Devon Ice Cap is a comparison between ocean and ice cap homologue patterns (MacInnis et al., 2017)." (P16, L7-L8)

We have further clarified by re-phrasing the description of the surfactant relationship:

"Water-to-air transport of PFAS is related to surfactant strength (Reth et al., 2011). Consistent with results from MacInnis et al. (2017), differences in surfactant strength cannot account for the different homologue profiles observed on the ice cap and in the ocean." (P16, L10-L12)

We agree with the Reviewer that post-depositional processes may be different for PFAS and sodium, although this has not been explicitly studied. On its own, these correlations would not provide sufficient evidence to discount the role of marine aerosols. However, the combination of the lack of correlation with sodium and sea ice extent, and the differing homologue patterns support our conclusion that marine aerosols are not the dominant source of PFAS to Devon Ice Cap.

14. Page 15, line 9. This is not true because the patterns in snow are different than in seawater even for a given site, and because we do not know the patterns in the surface microlayer, nor in remote aerosols.

Response: As described above in the response to comment 13, we do have information on the patterns of enrichment for the surface microlayer and marine aerosols relative to ocean water (Reth et al., 2011). To clarify this point, we have moved our discussion of water-to-air transport to directly follow this sentence. The section now reads as follows:

"If marine aerosols were/are a major source of PFAA contamination on Devon Ice Cap, then one would expect the homologue profiles to be similar between the ocean and the ice cap. Water-to-air transport of PFAS is related to surfactant strength (Reth et al., 2011). Consistent with results from MacInnis et al. (2017), differences in surfactant strength cannot account for the different homologue profiles observed on the ice cap and in the ocean (Fig S8)." (P16, L8-L12)

15. I suggest to plot the ratio of concentrations between Devon cap and arctic ocean (except for PFBA which has clearly a different origin and behavior), and plot this ratio versus the number of C of the pfas chain, and then discuss taking into account the literature.

Response: We thank the Reviewer for this suggestion. We actually initially plotted the ratios of concentrations in the Devon Ice Cap compared to ocean levels, similar to what was done in MacInnis et al. (2017), but included a proportional analysis of the molar concentrations in this paper instead, as to avoid duplicating a previous paper's figure. We have added Figure S8 to the SI (P31-P32)) and included a reference to it in the main text:

"Consistent with results from MacInnis et al. (2017), differences in surfactant strength cannot account for the different homologue profiles observed on the ice cap and in the ocean (Fig. S8)." (P16, L10-L12)



Figure S8. Ratios of observed concentrations in the Devon Ice Cap compared to levels in the Arctic Ocean (Benskin et al., 2012b)(Cai et al., 2012), Canadian Artic Archipelago (Benskin et al., 2012b), Greenland Sea (Zhao et al., 2012)(Busch et al., 2010), North Sea (Ahrens et al., 2010b), North Atlantic Ocean (Ahrens et al., 2010a)(Ahrens et al., 2009)(Zhao et al., 2012), and North Pacific Ocean (Cai et al., 2012) in 2005 and 2007 to 2010.

16. The authors insist that sea salt aerosol does not play a role, but I don't see concluding arguments. Which is the main source of aerosols in the region and how ionizable pfas behave after their formation? Ok, let's assume that sea-salt aerosols do not play an important role, then, to which aerosols are PFAS bound to? Are they in the gas phase and then scavenged by snow? Please, provide a plausible mechanistic explanation.

Response: As we have described above, PFAS formed in the gas phase will be deposited through wet and dry deposition (see response to comment 12). The identity of the aerosols with which PFAS might be associated is an open question. Our correlations with different tracers (e.g. for dust) were targeted to reduce uncertainty in this area.

17. Pages 16-17. A hypothetical dust source is commented, but this is not supported by the assessment of air mass back trajectories.

Response: Our discussion regarding dust is not based on our back trajectories, but rather on the well-established literature indicating both the presence of dust in the Arctic and that it can be coming from LRT (Darby et al., 1974; Rahn et al., 1977; Zdanowicz et al., 1998). To clarify this in the text, we have rephrased and added an additional reference:

"Mineral dust aerosols can accumulate acidic atmospheric contaminants, such as nitric and hydrochloric acids (Sullivan et al., 2007). **Dust can undergo LRT and deposit in the remote Arctic** (Rahn et al., 1977; **Zdanowicz et al., 1998**)." (P18, L6-L8)

18. Note that Ca and Mg are enriched in sea-salt aerosol coming from the sea surface microlayer (Jayarathne et al. EST 2016)! Then the correlations between Ca and PFAS would support sea salt as an important contributor to PFAS at the studied site!

Response: We thank the Reviewer for mentioning this. Although we did consider the enrichment of calcium and magnesium, we believe it has a negligible impact on our interpretation of the data. Enrichment in marine aerosols by calcium has been shown by a few studies (Jayarathne et al., 2016; Oppo et al., 1999; Salter et al., 2016). Aerosol enrichment by magnesium has been observed in a single study (Jayarathne et al., 2016), while another showed no enrichment (Oppo et al., 1999). Using established seawater cation ratios, we calculated average non-sea-salt (nss) fractions of calcium and magnesium of 99.5 % and 70.3 %, respectively (Table S19). Jayarathne et al. (2016) observed calcium enrichment factors were variable, but up to 3.38 in marine aerosols. If we assumed this maximum enrichment, nss-Ca on the ice cap would remain >98 %. It is extremely unlikely that this small change would impact the interpretation of our correlations. Given the uncertainty and observed variability in enrichment for magnesium, it is not possible at this time to determine the impact of possible magnesium marine aerosol enrichment on ice cap nss-Mg.

19. After reading this manuscript I think that the interpretation needs to be re-evaluated, and a new version prepared taking into account my comments above.

Response: We thank the Reviewer for taking the time to read our manuscript and provide important feedback. We have addressed all of the reviewer's comments and prepared a revised manuscript.

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Continuous Non-Marine Inputs of Per- and Polyfluoroalkyl Substances to the High Arctic: A Multi-Decadal Temporal Record

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- 10 Abstract. Perfluoroalkyl acids (PFAAs) are persistent, in some cases bioaccumulative compounds found ubiquitously within the environment. They can be formed from the atmospheric oxidation of volatile precursor compounds and undergo long-range transport (LRT) through the atmosphere and ocean to remote locations. Ice caps preserve a temporal record of PFAA deposition making them useful in studying the atmospheric trends in LRT of PFAAs in polar or mountainous regions, as well as understanding major pollutant sources and production changes over time. A 15 m ice core representing
- 15 38 years of deposition (1977-2015) was collected from the Devon Ice Cap in Nunavut, providing us with the first multidecadal temporal ice record in PFAA deposition to the Arctic. Ice core samples were concentrated using solid phase extraction and analyzed by liquid and ion chromatography methods. Both perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) were detected in the samples, with fluxes ranging from <LOD to 141 ng m⁻² yr⁻¹. Our results demonstrate that the PFCAs and **perfluorooctane** sulfonate (PFOS) have continuous and increasing deposition on
- 20 Devon Ice Cap, despite recent North American_and international regulations and phase-outs. We propose that this is the result of on-going <u>manufacture</u>, <u>use and emissions</u>_and <u>use</u> of these compounds, their precursors and other newly unidentified compounds in regions outside of North America. By modelling air mass transport densities, and comparing temporal trends in deposition with production changes of possible sources, we find that Eurasian sources, particularly from Continental Asia are large contributors to the global pollutants impacting Devon Ice Cap. Comparison of PFAAs to their
- 25 precursors and correlations of PFCA pairs showed that deposition of PFAAs is dominated by atmospheric formation from volatile precursor sources. Major ion analysis confirmed that marine aerosol inputs are unimportant to the long-range transport mechanisms of these compounds. Assessments of deposition, homologue profiles, ion tracers, air mass transport models, and production and regulation trends allow us to characterize the PFAA depositional profile on the Devon Ice Cap and further understand the LRT mechanisms of these persistent pollutants.

1 Introduction

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Per- and polyfluoroalkyl substances (PFAS) are a diverse group of compounds that have been used in surfactants and polymers for over 60 years (Buck et al., 2011). Perfluoroalkyl acids (PFAAs), a sub-group of PFASs are persistent contaminants that are ubiquitous in the environment. Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) are two of the most widely known and studied groups of PFAAs (Buck et al., 2011; Stock et al., 2007). PFAAs are prevalent in remote locations, such as the Arctic (Butt et al., 2010), due to their ability to undergo long-range transport through the atmosphere and/or the ocean (Prevedouros et al., 2006). Long-range transport can be a combination of both direct transport and indirect formation. With direct transport, PFAAs are directly transported in their carboxylic (PFCA)

- or sulfonic (PFSA) acid form to remote locations. This can occur through the atmosphere, in the gaseous or particle
 phase (including with marine aerosols), or via oceanic water currents (Prevedouros et al., 2006), via oceanic water currents or by marine aerosol formation (Benskin et al., 2012b). With indirect formation, PFAAs are produced through chemical transformation of PFAS precursors in the atmosphere (Young and Mabury, 2010). These compounds-PFAAs are environmentally persistent and longer chain acids (>6 carbons) have a tendency to bioaccumulate and biomagnify in food webs (Butt et al., 2010; Houde et al., 2006; Scheringer et al., 2014).
- 15 In the atmosphere, volatile and semi-volatile precursors such as fluorotelomer alcohols (FTOHs) and —N-alkyl perfluoroalkane_sulfonamides/sulfonamidoethanols ((N-Alkyl) FASAs/FASEs) NAFSAs/NAFSEs) and heat-transfer fluids (i.e. chlorofluorocarbon-replacements) undergo oxidation in the gas phase to form PFAAs (D'eon et al., 2006; Ellis et al., 2004; Young and Mabury, 2010). The atmospheric lifetime and persistence of these precursors is long enough to reach remote locations by wind and air transport, before subsequently oxidizing to the corresponding PFAAs and depositing
- to remote locations (Busch et al., 2010; Young et al., 2007).
 Once these PFAAs are formed indirectly-in the gas phaseatmosphere, they will-undergo wet or dry deposition_to the surface. The specifics of these processes have been considered in several modelling studies in the literature (Armitage et al., 2009a, 2009b; Schenker et al., 2008; Wallington et al., 2006; Yarwood et al., 2007). Further transport can occur via ocean currents (Armitage et al., 2006, 2009a, 2009c) andmarine aerosols (McMurdo et al., 2008). PFAAs are highly acidic, surface active compounds, usually present as anions in the aqueous phase under environmental conditions (Cheng et al., 2007).
- al., 2009). These surface active compounds will concentrate at the air water interface and are therefore expected to be in the sea surface microlayer (SSML) and to be present in marine aerosols (Lewis and Schwartz, 2004).

The long-range transport mechanisms of these compounds can be elucidated through the collection and analysis of remote samples, such as ice core samples. Ice caps receive their contamination solely from atmospheric deposition due to their high

30 elevation, and preserve a temporal record of that deposition. Devon Ice Cap, located on the Devon Island in Nunavut, Canada, was previously sampled for PFAAs in May of both 2006 and 2008 through collection from the sidewall of a snow pit (MacInnis et al., 2017; Young et al., 2007) This ice cap has a high latitude and elevation (Boon et al., 2010) and is not expected to receive any local or oceanic sources of contamination. These previous studies detected PFAAs in snow profiles

that spanned a 10 - 14 year period in deposition. In this study, a 15 m ice core was collected in 2015, allowing us to examine PFAA deposition over a much longer (38 year) period. Within this paper we discuss: (1) PFAA deposition and temporal trends; (2) homologue patterns and volatile precursor mechanisms; (3) transport of PFAAs to the Arctic via ion tracer analysis; and (4) PFAA source regions via transport modelling. This work represents the first multi-decadal analysis of PFAAs in an ice core from the summit region (2175 m above mean sea level) of a large Arctic ice cap.

2 Methods

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2.1 Sample Collection and Sectioning

15.5 collected from Nunavut А m ice core was the Devon Ice Cap, Devon Island, (75.2°N, 82.7°W, 2175 m above mean sea level (AMSL)) on May 17, 2015. Extensive measures were taken to avoid PFAS contamination during both sample collection and sectioning (i.e. PFAS-free apparel and equipment, methanol-10 rinsed sampling tools and equipment). Samples were collected using a stainless steel Kovacs ice drill with a 9 cm diameter (section S1). The samples were separated into 1 m ice core sections, packaged in polyethylene wrap, shipped frozen to the Canada Centre for Inland Waters (CCIW) in Burlington, Ontario, Canada and stored at -35°C prior to sectioning. Cores were sectioned in a -10°C freezer into discrete samples corresponding to individual years. Sectioning was done using stainless steel tools, cleaned with methanol (MeOH) (Omnisolv, 99.9%, EMD, ThermoFisher) before and after each sample. Ice core 15

sections were placed into pre-cleaned 4L high-density polypropylene bottles and kept frozen at -35°C prior to extraction and analysis.

2.2 Sample Preparation and Extraction

Sample extraction has been described previously (MacInnis et al., 2017). Briefly, samples were thawed immediately prior to extraction and aliquoted into 500 mL melted volumes for extraction. Sub-samples for extraction were spiked with 30 µL of a surrogate mixture (Table S1), which acted as the internal standard (IS) to monitor recovery (Table S2). Samples were shaken, sonicated for 10 minutes, and held for 30 minutes at room temperature.

Targeted analytes included: trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorobexanoic acid (PFHxA), perfluorobeptanoic acid (PFHpA), perfluoroctanoic

- 25 acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTrDA), perfluorobexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFOcDA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluoroheptane sulfonic acid (PFHpS), perfluorooctane sulfonic acid (PFOS), perfluorodecane sulfonic acid (PFDS), perfluorotetralecanoic acid (PFDS), perfluorobexane sulfonic acid (PFDS), perfluorotetralecanoic acid (PFDS), perfluorotetralecanoic acid (PFOS), perfluorodecane sulfonic acid (PFDS), perfluorotetralecanoic acid (PFDS), and perfluorotetralecanoic acid (PFDS), perfluorotetralecanoic acid (PFDS), and perfluorotetralecanoic acid (PFDS), perfluorotetralecanoic acid (PFDS), perfluorotetralecanoic acid (PFDS), perfluorotetralecanoic acid (PFDS), and perfluorotetralecanoic acid (PFDS), and perfluorotetralecanoic acid (PFDS), perfluorotetralecanoic
- 30 (FOSA).

Samples were concentrated using an OASIS® weak anion exchange solid phase extraction (SPE) cartridge (6 cm³, 150 mg, 30 µm). Cartridges were conditioned prior to sample loading with 5 mL 0.1% NH₄OH/MeOH, followed by 5 mL MeOH and 5 mL SPE-cleaned HPLC Grade water (Fisher). Following sample concentration, the cartridges were rinsed with 25 mM ammonium acetate buffer acidified to pH 4 with acetic acid, and centrifuged at 4000 rpm for 2 minutes to remove any residual water. Samples were eluted into two fractions: the first fraction was eluted with 6 mL of MeOH for FOSA, and the

5 residual water. Samples were eluted into two fractions: the first fraction was eluted with 6 mL of MeOH for FOSA, and the second fraction was eluted with 8 mL of 0.1% NH₄OH/MeOH for PFAAs. Both fractions were evaporated to dryness under a gentle stream of nitrogen and reconstituted in 0.5 mL 50/50 methanol – water containing the surrogate mixture (Table S1) to monitor matrix effects (Table S3). Reconstituted samples were sonicated for 5 minutes, vortexed and transferred to polypropylene vials for analysis.

10 2.3 Quality Assurance/Quality Control

Previous results from field blanks (HPLC grade water) transported and exposed to the atmosphere in the Canadian Arctic (Resolute Bay, Nunavut) have indicated that the environmental exposure and shipping do not contribute to background PFAS contamination. We have amassed an annual data set on these field blanks (Tables S4a-S4b). Cartridge blanks were used to validate the integrity of the extraction method, and isotopically labelled standards were used to

- 15 validate recovery and matrix effects. Three samples were extracted in triplicate and one sample in duplicate to evaluate reproducibility. A composite mixture of Devon Ice Cap samples was prepared for three types of QA/QC measures in triplicate: one sample was spiked with PFASs before extraction, one sample spiked with PFASs after extraction, and the third sample was spiked with the internal standard and processed akin to the larger sample set. The pre-extraction and postextraction spiked samples were compared to evaluate recovery and matrix effects. No quantifiable PFAA levels were
- 20 detected in the routinely analyzed methods blanks (SPE cartridge blanks, n=6). Method recoveries for the PFAAs ranged from 79 117% with the exception of PFOcDA (127 225%). PFOcDA recoveries indicated enhancement of analyte signal due to matrix effects and incorrect recovery and matrix correction due to using MPFHxDA as the internal standard. Since PFOcDA was below detection limit in all ice core samples, this was not explored any further.
- Matrix effects were evaluated by comparing the peak area of instrument performance standard (IP) compounds to peak areas at equivalent concentrations in a solvent standard. Recovery was evaluated by comparing the recovered analyte concentration in the spike and recovery sample to the theoretical spiked concentration. Each sample was corrected for recovery and matrix effects by quantifying the concentrations based on relative response to isotopically labelled standards added before extraction. A 15 level calibration curve was employed ranging from 0.02 – 8.5 ng mL⁻¹, along with analytical blanks. Analytical blanks (MeOH) and cartridge blanks were included in the method analysis. The method detection limit
- 30 (MDL) was based on three times the standard deviation of the cartridge blanks. Most PFAA analytes were not detected in the method blanks and were therefore below the instrument detection limit (IDL) (Table S54). The limit of detection (LOD) and limit of quantitation (LOQ) were quantified based on signal-to-noise (S/N) ratios of 3 and 10, respectively (Table S65).

2.4 Sample Analysis

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Samples were analyzed by ultra performance liquid chromatography (Waters Acquity UPLC I) with tandem mass spectrometry (Waters Xevo® TQ-S, UPLC-MS/MS) detection operated in electrospray negative ionization mode. Two analyses were conducted. For the first long-chain PFAA (PFCAs > C4, PFSAs > C4, FOSA) analysis, samples were separated using a C18 column (Waters Acquity UPLC® BEH, 2.1×50 mm, 1.7μ m) with a water – methanol 2 mM ammonium acetate gradient method. For the chort-chainsecond PFAA (PFCAs < C8, PFOS) analysis, samples were separated using a Shodex RSPak column (2.0×150 mm, 5μ m) with a water – methanol 50 mM ammonium acetate method (Tables S<u>76-S</u><u>8</u><u>7</u>). Analytes were quantified based on relative response to isotopically labelled internal standards (Wellington Laboratories, Guelph, ON).

10 2.5 Major Ion Analysis

Sub samples of the sectioned ice core (15 mL) were analyzed for major anions and cations. Anions were measured by ion chromatography with conductivity detection and cations were quantified using inductively coupled plasma and optical emission detection. A range of cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Al³⁺) and other metals (e.g. iron and silicon), and anions (F⁻, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, SO₄²⁻, PO₄³⁻) and organic acids (e.g. acetate, propionate, formate and butyrate) were measured. Further details on anion and cation analysis are provided in section S2.

2.6 Air Mass Transport Densities

To trace the origins of air masses arriving at the sampling site on Devon Ice Cap and characterize source regions, air mass back trajectories were computed using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015). Air parcel back trajectories were computed, allowing us to examine air mass moisture source regions and

- 20 transport to Devon Ice Cap. Back-trajectory analysis was performed using the National Centers for Environmental Protection and Atmospheric Research (NCEP/NCAR) global atmospheric reanalysis data set at 2.5 degrees resolution. Daily, 10-day back trajectories were initiated at 2175 meters AMSL at the Devon Ice Cap sample site location for years 1994 and 2013. Residence time analysis was used to identify air mass transport densities for 1994 and 2013 (Miller et al., 2002). This approach analyzes a large number of trajectories to reduce uncertainties, develop reliable pathways of airflow and account
- 25 for variations in transport speed and direction (Criscitiello et al., 2016). For this analysis, the total number of trajectory endpoints were summed within each equal-area pixel, and then divided by the zonal distance between the Devon ice core sampling site and each pixel to remove concentric patterning. The air mass transport densities were scaled on a 0-1 scale. In this study we focus on low-elevation air masses (0–500 m above terrain), which are more likely to be representative of evaporation moisture source.

3.1 PFAA Concentrations and Fluxes on the Devon Ice Cap: Comparisons to Previous Studies

A comprehensive analysis of perfluoroalkyl acid (PFAA) and FOSA annual deposition on the Devon Ice Cap was carried out on ice core samples dating from 1977 – 2015. In general, PFCAs from TFA (C2) to PFTrDA (C13) were detected on the
Devon Ice Cap. Deposition and temporal trends of TFA-(C2) to PFBA (C4) will be discussed in a separate paper. Observed PFCA concentrations from PFPeA (C5) to PFTrDA ranged from <3.21 to 755 pg L⁻¹ (Fig. S1, Table S28). PFCAs from PFHxA to PFUnDA (C6 – C11) were detected in almost every sample, with the exception of PFUnDA, which was not detected in one year. The long-chain PFCAs, PFDoDA (C12) and PFTrDA were only quantifiable in <3 years, while PFTeDA, PFHxDA, and PFOcDA were <LOQ throughout the 38-year time period and will not be discussed further. PFSAs
including PFBS, PFHpS and PFOS, as well as FOSA were detected in every sample while PFBS and PFHpS were only detected >LOD in two years. Evidence of the presence of PFHxS, PFDs and PFECHS was sought, but not found. FOSA was detected >LOD in most samples up until 2000 and only in three samples after 2000.

- Concentrations (pg L⁻¹) of the PFAAs were converted to fluxes (ng m⁻² yr⁻¹) (Section S3) to determine annual deposition of these compounds in the Canadian Arctic. The dating of the ice core itself is discussed in more detail in the SI (section S1). Annual snow accumulation was determined by measuring the length of the annual ice core sections. Annual snow accumulation was calculated as 0.15 - 0.64 m yr⁻¹, which is consistent with 0.22 - 0.24 m wet equivalents yr⁻¹ reported by (Pinglot et al., 2003) for Devon Ice Cap from 1963-2000. Fluxes of PFAAs, including PFOA to PFUnDA (C8 – C11) and PFOS (Tables S1<u>1</u>0, S1<u>2</u>4), were compared to fluxes of these PFAAs in two previous samples collected from snow pits on
- 20 Devon Ice Cap in 2006 (Young et al., 2007) and 2008 (MacInnis et al., 2017). The data sets generally agree within the uncertainty of the measurements, with the exception of PFOS (Fig. S2, S3). These slight discrepancies between Devon Ice Cap studies could be the result of multiple factors. In the 2006 study, there was limited availability of isotopically labelled and native standards of sufficient purity. Our study represents an improvement in analytical methods since that time, both in terms of instrument detection limits and accuracy. The 2006 and 2008 sampling strategies are also in contrast to the current
- 25 approach of ice core drilling. In the earlier efforts, depth samples were obtained by horizontal cylindrical sampling the face of an ice pit (2006) and vertically sampling the face of a snow pit continuously (2008). Those datasets represent semi-continuous depth measurements. In our current method, we obtained ice cores using a custom drill designed for Arctic sampling and conventional practices in ice sampling for temporal profiling (Boon et al., 2010; Readinger, 2006). Lastly, the Devon Ice Cap sampling locations in the earlier research were not at the summit of the ice cap as in the current research.
- 30 These differences in location may have resulted in some variability in fluxes. The most straightforwardaceurate temporal record of atmospheric deposition is obtained at the summit of an ice cap (Legrand and Mayewski, 1997); thus, the current research is hypothesized to be a better representation of PFAA deposition to Devon Island.

Concentrations and homologue trends of PFCAs and PFSAs detected in this study are comparable to a number of other studies (Table S1<u>3</u>2). Comparable levels of PFCAs ranging from PFPeA to PFUnDA were detected in remote snow core and surface snow samples from Cole Gnifetti (Kirchgeorg et al., 2013), Longyearbreen-yen (Kwok et al., 2013), and Livingston Island (Casal et al., 2017), and from glaciers on the Tibetan Plateau and Lake Namco (Wang et al., 2014a).

5 Short chain PFCAs had higher concentrations than other PFCAs detected in precipitation, lake and river water samples (Kwok et al., 2010; Müller et al., 2011; Scott et al., 2006; Taniyasu et al., 2008). In general, Concentrations of the PFCAs were generally much lower in the Arctic and Atlantic Oceans compared to the Devon Ice Cap concentrations. PFOS and FOSA concentrations were variable among all studies with no discernable trend for sample matrix or sample site.

3.2 Air Mass Transport Density Analysis

- 10 Previous studies using back trajectory analysis of air masses (Kahl et al., 1997; Meyer et al., 2012) have provided evidence for atmospheric LRT to the Devon Ice Cap from North America and Eurasia. Air masses on Devon Island originated three times more often from populated regions of Northern Europe and Asia compared to North America, and southern and eastern Asia were significant source regions. Little variation was observed in Devon Ice Cap air mass source regions over the time period 1994 – 2008 (Meyer et al., 2012). Previous studies on spatial patterns of pollen deposition in the High Arctic further
- 15 support these findings. Devon Ice Cap is located within an air mass boundary between 74° N and 76° N, between sites north of 76° that receive dominantly Eurasian pollen sources and sites south of 74° that receive dominantly North American pollen sources (Bourgeois et al., 2001). Devon Ice Cap therefore receives air masses and pollen/pollutant sources from both North America and Eurasia.

Air mass transport densities have previously been employed for investigating probable source regions and flow pathways of

- 20 air masses in the Canadian Arctic (Criscitiello et al., 2016). Air mass transport density analyses calculated using the HYSPLIT model for Devon Ice Cap for the years 1994 and 2013 are shown in Figure 1. The year 1994 was selected to compare to previous trajectory analyses conducted by Mever et als, and showed similar results. Because of the high PFOS fluxeur unusual PFAA observedations in 2013, we also examined this year to identify any transport anomalies, but found both years (1994 and 2013) to be comparable. Air mass transport densities for both 1994 and 2013 reveal elevated
- 25 residence time densities in parts of Asia, and particularly high residence time densities along the west coast of Greenland.



Figure 1: Air mass transport density maps (scaled 0-1) for air parcels reaching the Devon Ice Cap ice core site (red star), for a) 1994 and b) 2013.

5 3.3 PFCA Deposition and Temporal Trends on Devon Ice Cap

Annual fluxes of PFCAs ranged from <LOD to 141 ng m⁻² yr⁻¹ (Table S110). Temporal trends of shorter-chain PFCAs (C2 - C4) will be discussed separately, so this section will focus solely on PFCAs with more-thoust least five carbons. In general, the flux of PFCAs increased after 1985 (Fig. S4), but with diverging trends from 1995 - 2015. Various glaciology studies have shown that Devon Ice Cap has experienced strong summer warming since 2000 and especially after 2005 (Bezeau et al., 2013; Gascon et al., 2013; Sharp et al., 2011). This is consistent with Inuit traditional knowledge of overall 10 warming in the Arctic (Koihok et al., 2001). The variability in fluxes within the past 15-20 years could, therefore, be partially attributed to melting effects. When melting events occur, the ability to discern temporal trends in chemical deposition of various compounds can be compromised by the percolation of meltwater or elution of particles by meltwater flow (Eichler et al., 2001; Steinlin et al., 2016). These melting events could bias annual flux measurements of PFAAs in ice core samples during the melt period, since PFAAs on the ice cap surface can be eluted into the snowpack, before refreezing 15 at ice layer interfaces where temperatures at depth are below the pressure melting point (Bezeau et al., 2013). One study has examined elution behaviour of PFAAs from a melting snowpack and found that elution of PFAAs is <u>largely</u> driven by a number of factors including water solubility in the snowpack. PFAA chain length, and sorptive capacity of the snow grain surface (Plassmann et al., 2011). Due to melting at the surface, concentrations of PFAAs measured near the

surface layer can result in inaccurate estimations whereby one year might be overestimated and another year <u>underestimated</u>. MThis melting events on the ice cap haves likely happened periodically over the last 15 – 20 years, thereby blurring to some extent, the vertical profile. However, we expect any melting that occurred to have primarily affected the seasonal trends, as Koerner, 2005 states that the percolation of meltwater in a snowpack will refreeze

- 5 within an annual layer, and so seasonal cycles of PFAA deposition will be biased, but annual interpretations should not be affected (Koerner, 2005). Variability of \pm 1 year could be caused by inaccuracies in dating and/or error associated with ice core sectioning. To circumvent the compounding impacts of recent melt events and consequent meltwater percolation, and any error associated with ice core dating and sectioning, a 5-year moving average was applied to the flux measurements, thereby facilitating long-term temporal trend analysis of PFAS deposition to Devon Ice Cap.
- 10 Both PFOA and PFNA fluxes increased from 1977 up until at least 1995 (Figure 2). In the period post-1995 until 2013, fluxes have plateaued, with <25 ng m⁻² yr⁻¹ variance in annual flux. From 2012 to 2015, a large decline in PFOA and PFNA fluxes is apparent. The decrease in flux post-2012 was noted for the entire suite of PFCAs (Fig. S4). The most recent decrease in PFCA fluxes could be due to melting events or ice core dating and sectioning inaccuracies, but it also corresponds to anticipated PFCA emission reductions through the United States Environmental Protection Agency (EPA)
- 15 PFOA Stewardship Program (US EPA, 2016), as well as the Canadian Environmental Performance Agreement (Environment and Climate Change Canada, 2006). In 2006, the EPA invited eight major fluoropolymer and fluorotelomer manufacturers to commit to eliminating emissions and product content levels of PFOA, precursor compounds, and related longer chain length homologue chemicals. Corporations voluntarily committed to achieving a 95% reduction by 2010, measured from a year 2000 baseline, and full elimination of these products and emissions by 2015 (US EPA, 2016). In
- 20 Canada, the federal government established The Environmental Performance Agreement with the same commitment between Environment and Climate Change Canada (ECCC), Health Canada and four major manufacturers with known organofluorine products in Canadian commerce (Environment and Climate Change Canada, 2006). The most recent data for company-reported reductions in emission and product content for the U.S., Canada, and non-U.S. operations are summarized in Tables S143 S154. As of 2016, all companies participating in the PFOA Stewardship Program and Environmental
- 25 Performance Agreement reported they had met the goals of the program. As part of both agreements, all major manufacturers reduced their production and emissions of PFOA and related compounds by at least 95% from 2006 2010. The observed decrease in PFOA and PFNA fluxes from 2012 2015 cannot solely be attributed to these phase-outs, since it would be expected that the phase out would cause a large decrease in PFCA deposition between 2006 and 2010 and a small decrease after 2012. It is probable that existing products continued to emit after the stewardship program took effect, which could delay the detection of its impact (Prevedouros et al., 2006). This is evident in temporal trend analysis in Canada and
- 30 could delay the detection of its impact (Prevedouros et al., 2006). This is evident in temporal trend analysis in Canada and the U.S. such as in human serumblood, freshwater fish, and non-migratory birds, which do not show much of any declines in PFCAs from 1990s to 2012 (Braune and Letcher, 2013; Calafat et al., 2007; Gewurtz et al., 2016; Olsen et al., 2003)(Braune and Letcher, 2013; Gewurtz et al., 2016).





Figure 2: Annual deposition fluxes on the Devon Ice Cap: (a) PFOA and (b) PFNA. The solid black line represents the 5-year moving average, and the dotted coloured lines represent the estimated and reported consumption or production volumes of PFOAbased products including PTFE, perfluorinated ethylene-propylene copolymers (FEP), perfluoroalkoxyl polymers (PFA), and related ammonium and sodium salts (APFO/NaPFO), as well as PFNA-based products including polyvinylidene fluoride (PVDF) and related ammonium salts (APFN) (Wang et al., 2014b).

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In addition, other historical and on-going sources of **PFAS** have emerged. Manufacturers that were not signatories to the PFOA stewardship program have been producing **PFAS** since 1985. China started polytetrafluoroethylene (PTFE) production around 1985 and was producing up to 60 kt of PTFE in 2015 (Wang et al., 2014b). Some manufacturers have emerged more recently that produce PFAAs and precursor compounds (Land et al., 2015; Wang et al., 2014b). In general, from 2000 onward, long-chain (**PCS**) PFCAs have been phased-out through regulation or voluntary reduction by major producers in Japan, Western Europe, the United States and Canada (Wang et al., 2014b, 2014c). Meanwhile, new manufacturers (e.g. China) have begun producing these long-chain PFCAs and their precursors (Land et al., 2015). The total

estimated annual emissions of PFBA to PFTeDA for Canada, the United States, Western Europe, and Japan were 25 - 50 t yr⁻¹ in 2010, while estimated emissions of PFBA to PFTeDA were 40 - 193 t yr⁻¹ in China in 2013 (Wang et al., 2014b). Thus, global emissions of PFAAs and their precursors have not decreased significantly, which is consistent with observed temporal trends on Devon Ice Cap. Furthermore, the phase-out has created a market for numerous alternative fluorinated products (Wang et al., 2016, 2013), some of which may be precursors to the stewardship program in North America and increasing production and emissions in other regions.

3.4 PFSA and FOSA Deposition and Temporal Trends on Devon Ice Cap

- The observed concentrations of PFSAs and FOSA correspond to annual fluxes from <LOD to 80.3 ng m⁻² yr⁻¹ (Table S124).
 Since PFBS and PFHpS were only detected in three samples, there are no observable trends. PFOS and FOSA each show distinct temporal trends. PFOS was detected at consistent levels below 10 ng m⁻² yr⁻¹, with an anomaly (80 ng m⁻² yr⁻¹) detected in 20122 (Fig. 3a). FOSA was measured in almost every year from 1977 2000 with fluxes increasing until 1995. After 2000, FOSA was only detected in three samples with levels <0.76 ng m⁻² yr⁻¹ (Fig. 3b). FOSA is a known volatile precursor and can degrade to PFOS (D'eon et al., 2006); however, PFOS was continually measured after 2000, whereas FOSA was not. In addition, there was no correlation between PFOS and FOSA measurements (Table S1<u>6</u>5). Therefore, it is
 - reasonable to assume that there are sources of PFOS that are independent of FOSA and other sulfonamido derivatives, is suggests FOSA is not the primary source of PFOS to the Devon Ice Cap.




Figure 3: Annual deposition fluxes on the Devon Ice Cap: (a) PFOS and (b) FOSA, with global POSF production from 1977 – 2003 and POSF production for Western Europe, Japan, United States and China from 2003 – 2015 (Wang et al., 2014b, 2017). Solid black lines represent 5-year moving averages.

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From 2000 – 2002, 3M, one of the major global producers of perfluoroalkyl substances phased out the production of the synthetic precursor to FOSA and PFOS, perfluorooctane sulfonyl fluoride (POSF), as well as related products based on C6, C8, and C10 chemistry (Wang et al., 2013; Weppner, 2000). These were replaced with C4-based chemistry, where products were derived from perfluorobutane sulfonyl fluoride (PBSF). These compounds are believed to have lower bioaccumulative and toxicological effects (Stahl et al., 2011). Reported production of PBSF in the United States almost doubled from 2002 to 2006, while that of POSF decreased by more than two orders of magnitude between 1998 and 2002, with no known

production after 2006 (Wang et al., 2014c). This is interesting because we actually detected quantifiable levels of PFBS in the ice core in two recent years, and so our understanding of LRT of these PFASs is incomplete and warrants further research. Before 2003, 3M was responsible for most global PFOS production (Carloni, 2009). By 2006, PFOS and related substances derived from POSF were regulated under the European Union (EU) Directive 2006/122/EC and by 2009,

- 5 were listed under Annex B (restriction of production and use) of the Stockholm Convention on Persistent Organic Pollutants coordinated by the United Nations Environment Programme (UNEP) (Land et al., 2015). These production changes in PFOS in the early 2000s were used to explain temporal trends in the Canadian Arctic (Butt et al., 2007). The decline of precursor POSE-in production, and hence of all C8 sulfonamido derivatives, including FOSA, of the preeursor-FOSA-by 3M is consistent with FOSA trends observed on the Devon Ice Cap, in which the majority of FOSA is <LOD after 2000,</p>
- 10 suggesting an effective phase out of this compound (Fig. 3b). This was similarly observed in samples collected from Devon Ice Cap in 2008 (MacInnis et al., 2017), in North Atlantic pilot whales harvested between 1986 and 2013 (Dassuncao et al., 2017), and in Arctic air at Alert (Hung et al., 2016).

Temporal trends of PFOS deposition to the Devon Ice Cap do not reflect the production phase out of PFOS by 3M in the early 2000s (Fig. 3a). Rather, PFOS production and manufacturing, along with replacements (e.g. PFBS), have increased

- 15 dramatically in Asia since 2001, and China is now the dominant producer of these compounds (Lam et al., 2016; Xie et al., 2013; Yao et al., 2016). PFOS production in China began increasing rapidly around 2000 and is currently steady at 100 200 t yr⁻¹ (Wang et al., 2016). China was reported to be the main producer and user of PFOS substances between 2003 2008 with less than 50 t in 2003 and up to 250 t of POSF-based products produced in 2008 (Carloni, 2009). During this time, over 100 t of PFOS was also used annually in China to produce aqueous film forming foams (AFFFs) (Armitage et al.,
- 20 2009b) used for extinguishing fuel-based fires. According to available 2006 inventories, 15 Chinese enterprises were producing over 200 t of POSF, of which 100 t were for export (Ruisheng, 2008). This suggests the annual volume of PFOS production in China in the mid-2000s was similar to the annual production by 3M in the late 1990s (Armitage et al., 2009b). Although it is known that the production of perfluoroalkane sulfonyl fluorides has increased in China, global emission data for individual compounds are currently unavailable and cannot be correlated with the temporal trends observed on the Devon
- 25 Ice Cap (Lim et al., 2011). However, the continuous detection of PFOS after the early 2000s on Devon Ice Cap may be related to the on-going production and use of PFOS substances by manufacturers in Asia (Wang et al., 2017). Production of other PFOS-related perfluorinated chemicals is on-going in China, as well as in Russia and India (Jiang et al., 2015) which is supported by higher levels of PFOS after 2011 in the Devon Ice Cap. An anomalously high PFOS flux was observed in 2013. This flux was between five and eight times greater than both previous and following years. There was no signal
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enhancement for other **PFAS** in 2013 and the air mass transport model showed no transport anomaly for this year. Therefore, the large 2013 PFOS flux in Devon Ice Cap is unlikely attributed to contamination during method collection or analysis, or due to air mass movements. The reason for the high 2013 PFOS flux is unknown but may suggest other sources. Arctic air samples collected at Alert also showed the highest levels of PFOS in 2013 (Hung et al., 2016), and anomalously high PFOS levels were observed in landlocked Arctic Char from Cape Bounty, Melville Island in Nunavut, Canada,



collected between 2011 – 2015 (Cabrerizo et al., 2016). This increasing PFOS trend warrants further consideration in order to determine the efficacy of current POSF restrictions.

3.5 PFCA Homologues and Volatile Precursors

Indirect sources of PFAAs are contributors to the global presence of these compounds, particularly in locations such as but

- contamination is more important for certain homologues in some locations, for example the Canadian Archipelago (Benskin 5 et al., 2012a). This has been demonstrated in multiple studies that detected the presence of volatile precursors (e.g. FTOHs, (N-Alkyl) FASAs/FASEsNAFSAs, NAFSEs), and FTOH-precursor degradation products (e.g. fluorotelomer unsaturated carboxylic acids (FTUCAs)), in the Canadian Arctic (Benskin et al., 2011; Schenker et al., 2008; Shoeib et al., 2006; Stock et al., 2007). Volatile precursor compounds will oxidize in the atmosphere to produce PFCAs. Patterns of PFCA homologues are useful in examining the role that fluorotelomer-derived compounds play in gas-phase atmospheric oxidation (Young et 10 al., 2007). If these compounds are coming from the same source, then sequential pair concentrations are expected to vary through time together. There will be some variability in the ratios depending on the relative atmospheric levels of NO_x (NO + NO₂) and peroxy radicals (Young and Mabury, 2010). In this study, comparisons were made between observed concentrations of 366 pairs of PFCA homologues ranging from PFPeTFA to PFTrDA (Table S165). Most sequential pairs of 15 PFCA homologues were deposited in similar amounts on the ice cap. Correlations between sequential pairs from PFPeA and PFDoDA were all statistically significant (two-tailed t-test) with strong correlations (all p-values ≤ 0.0001 ; $0.527 \leq R^2 \leq$ 0.889; Table S165). Similar correlations were observed for a number of PFCA homologues in previous ice samples from the Devon Ice Cap (MacInnis et al., 2017) and from Longvearbyen, the Longvearbreen glacier in Svalbard (Kwok et al., 2013). The correlations are consistent with expected PFCA homologue production via gas phase atmospheric oxidation of fluorotelomer-derived compounds (Ellis et al., 2004). Flux measurement ratios were calculated for six pairs of PFCA 20 homologues from PFPeA to PFUnDA over the time series (Fig. S5). The three major even-odd pairs expected to be formed from 6:2, 8:2, and 10:2 fluorotelomer compounds are PFHxA:PFHpA, PFOA:PFNA, and PFDA:PFUnDA, respectively. The majority (82%) of the flux ratio measurements were within a factor of two, supporting the hypothesis that these sequential, even-odd homologues are likely coming from fluorotelomer-derived sources (Fig. 4a) (Ellis et al., 2004; Wallington et al., 2006). Fluorotelomer compounds of different chain lengths were produced and used to different extents. We can compare 25 these using odd-odd PFCA homologue ratios, comparing PFNA to PFPeA, PFHpA, and PFUnDA, as products of 8:2, 4:2, 6:2, and 10:2 fluorotelomer compounds, respectively (Fig. 4b). The dominant homologues are PFNA and PFHpA, followed by PFPeA, then PFUnDA. This suggests that 8:2 and 6:2 fluorotelomer compounds dominate as precursors, followed by the 4:2 and 10:2 fluorotelomer compounds. This trend is consistent with our knowledge of commercial product formulations and atmospheric measurements (Dinglasan-Panlilio and Mabury, 2006; Heydebreck et al., 2016; Young and Mabury, 2010).
- Despite producers moving from 8:2 to shorter-chain formulations, recent FTOH atmospheric measurements have found that the 8:2 FTOH remains the dominant compound in the High European Alps (Xu et al., 2017). Therefore, it is likely that

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PFCAs from PFPeA to PFUnDA on the Devon Ice Cap are derived from common emission sources due to prominent quantities of residual volatile precursors in fluoropolymer products.



5 Figure 4: Molar flux ratios for (a) three even-odd pairs of PFCAs and (b) three odd pairs of PFNA with PFPeA, PFHpA, and PFUnDA homologues, as a function of depth and year.

The atmospheric oxidation of perfluoroalkane sulfonamido substances may provide an additional source of PFCAs to the Devon Ice Cap. The oxidation of FOSA could contribute to the observed flux of PFOA and shorter-chain PFCAs in the High Arctic (Martin et al., 2006). However, since there were no observed correlations between FOSA and PFOA or FOSA and any of the other PFCAs ($p \ge 0.0021$; $R^2 \le 0.24$, Table S165), it is likely that PFOA deposition to the Devon Ice Cap is driven by other sources.

3.6 Elucidating the Role of Marine-Driven Transport of PFAAs to the Arctic

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Thus far, evidence <u>supportswas provided for</u> indirect formation of PFAAs in the atmosphere from volatile precursor compounds, as <u>being-the major source</u>, indicating that direct transport is <u>likely a minor unlikely</u> source of PFAAs to the ice cap. Atmospherically formed PFAAs can deposit to any terrestrial or oceanic system. Those PFAAs deposited to oceans <u>can</u>, and to the atmosphere into the ocean before reaching the Arctic, and then re-enter the atmosphere in the form of from oceanic currents and marine aerosols (McMurdo et al., 2008). It is therefore important to understand the extent to which the

oceans contribute to PFAA ice cap deposition. Other sources, such as dust or biomass burning, must also be considered as possible contributors of PFAAs to the ice cap. Gas-phase PFAAs will deposit through wet or dry deposition and <u>PFAAs</u> may also be transported on aerosols (Thackray and Selin, 2017). (Thackray and Selin, 2017). Major ions are useful source markers for atmospheric aerosols, and were measured in the ice core to further understand these transport mechanisms (Tables $S1\underline{76} - S1\underline{87}$, Fig. S6 – S7).

The non-sea salt (nss) component of the ice core samples was calculated to understand the atmospheric origin in the samples (Keene et al., 1986). All sodium (Na⁺) in the ice core samples was assumed to come from sea salt. Most other ions were attributed to the nss component, suggesting limited oceanic sources depositing on Devon Ice Cap (Table S1<u>9</u>8). Further, no correlations were observed between Na⁺ flux and any of the PFAAs ($p \ge 0.0093$; $R^2 \le 0.218$; Table S<u>20</u>19).

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- 10 Another technique used to assess the influence of marine aerosol deposition of PFAAs to the Devon Ice Cap is a comparison between ocean and ice cap homologue patterns (MacInnis et al., 2017). If marine aerosols were/are a major source of PFAA contamination on Devon Ice Cap, then one would expect the homologue profiles to be similar between the ocean and the ice cap (Fig. S8). Water-to-air transport of PFAS is related to surfactant strength (Reth et al., 2011). Consistent with results from MacInnis et al. (2017), differences in surfactant strength cannot account for the different homologue
- 15 profiles observed on the ice cap and in the ocean (Fig. S8). Figure 5 illustrates the proportional analysis of the molar concentration (pmol L⁻¹) fraction between PFAAs on the Devon Ice Cap and ocean levels in the Canadian Arctic Archipelago (Benskin et al., 2012b), Arctic Ocean (Benskin et al., 2012b; Cai et al., 2012a), North Atlantic Ocean (Zhao et al., 2012), and North Pacific Ocean (Cai et al., 2012a) for the years 2005 and 2010. Molar concentration concentrations fractions of PFAAs on the ice cap differed from ocean PFAA concentrations fractions, with higher molar concentration
- 20 **fractions**s of PFBA and PFNA, and lower molar **concentration_fractions**s of PFSAs found on Devon Ice Cap. PFHxS was not detected on the ice cap, but was measured in most ocean samples. <u>As described by MacInnis et al. (2017), PFHxS can act as a marker for direct transportIn_general, PFHxS is regularly detected in the terrestrial and oceanic environment, but rarely in the atmospheric environment Therefore the absence of PFHxS on the ice cap is further confirmation that marine aerosols are not a significant source for PFAA deposition to the Arctic environment.</u>
- 25 suggesting that indirect sources are of importance for Arctic deposition, due to the absence of PFHxS on the ice cap. The differences in homologue profiles between the ice cap and the ocean can also not be accounted for by different surfactant properties (MacInnis et al., 2017), suggesting the two may have different sources of PFAA contamination. Additionally, correlations between annual PFAS deposition and Arctic sea ice minimum were calculated (NSIDC, 2017) (Table S22). If marine aerosols were a major source of PFAS to the ice cap, then a negative correlation between annual sea
- 30 <u>ice extent and deposition would be expected, but the majority (12 of 14) showed a positive correlation</u>. The discrepancies between the Na⁺/PFAA flux ratios and the ice cap/ocean proportional analysis provide further evidence to imply that marine aerosols are not a significant source of PFAAs to the Devon Ice Cap.



Figure 5: Molar concentration fraction of sum of PFAAs on the Devon Ice Cap (from the current 2015 ice core collection) compared to levels in the Canadian Arctic Archipelago (Benskin et al., 2012b), Arctic Ocean (Benskin et al., 2012b; Cai et al., 2012a), North Atlantic Ocean (Zhao et al., 2012), and North Pacific Ocean (Cai et al., 2012a) in 2005 and 2010. Ocean 5 concentrations are compared to ice cap concentrations for two years to show a better overall comparison with different ocean samples that were collected in multiple field campaigns.

3.7 Understanding Atmospheric Inputs of PFAAs Using Ion Tracers

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Weak correlations were observed between short-chain PFCAs <u>(C2-C4)</u> and nss-F⁻ ($p \le 0.0015$; $0.306 \le R^2 \le 0.455$). A small percentage of the F⁻ being detected in the ice core samples may be derived from the atmospheric formation of PFCAs. The degradation of many PFCA precursors <u>rincluding heat transfer fluids</u>, formforms both PFCA and HF. For example, the hydrolysis of perfluoroacyl fluorides forms the corresponding PFCAs along with the loss of HF (Calvert et al., 2008):

(1)

$$CF_3(CF_2)_x COF + H_2 O \rightarrow CF_3(CF_2)_x COOH + HF$$

By this mechanism in Eq. (1), PFCAs could account for between 0.80 - 14% of the F⁻ present on the ice cap, depending on the year. These numbers are upper limits as PFCAs can also be formed by mechanisms that do not form HF (Young and Mabury, 2010). It is difficult to assess the exact contribution of this anthropogenic source to the overall burden of F⁻, due to the lack of available data on F⁻ sources. This is further confounded by the high mobility of F⁻ in both firm and ice layers, which makes it difficult to study temporal trends in F⁻ deposition (Preunkert et al., 2001). Both natural and anthropogenic sources contribute to the overall budget of F⁻ in the troposphere, including primary sea-salt, soil dust aerosols, volcanic emissions, coal burning, and industrial processing (Preunkert et al., 2001). We are currently unable to assess the exact contributions of each source of F^- , but the correlations observed here suggest that short-chain PFCA precursor degradation could account for up to 14% of the observed F^- . Furthermore, these correlations lend further support to indirect formation as a major pathway to PFCA contamination on the Devon Ice Cap. The role of ice in the formation of PFAAs from precursors is currently unknown and future work should also focus on ice-mediated PFAA formation.

- 5 There were weak to moderate correlations between several PFAAs and nss-Ca²⁺ and nss-Mg²⁺ (0.300 ≤ R² ≤ 0.54931), both of which are indicators of mineral dust (Mochizuki et al., 2016). Mineral dust aerosols can accumulate acidic atmospheric contaminants, such as nitric and hydrochloric acids (Sullivan et al., 2007). Dust can undergo LRT and deposit in the remote Arctic, and undergo LRT during dust storms, where they can travel long distances from Asian and African dust sources to the remote Arctic (Rahn et al., 1977; Zdanowicz et al., 1998). (Rahn et al., 1977; Sullivan et al., 2007).
- 10 Dust entrainment in deserts is one of the most important sources of mineral dust in the global atmosphere and North African (e.g. Sahara) and Central Asian (e.g. Gobi desert) dust sources contribute the most global dust to the Northern Hemisphere (Luo et al., 2003). Several studies have found dust particles associated with LRT in snow and ice samples from the Canadian Arctic (Bullard et al., 2016; Groot Zwaaftink et al., 2016; Zdanowicz et al., 1998). Dust deposition to the Arctic shows a seasonal effect, with dust storms in major deserts occurring more frequently in the spring, leading to higher concentrations of
- 15 mineral dust tracers in the spring and autumn (Barrie and Barrie, 1990). We detected high concentrations $(199 786 \ \mu g \ L^{-1})$ of Ca²⁺ on Devon Ice Cap, and calculated that the majority (99.5%) of Ca²⁺ contributed to the nss component. Substantial concentrations (<2.00 - 78.3 $\mu g \ L^{-1}$) of other mineral dust (Al³⁺, Fe³⁺, Si⁴⁺) tracers were also detected. Correlations between nss-Ca²⁺ and PFAAs suggest there is a relationship between the transport of mineral dust and PFAAs to the Devon Ice Cap. This could be caused by both mineral dust and PFAAs originating from the same regions. Alternatively, it could indicate a
- 20 mechanistic relationship. Atmospheric acids are known to interact with mineral dust through reactive uptake (Sullivan et al., 2007). It is possible that PFAAs, as strong atmospheric acids, could behave in the same way and be taken up onto mineral dust aerosols and subsequently transported to the Arctic. We cannot distinguish between these mechanisms at this time, and suggest that further studies explore this relationship between mineral dust and PFAA LRT.

4 Conclusions

25 Monitoring of temporal trends in persistent organic pollutant deposition in remote areas is an important initiative to determine the impact of regulation on contamination of pristine environments. This study demonstrates the value of ice cores to understanding contaminant LRT. Herein we report the first multi-decadal record of long chain-PFAA deposition in the Canadian Arctic. Continuous and increasing deposition of many PFAAs on Devon Ice Cap was observed, suggesting on-going emission and use of these PFAAs and compounds, their their precursors in areas such as North America and <u>Eurasia and likely new unidentified compounds</u>. These results indicate that Devon Ice Cap is likely impacted by global pollutants from both North American and Eurasian Sources, with Continental Asia becoming a greater contributor in recent years. Use of major ion tracers provided new information regarding the transport of PFAAs in the atmosphere, confirming

that marine aerosol inputs are unimportant and suggesting a relationship with mineral dust. We also observed that a small percentage of fluoride detected in the Arctic could be coming from the reactive mechanisms forming the PFAAs. Further efforts are necessary to continue monitoring the long-range transport of PFAAs and their deposition to the remote Canadian Arctic. It is important to understand these LRT mechanisms and determine the geographical sources of PFAAs and their precursors. Ice cores can aid in elucidating these mechanisms and further collection and analysis of ice cores is

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Supplement Link

recommended.

Author Contribution

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H.M.P sectioned, extracted and analyzed the ice core, conducted the data analysis and wrote the manuscript. C.J.Y. designed and led the project, directed ice core sectioning, assisted with data analysis, and edited the manuscript. A.D.S. assisted in ice core analysis, data interpretation and edited the manuscript. C.S. aided in ice core extraction and conducted analysis. A.S.C. conducted transport modelling and A.S.C. and M.J.S. coordinated field operations, collected the ice core, and performed the dating of the ice core. D.C.G.M. provided input on the manuscript.

Competing Interests

15 The authors declare that they have no conflict of interest.

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Supplementary Information for:

Continuous Non-Marine Inputs of Per- and Polyfluoroalkyl Substances to the High Arctic: A Multi-Decadal Temporal Record

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between PFAS deposition and Arctic sea ice extent and area. Sea ice time series are based on SMMR/ SMM/I satellite obersvations. The slope sign is indicated as either

positive (+) or negative (-) for each PFAA compound. Correlations are ranked in				
terms of significance by purple>blue>orange, but in g	eneral, the correlations are not			
very significant between PFASs and sea ice minimum.				
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Section S1. Methods – Sample Collection

Dating of the Devon Ice Cap ice core was completed using the oxygen isotope record and other glaciochemical records measured in a replicate core drilled at the same location. Oxygen isotope analyses were run on a Picarro cavity ring-down spectroscopy analyzer (precision for δ^{18} O of water samples is $\leq 0.1\%$). Sample isotope ratios were standardized using three working standards calibrated against the IAEA standards VSMOW and SLAP. Final δ^{18} O values are on the VSMOW/SLAP scale. The δ^{18} O time series was used to establish an age-depth relationship by matching the δ^{18} O core record with local summer and winter solstice dates (linearly interpolating between solstices) (Criscitiello et al., 2014). Elemental, ion, and H₂O₂ analyses were performed on an ICP-MS (McConnell et al., 2002). Where δ^{18} O records were ambiguous, we additionally used the non-sea salt sulfur/sodium (nssS/Na) summer peak (indicative of summer solstice) as well as H₂O₂ to ascertain the annual δ^{18} O maxima. We counted annual peaks in the remaining major ionic species to validate and confirm the accuracy of the age assignment. Validation of the oxygen isotope based dating was done using (in this order): nssS, Na⁺, H₂O₂, Mg²⁺, Cl⁻, and Ca²⁺. Further confirmation of dating assignment was conducted using the Pb-enrichment time series wherein the 1979 spike in Pb enrichment was used as a tie-point. Total dating error is ± 1 year.

The 15.5-meter ice core was separated and packaged into 1-meter sections for transport. Extensive care was taken in handling the ice core to avoid any introduction of contamination that could compromise the trace analysis. During collection process, handling, and sample preparation, no products containing fluoropolymer coatings came into contact with the ice cores. Additionally, care was taken to scrape the potentially contaminated outer "rind" of the core sections, using only the inner uncontaminated ice for analysis. Depths corresponding to calendar years were determined as described above. Using this data, the dates for each 1meter section were determined. For sectioning the 1-meter ice cores into the equivalent years, we removed each 1-meter section from the packaging, and placed the firn and ice pieces onto aluminum foil, cleaned with methanol. We cut the firn or ice pieces at the depth that corresponded to each year with a pre-cleaned saw and then added the sectioned firn and ice for one year into a labeled pre-cleaned polypropylene bottle. Using the aluminum foil underneath the firn and ice pieces, we were able to easily pick up the foil and pour the firn and ice pieces into the labeled bottle, with minimal loss.

Section S2. Methods – Sample Preparation and Analysis

Prior to extraction, sub-samples were spiked with internal standards (IS) to monitor recovery and matrix effects. Prior to analysis, extracted samples were spiked with instrument performance standards (IP) to account for matrix effects and instrumental drift. Table S1 outlines the IS and IP standards as well as the analyte ion transitions used in the method analysis.

Table S1. Analyte quantifier and qualifier ion transitions (m/z) and internal standards used for PFAA analysis. Internal standards (IS) were used to evaluate recovery and matrix effects, while instrument performance (IP) standards were used to evaluate matrix effects only. Precursor ion/product ion transitions (m/z) are indicated in brackets.

Analyte	Quantifier/Qualifier Ion	Internal Standard	Instrument
	Transition (m/z)		Performance Standard
TFA	113 > 69		
PFPrA	163 > 119		
PFBA	213 > 169	¹³ C ₄ PFBA (217/172)	¹³ C ₃ PFBA (216/172)
PFPeA	263 > 219	¹³ C ₅ PFPeA (268/223)	¹³ C ₃ PFPeA (266/222)
PFHxA	313 > 269 / 313 > 119	¹³ C ₂ PFHxA (315/270)	¹³ C ₅ PFHxA (318/273)
PFHpA	363 > 319 / 363 > 119, 169	¹³ C ₄ PFHpA (367/322)	
PFOA	413 > 369 / 413 > 169	¹³ C ₄ PFOA (417/372)	¹³ C ₂ PFOA (415/370)
PFNA	463 > 419 / 463 > 219	¹³ C ₅ PFNA (468/423)	¹³ C ₉ PFNA (472/427)
PFDA	513 > 469 / 513 > 219	¹³ C ₂ PFDA (515/470)	¹³ C ₆ PFDA (519/474)
PFUnDA	563 > 519 / 563 > 319, 269	¹³ C ₂ PFUnDA (565/520)	¹³ C ₇ PFUnDA (570/525)
PFDoDA	613 > 569 / 613 > 169	¹³ C ₂ PFDoDA (615/570)	
PFTrDA	663 > 619 / 663 > 169	¹³ C ₂ PFDoDA (615/570)	
PFTeDA	713 > 669 / 713 > 169	¹³ C ₂ PFTeDA (715/670)	
PFHxDA	813 > 769 / 813 > 169	¹³ C ₂ PFHxDA (815/770)	
PFOcDA	913 > 869 / 913 > 169	¹³ C ₂ PFHxDA (815/770)	
PFBS	299 > 80 / 299 > 99	¹³ C ₃ PFBS (302/99)	
PFHxS	399 > 80 / 399 > 99	¹⁸ O ₂ PFHxS (403/103)	¹³ C ₃ PFHxS (402/99)
PFHpS	449 > 80 / 449 > 99	¹⁸ O ₂ PFHxS (403/103)	
PFOS	499 > 80 / 499 > 99	¹³ C ₄ PFOS (503/99)	¹³ C ₈ PFOS (507/99)
PFDS	599 > 80 / 599 > 99	¹³ C ₄ PFOS (503/99)	
FOSA	498 > 78	¹³ C ₈ FOSA (506/78)	
PFECHS	461 > 381 / 461 > 99	¹⁸ O ₂ PFHxS (403/103)	

The mean recoveries and standard errors for the IS and IP standards are provided

in Tables S2-S3. Recoveries are based on peak area comparisons to the solvent standards.

Table S2. Recovery of IS in sample extracts. IS analytes with numbers refers to the	e
different ion transitions (m/z). Samples (500 mL) were spiked with internal standar	ď
(30µL) prior to extraction. Recovery based on peak area comparison to solvent	
standard. Mean (standard error) recovery reported for n=42 samples from the	
Devon Ice Cap.	

IS	Recovery (%)
¹³ C ₄ PFBA	89 (1)
¹³ C ₅ PFPeA	79 (1)
¹³ C ₂ PFHxA	90 (1)
¹³ C ₄ PFHpA	94 (1)
¹³ C ₄ PFOA	96 (1)
¹³ C ₅ PFNA	102 (1)
$^{13}C_2 PFDA$	104 (1)
¹³ C ₇ PFUnDA	99 (1)
$^{13}C_2 PFDoDA$	70(1)
¹³ C ₂ PFTeDA	31 (1)
¹³ C ₂ PFHxDA	61 (2)
¹³ C ₄ PFOS 80	101 (1)
¹³ C ₄ PFOS 99	101 (1)
¹⁸ O ₂ PFHxS 103	101 (1)
¹⁸ O ₂ PFHxS 84	100(1)
¹³ C ₃ PFBS 80	101 (1)
¹³ C ₃ PFBS 99	102 (1)

Table S3. Recovery of IP in sample extracts. IP analytes with numbers refers to the different ion transitions (m/z). Samples (500 mL) were spiked with instrument performance standard (30μL) prior to extraction. Mean (standard error) recovery reported for n=42 samples from the Devon Ice Cap.

IP	Recovery (%)
¹³ C ₃ PFBA	110(1)
¹³ C ₃ PFPeA	96 (2)
¹³ C ₅ PFHxA	105 (1)
¹³ C ₂ PFOA	104 (1)
¹³ C ₉ PFNA	108 (1)
¹³ C ₆ PFDA	111 (1)
¹³ C ₂ PFUnDA	109 (2)
¹³ C ₈ PFOS 80	105 (1)
¹³ C ₈ PFOS 99	104 (1)
¹³ C ₃ PFHxS 99	104 (1)

We have amassed an annual data set on field blanks (HPLC grade water)

transported and exposed to the atmosphere in the Arctic location Resolute Bay, Nunavut

since 2010. These samples are shipped back to the lab, extracted and analyzed with methods analogous to the ice samples and compared to the same HPLC grade water stored in the lab. These results indicate that the environmental exposure and shipping do

not contribute to PFAS background contamination.

Table S4a. Concentrations of PFAS (ng L-1) in HPLC-grade water transported to Resolute Bay (Field) and HPLC-grade water kept in lab (Stay). Analytes PFUnDA, PFDoA, PFTrA, PFTeDA, PFBS, PFDS, PFOSA were <LOD in all field and stay

Dianks.										
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFOS	PFECHS	PFHxS
2011 Field	<lod< td=""><td>0.030</td><td>0.165</td><td>0.071</td><td>2.103</td><td>0.494</td><td>0.141</td><td>0.006</td><td>0.021</td><td><lod< td=""></lod<></td></lod<>	0.030	0.165	0.071	2.103	0.494	0.141	0.006	0.021	<lod< td=""></lod<>
2011 Stay	<lod< th=""><th>0.100</th><th>0.153</th><th>0.074</th><th>1.574</th><th>0.376</th><th>0.028</th><th>0.006</th><th>0.021</th><th><lod< th=""></lod<></th></lod<>	0.100	0.153	0.074	1.574	0.376	0.028	0.006	0.021	<lod< th=""></lod<>
2012 field	<lod< td=""><td><lod< td=""><td>0.210</td><td>0.057</td><td>1.818</td><td>0.068</td><td>0.011</td><td>0.037</td><td>0.030</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.210</td><td>0.057</td><td>1.818</td><td>0.068</td><td>0.011</td><td>0.037</td><td>0.030</td><td><lod< td=""></lod<></td></lod<>	0.210	0.057	1.818	0.068	0.011	0.037	0.030	<lod< td=""></lod<>
2012 field	<lod< td=""><td>0.045</td><td>0.208</td><td>0.045</td><td>2.268</td><td>0.091</td><td>0.024</td><td>0.091</td><td>0.138</td><td>0.011</td></lod<>	0.045	0.208	0.045	2.268	0.091	0.024	0.091	0.138	0.011
2012 stay	<lod< th=""><th>0.045</th><th>0.174</th><th>0.078</th><th>2.193</th><th>0.339</th><th>0.084</th><th>0.085</th><th>0.117</th><th>0.007</th></lod<>	0.045	0.174	0.078	2.193	0.339	0.084	0.085	0.117	0.007
2014 field	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>0.017</td><td>0.019</td><td><lod< td=""><td><lod< td=""><td>0.006</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.017</td><td>0.019</td><td><lod< td=""><td><lod< td=""><td>0.006</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.017</td><td>0.019</td><td><lod< td=""><td><lod< td=""><td>0.006</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.017</td><td>0.019</td><td><lod< td=""><td><lod< td=""><td>0.006</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	0.017	0.019	<lod< td=""><td><lod< td=""><td>0.006</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.006</td><td><lod< td=""></lod<></td></lod<>	0.006	<lod< td=""></lod<>
2014 stay	<lod< th=""><th><lod< th=""><th>0.020</th><th><lod< th=""><th>0.034</th><th>0.259</th><th>0.005</th><th>0.015</th><th>0.015</th><th><lod< th=""></lod<></th></lod<></th></lod<></th></lod<>	<lod< th=""><th>0.020</th><th><lod< th=""><th>0.034</th><th>0.259</th><th>0.005</th><th>0.015</th><th>0.015</th><th><lod< th=""></lod<></th></lod<></th></lod<>	0.020	<lod< th=""><th>0.034</th><th>0.259</th><th>0.005</th><th>0.015</th><th>0.015</th><th><lod< th=""></lod<></th></lod<>	0.034	0.259	0.005	0.015	0.015	<lod< th=""></lod<>
2015 field	0.17	0.007	0.022	0.016	0.044	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<>	0.002	<lod< td=""></lod<>
2015 field	<lod< td=""><td><lod< td=""><td>0.022</td><td>0.021</td><td>0.036</td><td>0.012</td><td><lod< td=""><td><lod< td=""><td>0.001</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.022</td><td>0.021</td><td>0.036</td><td>0.012</td><td><lod< td=""><td><lod< td=""><td>0.001</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	0.022	0.021	0.036	0.012	<lod< td=""><td><lod< td=""><td>0.001</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.001</td><td><lod< td=""></lod<></td></lod<>	0.001	<lod< td=""></lod<>
2015 stay	0.22	<lod< th=""><th>0.048</th><th>0.009</th><th>0.026</th><th><lod< th=""><th><lod< th=""><th><lod< th=""><th>0.006</th><th><lod< th=""></lod<></th></lod<></th></lod<></th></lod<></th></lod<>	0.048	0.009	0.026	<lod< th=""><th><lod< th=""><th><lod< th=""><th>0.006</th><th><lod< th=""></lod<></th></lod<></th></lod<></th></lod<>	<lod< th=""><th><lod< th=""><th>0.006</th><th><lod< th=""></lod<></th></lod<></th></lod<>	<lod< th=""><th>0.006</th><th><lod< th=""></lod<></th></lod<>	0.006	<lod< th=""></lod<>
2016 field	<lod< td=""><td><lod< td=""><td>0.443</td><td>0.294</td><td>0.070</td><td>0.057</td><td>0.065</td><td><lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.443</td><td>0.294</td><td>0.070</td><td>0.057</td><td>0.065</td><td><lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<></td></lod<>	0.443	0.294	0.070	0.057	0.065	<lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<>	0.002	<lod< td=""></lod<>
2016 field	<lod< td=""><td><lod< td=""><td>0.545</td><td>0.272</td><td>0.061</td><td>0.042</td><td>0.052</td><td><lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.545</td><td>0.272</td><td>0.061</td><td>0.042</td><td>0.052</td><td><lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<></td></lod<>	0.545	0.272	0.061	0.042	0.052	<lod< td=""><td>0.002</td><td><lod< td=""></lod<></td></lod<>	0.002	<lod< td=""></lod<>
2016 stay	<lod< th=""><th><lod< th=""><th>0.472</th><th>0.190</th><th>0.032</th><th>0.017</th><th>0.007</th><th>0.021</th><th>0.003</th><th>0.007</th></lod<></th></lod<>	<lod< th=""><th>0.472</th><th>0.190</th><th>0.032</th><th>0.017</th><th>0.007</th><th>0.021</th><th>0.003</th><th>0.007</th></lod<>	0.472	0.190	0.032	0.017	0.007	0.021	0.003	0.007
2017 field	<lod< td=""><td><lod< td=""><td>0.013</td><td>0.012</td><td>0.006</td><td><lod< td=""><td>0.009</td><td>0.062</td><td><lod< td=""><td>0.004</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.013</td><td>0.012</td><td>0.006</td><td><lod< td=""><td>0.009</td><td>0.062</td><td><lod< td=""><td>0.004</td></lod<></td></lod<></td></lod<>	0.013	0.012	0.006	<lod< td=""><td>0.009</td><td>0.062</td><td><lod< td=""><td>0.004</td></lod<></td></lod<>	0.009	0.062	<lod< td=""><td>0.004</td></lod<>	0.004
2017 field	0.093	<lod< td=""><td>0.007</td><td><lod< td=""><td>0.015</td><td><lod< td=""><td>0.012</td><td>0.001</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	0.007	<lod< td=""><td>0.015</td><td><lod< td=""><td>0.012</td><td>0.001</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	0.015	<lod< td=""><td>0.012</td><td>0.001</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	0.012	0.001	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
2017 stay	0.089	<lod< td=""><td>0.007</td><td><lod< td=""><td>0.019</td><td><lod< td=""><td>0.011</td><td>0.077</td><td><lod< td=""><td>0.004</td></lod<></td></lod<></td></lod<></td></lod<>	0.007	<lod< td=""><td>0.019</td><td><lod< td=""><td>0.011</td><td>0.077</td><td><lod< td=""><td>0.004</td></lod<></td></lod<></td></lod<>	0.019	<lod< td=""><td>0.011</td><td>0.077</td><td><lod< td=""><td>0.004</td></lod<></td></lod<>	0.011	0.077	<lod< td=""><td>0.004</td></lod<>	0.004

Table S4b. Difference in PFAS Concentrations (ng L⁻¹) between field and stay blanks in Table S4a. Numbers in red indicate higher field blank concentration compared to stay blank

compared to stay blank.										
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFOS	PFECHS	PFHxS
2011 Field	<lod< td=""><td>-0.070</td><td>0.012</td><td>-0.004</td><td>0.530</td><td>0.117</td><td>0.113</td><td>-0.000</td><td>-0.000</td><td><lod< td=""></lod<></td></lod<>	-0.070	0.012	-0.004	0.530	0.117	0.113	-0.000	-0.000	<lod< td=""></lod<>
2012 field	<lod< td=""><td><lod< td=""><td>0.036</td><td>-0.021</td><td>-0.375</td><td>-0.271</td><td>-0.073</td><td>-0.048</td><td>-0.087</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.036</td><td>-0.021</td><td>-0.375</td><td>-0.271</td><td>-0.073</td><td>-0.048</td><td>-0.087</td><td><lod< td=""></lod<></td></lod<>	0.036	-0.021	-0.375	-0.271	-0.073	-0.048	-0.087	<lod< td=""></lod<>
2012 field	<lod< td=""><td>-0.000</td><td>0.033</td><td>-<mark>0</mark>.033</td><td>0.076</td><td>-0.248</td><td>-0.060</td><td>0.006</td><td>0.021</td><td>0.004</td></lod<>	-0.000	0.033	- <mark>0</mark> .033	0.076	-0.248	-0.060	0.006	0.021	0.004
2014 field	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>-0.017</td><td>-0.240</td><td><lod< td=""><td><lod< td=""><td>-0.009</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>-0.017</td><td>-0.240</td><td><lod< td=""><td><lod< td=""><td>-0.009</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>-0.017</td><td>-0.240</td><td><lod< td=""><td><lod< td=""><td>-0.009</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>-0.017</td><td>-0.240</td><td><lod< td=""><td><lod< td=""><td>-0.009</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	-0.017	-0.240	<lod< td=""><td><lod< td=""><td>-0.009</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>-0.009</td><td><lod< td=""></lod<></td></lod<>	-0.009	<lod< td=""></lod<>
2015 field	<lod< td=""><td><lod< td=""><td>0.000</td><td>0.007</td><td>0.019</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>-0.004</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.000</td><td>0.007</td><td>0.019</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>-0.004</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	0.000	0.007	0.019	<lod< td=""><td><lod< td=""><td><lod< td=""><td>-0.004</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>-0.004</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>-0.004</td><td><lod< td=""></lod<></td></lod<>	-0.004	<lod< td=""></lod<>
2015 field	0.051	<lod< td=""><td>0.026</td><td>0.012</td><td>0.010</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>-0.005</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	0.026	0.012	0.010	<lod< td=""><td><lod< td=""><td><lod< td=""><td>-0.005</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>-0.005</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>-0.005</td><td><lod< td=""></lod<></td></lod<>	-0.005	<lod< td=""></lod<>
2016 field	<lod< td=""><td><lod< td=""><td>-0.029</td><td>0.104</td><td>0.038</td><td>0.040</td><td>0.058</td><td><lod< td=""><td>-0.001</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>-0.029</td><td>0.104</td><td>0.038</td><td>0.040</td><td>0.058</td><td><lod< td=""><td>-0.001</td><td><lod< td=""></lod<></td></lod<></td></lod<>	-0.029	0.104	0.038	0.040	0.058	<lod< td=""><td>-0.001</td><td><lod< td=""></lod<></td></lod<>	-0.001	<lod< td=""></lod<>
2016 field	<lod< td=""><td><lod< td=""><td>0.073</td><td>0.082</td><td>0.029</td><td>0.025</td><td>0.045</td><td><lod< td=""><td>-0.001</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.073</td><td>0.082</td><td>0.029</td><td>0.025</td><td>0.045</td><td><lod< td=""><td>-0.001</td><td><lod< td=""></lod<></td></lod<></td></lod<>	0.073	0.082	0.029	0.025	0.045	<lod< td=""><td>-0.001</td><td><lod< td=""></lod<></td></lod<>	-0.001	<lod< td=""></lod<>
2017 field	0.004	<lod< td=""><td>0.006</td><td><lod< td=""><td>-0.013</td><td><lod< td=""><td>0.000</td><td>-0.015</td><td><lod< td=""><td>0.001</td></lod<></td></lod<></td></lod<></td></lod<>	0.006	<lod< td=""><td>-0.013</td><td><lod< td=""><td>0.000</td><td>-0.015</td><td><lod< td=""><td>0.001</td></lod<></td></lod<></td></lod<>	-0.013	<lod< td=""><td>0.000</td><td>-0.015</td><td><lod< td=""><td>0.001</td></lod<></td></lod<>	0.000	-0.015	<lod< td=""><td>0.001</td></lod<>	0.001
2017 field	<lod< td=""><td><lod< td=""><td>0.000</td><td><lod< td=""><td>-0.003</td><td><lod< td=""><td>0.003</td><td>-0.076</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.000</td><td><lod< td=""><td>-0.003</td><td><lod< td=""><td>0.003</td><td>-0.076</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	0.000	<lod< td=""><td>-0.003</td><td><lod< td=""><td>0.003</td><td>-0.076</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	-0.003	<lod< td=""><td>0.003</td><td>-0.076</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	0.003	-0.076	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>

Analytical blanks (MeOH) and cartridge blanks were included in the method analysis. The method detection limit (MDL) is based on 3x the standard deviation of the cartridge

blanks. The majority of the PFAA analytes were not detected in the method blanks and are therefore below the instrument detection limit (IDL).

Perfluoroalkyl Substance	Method Blanks (ng/L)
TFA	<idl*< td=""></idl*<>
PFPrA	<idl< td=""></idl<>
PFBA	<idl< td=""></idl<>
PFPeA	<idl< td=""></idl<>
PFHxA	<idl< td=""></idl<>
PFHpA	<idl< td=""></idl<>
PFOA	0.010
PFNA	0.0042
PFDA	<idl< td=""></idl<>
PFUnDA	0.0070
PFDoDA	<idl< td=""></idl<>
PFTrDA	<idl< td=""></idl<>
PFTeDA	<idl< td=""></idl<>
PFHxDA	<idl< td=""></idl<>
PFOcDA	<idl< td=""></idl<>
PFBS	<idl< td=""></idl<>
PFHxS	0.0036
PFHpS	<idl< td=""></idl<>
PFOS	0.0017
PFDS	<idl< td=""></idl<>
PFECHS	<idl< td=""></idl<>
FOSA	0.0055

 Table S<u>5</u>4. Method detection limit (ng/L) based on 3x the standard deviation of the blanks.

*Analytes <IDL (instrument detection limit) were not detected in the method blanks. The limit of detection (LOD) and limit of quantitation (LOQ) respectively refer to the lowest quantity reliably distinguished from the blank and the lowest quantity quantified accurately. These values were calculated from two sets of MeOH blanks and three sets of standard calibration curves. The average noise from the calibration standards was subtracted from the max peak value to calculate the signal, which was divided by the average of the two standard deviations (SD) calculated from the blanks, to get signal/noise (S/N) ratios for each of the standards. The linear regression was determined for S/N vs. calculated concentration (ng/mL) of the standards, and LOD and LOQ were calculated based on the slope: LOD= 3/m and LOQ=10/m (m=slope) (y=mx).

Compound	Ion	LOD (pg/L) ¹	LOQ $(pg/L)^2$	Reproducibility ³
TFA		151	503	5.95
PFPrA		154	514	10.9
PFBA		39.8	133	7.37
PFPeA		10.4	34.7	8.53
PFHxA	269	2.52	8.41	9.67
	119	14.6	48.5	11.9
PFHpA	319	3.05	10.2	11.0
	169	1.79	5.96	11.4
PFOA	369	2.44	8.12	9.76
	169	1.44	4.81	3.48
PFNA	419	3.49	11.6	6.48
	219	1.44	4.80	7.67
PFDA	469	3.75	12.5	2.50
	219	1.18	3.94	15.1
PFUnDA	519	4.72	15.7	1.10
	269	1.17	3.91	4.25
PFDoDA	569	3.61	12.0	9.53
	169	1.54	5.12	9.67
PFTrDA	619	3.21	10.7	11.6
	169	0.98	3.25	5.65
PFTeDA	669	3.73	12.4	5.79
	169	1.02	3.39	6.02
PFHxDA	769	4.64	15.5	4.42
	169	1.85	6.16	1.23
PFOcDA	869	24.4	81.2	9.90
	169	31.9	106	13.4
PFBS	80	0.91	3.04	12.9
	99	3.62	12.1	7.56
PFHxS	80	0.37	1.23	7.40
	99	1.83	6.09	6.76
PFHpS	80	1.16	3.86	6.30
1	99	1.43	4.77	13.2
PFOS	99	1.27	4.23	25.8
PFDS	80	0.28	0.94	15.0
	99	1.33	4.44	9.21
PFECHS	99	0.94	3.14	3.25
	381	1.09	3.63	4.80
FOSA		0.18	0.59	14.8

Table S₆5. Instrument limit of detection (LOD) and quantitation (LOQ) for PFAAs.

l

¹LOD is concentration corresponding to signal-to-noise (S/N) ratios of 3. ²LOQ is concentration corresponding to S/N of 10. ³Reproducibility is given by the percent relative standard deviation for triplicate extraction and analysis of a sample.

Two analyses were conducted. For the first analysis, all of the PFCAs >C4 and the PFSAs were monitored. A summary of the chromatographic conditions for this gradient method is shown in Table S<u>76</u>. The inlet and mass spectrometric conditions for this analysis are summarized in Table S<u>87</u>. For the second analysis, the short chain PFCAs <C8 and PFOS were monitored. The method was a 15 minute run, at a flow rate of 0.300 mL min⁻¹, at 20% H₂O and 80% MeOH. The inlet and mass spectrometric conditions for this analysis were the same as the first (Table S<u>87</u>), except for column temperature, which was 40°C.

Time (minutes)	Flow rate (mL min ⁻¹)	% H ₂ O	% MeOH
0	0.400	75	25
0.5	0.400	75	25
5.0	0.400	15	85
5.1	0.400	0	100
5.6	0.400	0	100
7.0	0.550	0	100
9.0	0.400	75	25
12.0	0.400	75	25

Table S₇₆. Summary of chromatographic conditions.

Table S87. Summary of inlet and mass spectrometric conditions.

Capillary Voltage (kV)	1.7
Cone Voltage (V)	10
Source Offset (V)	50
Source Temperature (°C)	150
Desolvation Gas Temperature (°C)	450
Cone Gas Flow (L hr ⁻¹)	150
Desolvation Gas Flow (L hr ⁻¹)	800
Collision Gas Flow (mL min ⁻¹)	0.15
Nebulizer Pressure (bar)	7.0
Column Temperature (°C)	50 / 40
Injection Volume (µL)	9.0

Sub samples of the sectioned ice core (15 mL) were analyzed for major anions

and cations. Anion analysis was conducted using a Dionex ICS 2100 Ion

Chromatography System coupled to a conductivity detector, DS6 heated conductivity cell (Thermo Scientific, Mississauga, ON, Canada). Injection volumes were 1 mL using an autosampler (Dionex AS-DV) and preconcentrated on a concentrator column (TAC-ULP1, 5 mm x 23 mm). Anions were separated on an anion exchange column (DionexTM IonPacTM AS19, 4 mm x 250 mm) with guard column (AG19, 4 mm x 50 mm) using gradient elution with potassium hydroxide at 1.5 mL/min flow rate. The eluent was suppressed (AERS 500 ion suppressor, 4 mm) before the analytes were measured. Calibration standards were prepared by serial dilution from the stock standard (Dionex Seven Anion Standard II) and run with the sample analysis, check standards, and analytical blanks. LOD and LOQ values for the anions were calculated based on S/N 3 and 10, respectively. Detection limits ranged from 0.079 – 27 ppb.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis for cations was performed using an iCap 6500 Series ICP-OES (Thermo Scientific, Mississauga, ON, Canada). Thirty ice core samples were prepared by acidifying 10 mL water samples with 2% (v/v) HNO₃ prior to analysis. Calibration standards were prepared by serial dilution from the stock standard (Dionex Six Cation Standard). In addition to calibration standards, two check standards and a reagent blank were run every 20 samples. Yttrium was added inline as an internal standard. Each sample was analyzed four times using the following settings: nebulizer pump flush rate 100 rpm, analysis pump rate 50 rpm, pump relaxation time: 20 s, RF power: 1150 W, nebulizer gas: 0.55 L/min, auxillary gas: 0.5 L/min. Detection limits ranged from 0.40 – 20 ppb.

Section S3. PFAA Concentrations/Fluxes in the Devon Ice Cap and Comparisons

A number of PFCAs and PFSAs, including as well as FOSA were detected on the Devon Ice Cap. The concentrations of all the detected analytes for a single representative year (1996) are illustrated in Figure S1.



Figure S1. Concentrations of detected PFAS analytes (excluding C2 – C4 PFCAs) for the year 1996, as a single representative year. Light grey bars represent the LOD for measurements <LOD.

Concentrations (pg L⁻¹) of all the PFCA analytes detected on the Devon Ice Cap with depth and over time, are given in Table S<u>9</u>8, including values below the LOD and LOQ. PFSA and FOSA concentrations are given in Table S<u>10</u>9. No values are provided for the years 1980-1981, as there were no ice core samples available for those two years. Fluxes (ng m⁻² yr⁻¹) for the PFCAs and PFSAs are given in Tables S1<u>1</u>0-S1<u>2</u>4.

	-	Concentration (pg/L)								
Depth (cm)	Voor	DEDoA	ргн _у а	DFHnA	DEUV	DENA	DEDA	DEUnDA	DEDODA	DETrDA
10	2015	<10.4	43.0	55.0	102	140	17.0	<15.7	<3.61	<3.21
78	2013	<10.4	42.8	94.4	129	284	54.0	41.1	<3.61	<3.21
13/	2014	<10.4	95.2	235	207	440	72.3	66.8	<3.61	<3.21
134	2013	<10.4	193	438	207	596	84.2	145	<12.0	<3.21
1//	2012	<10.4	280	578	273	382	47.6	53.8	<3.61	<3.21
195	2011	<10.4	130	317	105	127	47.0	62 A	<3.61	<3.21
255	2010	<10.4	63.7	173	173	262	43.3	53.8	<3.61	<3.21
200	2009	73.8	104	175	181	310	45.5 70.8	75.2	<3.61	<3.21
262	2008	/ 5.0	38.7	135	156	274	20.0	70.1	<3.61	<3.21
200	2007	51.3	73 /	195	258	755	113	218	<12.0	1.96
390	2006	108	122	231	180	103	65.6	128	<5.12	<3.21
429 454	2005	88.8	94.9	198	226	403	69 2	75.4	<3.12	<3.21
487	2001	74.0	73.5	183	144	274	41.7	68.6	<3.61	<3.21
547	2003	126	120	241	185	302	70.8	88.6	5.71	<3.21
606	2002	54.2	48.9	93.1	116	159	31.0	29.3	<3.61	<3.21
648	2001	92.9	68.3	155	142	306	72.5	102	<3.61	<3.21
684	1999	54.5	80.8	178	195	555	72.6	98.1	6.84	<3.21
730	1008	<10.4	29.2	80.1	166	385	56.0	88.7	<3.61	<3.21
750	1990	<34.7	42.7	91.9	181	299	38.8	74.4	<3.61	<3.21
825	1006	62.9	101	243	333	584	81.8	106	<3.61	<3.21
857	1990	95.0	101	180	186	225	24.2	52.6	<3.61	<3.21
007	1004	81.0	90.8	140	221	223	37.1	45.2	<3.61	<3.21
902	1994	79.9	107	162	159	173	24.9	30.2	<3.61	<3.21
1006	1002	87.1	112	145	129	147	18.1	<15.7	<3.61	<3.21
1047	1992	79.4	82.0	145	178	213	37.8	41.9	<3.61	<3.21
1047	1991	81.4	67.5	173	145	163	28.5	25.7	<3.61	<3.21
1000	1990	<34.7	49.7	95.1	105	162	18.7	35.2	<3.61	<3.21
1144	1909	87.1	87.1	174	209	262	39.4	41.2	<3.61	<3.21
1216	1988	35.4	50.0	86.5	122	138	25.8	18.9	<3.61	<3.21
1210	1987	46.1	65.2	124	122	125	35.0	<15.7	<3.61	<3.21
1201	1980	39.2	44.2	98.3	93.8	101	<12.5	17.9	<3.61	<3.21
1294	1965	<34.7	67.1	115	112	117	16.4	16.4	<3.61	<3.21
1259	1904	<34.7	34.6	68.1	82.2	81.0	<12.5	<1.72	<3.61	<3.21
1336	1965	<34.7	56.2	113	107	133	19.9	<4.72	<3.61	<3.21
1394	1982	5,	50.2	115	107	155	17.7	\$15.7	5.01	0.21
1420	1901									
1438	1980	<34 7	40.4	85 5	82.5	70.4	<12.5	<4.72	<3.61	<3.21
14/3	19/9	<34.7		130	96.6	137	16.5	<15.7	<3.61	<3.21
1514	1970	<34.7	47.2	86.7	107	110	12.6	<4.72	<3.61	<3.21

Table S₂8. Depth profile (cm) of PFCA concentrations (pg L⁻¹) on the Devon Ice Cap. Values <LOD are identified in red and values <LOQ are identified in blue. All samples are <LOQ for PFTeDa, PFHxDA and PFOcDA and are therefore not shown here.

		Concentration (pg/L)					
Depth (cm)	Year	PFBS	PFHpS	PFOS	FOSA		
19	2015	6.80	<1.43	52.2	< 0.18		
78	2014	<3.62	9.28	94.8	< 0.18		
134	2013	4.19	8.77	391	< 0.18		
177	2012	<3.62	<1.43	50.8	1.50		
193	2011	<3.62	<1.43	103	< 0.18		
235	2010	<3.62	<1.43	32.0	< 0.18		
280	2009	<3.62	<1.43	27.8	< 0.18		
331	2008	<3.62	<1.43	30.5	< 0.18		
363	2007	<3.62	<1.43	21.9	< 0.18		
390	2006	<3.62	<1.43	29.8	< 0.18		
429	2005	<3.62	<1.43	29.0	1.69		
454	2004	<3.62	<1.43	32.7	< 0.18		
487	2003	<3.62	<1.43	24.8	7.00		
547	2002	<3.62	<1.43	32.5	< 0.18		
606	2001	<3.62	<1.43	11.9	< 0.18		
648	2000	<3.62	<1.43	24.6	1.48		
684	1999	<3.62	<1.43	21.5	13.2		
730	1998	<3.62	<1.43	37.5	71.9		
776	1997	<3.62	<1.43	17.8	43.6		
825	1996	<3.62	<1.43	19.7	41.9		
857	1995	<3.62	<1.43	29.5	41.2		
902	1994	<3.62	<1.43	35.7	76.8		
964	1993	<3.62	<1.43	20.2	29.7		
1006	1992	<3.62	<1.43	26.6	24.5		
1047	1991	<3.62	<1.43	26.6	37.5		
1088	1990	<3.62	<1.43	13.7	26.6		
1144	1989	<3.62	<1.43	21.7	33.1		
1187	1988	<3.62	<1.43	15.9	30.2		
1216	1987	<3.62	<1.43	22.8	22.2		
1251	1986	<3.62	<1.43	19.8	25.0		
1294	1985	<3.62	<1.43	16.9	27.9		
1317	1984	<3.62	<1.43	50.3	13.6		
1358	1983	<3.62	<1.43	18.7	3.72		
1394	1982	<3.62	<1.43	22.6	14.8		
1420	1981						
1458	1980						
1473	1979	<3.62	<1.43	15.8	< 0.18		
1514	1978	<3.62	<1.43	14.8	13.7		
1542	1977	<3.62	<1.43	13.8	10.2		

Table S109. Depth profile (cm) of PFSA concentrations (pg L⁻¹) on the Devon Ice Cap. Values <LOD are identified in red. All samples are <LOD for PFHxS, PFDA and PFECHS, and are therefore not shown here.

|

_	-	Flux (ng m ⁻² yr ⁻¹)								
Depth (cm)	Vear	PFPeA	PFHvA	PFHnA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA
19	2015	<lod< td=""><td>4 58</td><td>5.86</td><td>10.9</td><td>15.0</td><td>1.81</td><td>0.84</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	4 58	5.86	10.9	15.0	1.81	0.84	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
78	2013	<lod< td=""><td>6.91</td><td>15.2</td><td>20.8</td><td>45.8</td><td>8.70</td><td>6.63</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	6.91	15.2	20.8	45.8	8.70	6.63	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
134	2013	<lod< td=""><td>19.6</td><td>48.4</td><td>42.6</td><td>90.5</td><td>14.9</td><td>13.7</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	19.6	48.4	42.6	90.5	14.9	13.7	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
177	2012	33.9	38.2	86.7	54.5	118	16.7	28.6	1.19	<lod< td=""></lod<>
193	2011	13.7	18.8	38.7	18.6	25.6	3.19	3.60	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
235	2010	<lod< td=""><td>19.6</td><td>48.0</td><td>29.4</td><td>64.6</td><td>6.50</td><td>9.43</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	19.6	48.0	29.4	64.6	6.50	9.43	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
280	2009	<lod< td=""><td>10.5</td><td>28.5</td><td>28.4</td><td>43.1</td><td>7.11</td><td>8.85</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	10.5	28.5	28.4	43.1	7.11	8.85	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
331	2008	16.7	23.6	32.6	40.9	72.1	11.3	17.0	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
363	2007	<lod< td=""><td>5.50</td><td>19.2</td><td>22.1</td><td>38.9</td><td>4.12</td><td>10.0</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	5.50	19.2	22.1	38.9	4.12	10.0	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
390	2006	6.13	8.78	23.5	30.8	90.3	13.6	26.0	0.718	0.593
429	2005	17.7	19.9	37.8	29.4	66.0	10.7	20.9	0.419	<lod< td=""></lod<>
454	2004	9.19	9.82	20.5	23.4	45.9	7.16	7.81	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
487	2003	8.01	7.96	19.8	15.6	29.7	4.52	7.43	<lod< td=""><td>0.176</td></lod<>	0.176
547	2002	37.0	35.4	71.0	54.5	88.9	20.8	26.1	1.68	<lod< td=""></lod<>
606	2001	13.8	12.4	23.7	29.6	40.5	7.87	7.44	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
648	2000	16.7	12.3	27.9	25.5	55.1	13.1	18.3	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
684	1999	12.0	17.8	39.2	43.0	122	16.0	21.6	1.51	<lod< td=""></lod<>
730	1998	<lod< td=""><td>4.00</td><td>11.0</td><td>22.7</td><td>52.7</td><td>7.65</td><td>12.1</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	4.00	11.0	22.7	52.7	7.65	12.1	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
776	1997	3.15	7.76	16.7	32.9	54.4	7.06	13.5	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
825	1996	15.2	24.3	58.7	80.5	141	19.8	25.7	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
857	1995	14.2	18.3	27.0	27.8	33.7	3.62	7.86	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
902	1994	17.1	19.2	29.6	46.7	50.9	7.83	9.55	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
964	1993	24.1	32.2	48.8	48.1	52.3	7.53	9.10	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1006	1992	16.9	21.6	28.2	25.1	28.6	3.51	1.53	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1047	1991	15.9	16.4	28.9	35.6	42.6	7.57	8.38	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1088	1990	16.4	13.6	25.0	29.2	32.8	5.73	5.16	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1144	1989	4.80	13.8	26.3	29.0	44.9	5.17	9.73	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1187	1988	19.7	19.7	39.4	47.3	59.2	8.90	9.32	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1216	1987	5.44	7.67	13.3	18.7	21.2	3.96	2.89	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1251	1986	9.23	13.1	24.8	24.5	25.1	7.02	1.58	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1294	1985	8.33	9.41	20.9	20.0	21.4	1.33	3.81	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1317	1984	2.21	8.57	14.7	14.3	14.9	2.09	2.09	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1358	1983	3.79	7.56	14.9	18.0	17.7	1.37	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1394	1982	3.56	11.6	23.3	22.0	27.4	4.08	1.62	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1420	1981									
1458	1980									
1473	1979	1.38	3.21	6.79	6.56	5.59	0.50	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1514	1978	4.03	12.7	30.2	22.5	31.9	3.83	1.83	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
1542	1977	2.65	7.22	13.3	16.3	16.9	1.93	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>

Table S110. Depth profile (cm) of PFCA fluxes (ng m ⁻² yr ⁻¹) on the Devon Ice Cap
Values <lod <loq="" and="" are="" blue.<="" identified="" in="" red="" td="" values=""></lod>

		Flux (ng m ⁻² yr ⁻¹)					
Depth (cm)	Year	PFBS	PFHpS	PFOS	FOSA		
19	2015	0.725	<lod< td=""><td>5.57</td><td><lod< td=""></lod<></td></lod<>	5.57	<lod< td=""></lod<>		
78	2014	<lod< td=""><td>1.50</td><td>15.3</td><td><lod< td=""></lod<></td></lod<>	1.50	15.3	<lod< td=""></lod<>		
134	2013	0.861	1.80	80.3	<lod< td=""></lod<>		
177	2012	<lod< td=""><td><lod< td=""><td>10.1</td><td>0.297</td></lod<></td></lod<>	<lod< td=""><td>10.1</td><td>0.297</td></lod<>	10.1	0.297		
193	2011	<lod< td=""><td><lod< td=""><td>6.88</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>6.88</td><td><lod< td=""></lod<></td></lod<>	6.88	<lod< td=""></lod<>		
235	2010	<lod< td=""><td><lod< td=""><td>4.84</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>4.84</td><td><lod< td=""></lod<></td></lod<>	4.84	<lod< td=""></lod<>		
280	2009	<lod< td=""><td><lod< td=""><td>4.56</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>4.56</td><td><lod< td=""></lod<></td></lod<>	4.56	<lod< td=""></lod<>		
331	2008	<lod< td=""><td><lod< td=""><td>6.91</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>6.91</td><td><lod< td=""></lod<></td></lod<>	6.91	<lod< td=""></lod<>		
363	2007	<lod< td=""><td><lod< td=""><td>3.11</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>3.11</td><td><lod< td=""></lod<></td></lod<>	3.11	<lod< td=""></lod<>		
390	2006	<lod< td=""><td><lod< td=""><td>3.56</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>3.56</td><td><lod< td=""></lod<></td></lod<>	3.56	<lod< td=""></lod<>		
429	2005	<lod< td=""><td><lod< td=""><td>4.75</td><td>0.277</td></lod<></td></lod<>	<lod< td=""><td>4.75</td><td>0.277</td></lod<>	4.75	0.277		
454	2004	<lod< td=""><td><lod< td=""><td>3.39</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>3.39</td><td><lod< td=""></lod<></td></lod<>	3.39	<lod< td=""></lod<>		
487	2003	<lod< td=""><td><lod< td=""><td>2.69</td><td>0.758</td></lod<></td></lod<>	<lod< td=""><td>2.69</td><td>0.758</td></lod<>	2.69	0.758		
547	2002	<lod< td=""><td><lod< td=""><td>9.57</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>9.57</td><td><lod< td=""></lod<></td></lod<>	9.57	<lod< td=""></lod<>		
606	2001	<lod< td=""><td><lod< td=""><td>3.03</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>3.03</td><td><lod< td=""></lod<></td></lod<>	3.03	<lod< td=""></lod<>		
648	2000	<lod< td=""><td><lod< td=""><td>4.43</td><td>0.266</td></lod<></td></lod<>	<lod< td=""><td>4.43</td><td>0.266</td></lod<>	4.43	0.266		
684	1999	<lod< td=""><td><lod< td=""><td>4.74</td><td>2.91</td></lod<></td></lod<>	<lod< td=""><td>4.74</td><td>2.91</td></lod<>	4.74	2.91		
730	1998	<lod< td=""><td><lod< td=""><td>5.13</td><td>9.83</td></lod<></td></lod<>	<lod< td=""><td>5.13</td><td>9.83</td></lod<>	5.13	9.83		
776	1997	<lod< td=""><td><lod< td=""><td>3.23</td><td>7.93</td></lod<></td></lod<>	<lod< td=""><td>3.23</td><td>7.93</td></lod<>	3.23	7.93		
825	1996	<lod< td=""><td><lod< td=""><td>4.76</td><td>10.1</td></lod<></td></lod<>	<lod< td=""><td>4.76</td><td>10.1</td></lod<>	4.76	10.1		
857	1995	<lod< td=""><td><lod< td=""><td>4.42</td><td>6.16</td></lod<></td></lod<>	<lod< td=""><td>4.42</td><td>6.16</td></lod<>	4.42	6.16		
902	1994	<lod< td=""><td><lod< td=""><td>7.54</td><td>16.2</td></lod<></td></lod<>	<lod< td=""><td>7.54</td><td>16.2</td></lod<>	7.54	16.2		
964	1993	<lod< td=""><td><lod< td=""><td>6.10</td><td>8.95</td></lod<></td></lod<>	<lod< td=""><td>6.10</td><td>8.95</td></lod<>	6.10	8.95		
1006	1992	<lod< td=""><td><lod< td=""><td>5.15</td><td>4.75</td></lod<></td></lod<>	<lod< td=""><td>5.15</td><td>4.75</td></lod<>	5.15	4.75		
1047	1991	<lod< td=""><td><lod< td=""><td>5.33</td><td>7.49</td></lod<></td></lod<>	<lod< td=""><td>5.33</td><td>7.49</td></lod<>	5.33	7.49		
1088	1990	<lod< td=""><td><lod< td=""><td>2.75</td><td>5.36</td></lod<></td></lod<>	<lod< td=""><td>2.75</td><td>5.36</td></lod<>	2.75	5.36		
1144	1989	<lod< td=""><td><lod< td=""><td>6.02</td><td>9.17</td></lod<></td></lod<>	<lod< td=""><td>6.02</td><td>9.17</td></lod<>	6.02	9.17		
1187	1988	<lod< td=""><td><lod< td=""><td>3.59</td><td>6.81</td></lod<></td></lod<>	<lod< td=""><td>3.59</td><td>6.81</td></lod<>	3.59	6.81		
1216	1987	<lod< td=""><td><lod< td=""><td>3.50</td><td>3.40</td></lod<></td></lod<>	<lod< td=""><td>3.50</td><td>3.40</td></lod<>	3.50	3.40		
1251	1986	<lod< td=""><td><lod< td=""><td>3.97</td><td>5.01</td></lod<></td></lod<>	<lod< td=""><td>3.97</td><td>5.01</td></lod<>	3.97	5.01		
1294	1985	<lod< td=""><td><lod< td=""><td>3.59</td><td>5.93</td></lod<></td></lod<>	<lod< td=""><td>3.59</td><td>5.93</td></lod<>	3.59	5.93		
1317	1984	<lod< td=""><td><lod< td=""><td>6.42</td><td>1.73</td></lod<></td></lod<>	<lod< td=""><td>6.42</td><td>1.73</td></lod<>	6.42	1.73		
1358	1983	<lod< td=""><td><lod< td=""><td>4.08</td><td>0.81</td></lod<></td></lod<>	<lod< td=""><td>4.08</td><td>0.81</td></lod<>	4.08	0.81		
1394	1982	<lod< td=""><td><lod< td=""><td>4.65</td><td>3.03</td></lod<></td></lod<>	<lod< td=""><td>4.65</td><td>3.03</td></lod<>	4.65	3.03		
1420	1981						
1458	1980						
1473	1979	<lod< td=""><td><lod< td=""><td>1.26</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>1.26</td><td><lod< td=""></lod<></td></lod<>	1.26	<lod< td=""></lod<>		
1514	1978	<lod< td=""><td><lod< td=""><td>3.44</td><td>3.18</td></lod<></td></lod<>	<lod< td=""><td>3.44</td><td>3.18</td></lod<>	3.44	3.18		
1542	1977	<lod< td=""><td><lod< td=""><td>2.11</td><td>1.56</td></lod<></td></lod<>	<lod< td=""><td>2.11</td><td>1.56</td></lod<>	2.11	1.56		

Table S124. Depth profile (cm) of PFSA fluxes (ng m-2 yr-1) on the Devon Ice Cap.Values <LOD are identified in red.</td>

Fluxes, for each analyte per year, were calculated and given in ng m⁻² yr⁻¹. Fluxes were calculated as follows:

Flux =
$$\left[\frac{\text{Analyte Concentration } (ng \ L^{-1}) \times \text{ Total ice volume per year (L)}}{\text{Area } (m^2)}\right]$$
$$(\text{Area} = \pi r^2 \text{ where } r = 4.5 \text{ cm})$$

Temporal flux trend comparisons between the current study and the 2008 Devon Ice Cap study are provided in Figure S2 for the various PFCA analytes ranging from C4-C12. Figure S3 shows the calculated enrichment factor comparison between the three studies, for two sets of years; 1995-2000 and 2001-2006. The data sets generally agree albeit with some subtle differences (i.e. the mean +/- uncertainty overlap between the three studies), the exception being PFOS.








Figure S2. Temporal flux trends for a) PFPeA, b) PFHxA, c) PFHpA, d) PFOA, e) PFNA, f) PFDA, g) PFUnDA, and h) PFDoDA calculated from samples collected in 2008 (green) and 2015 (blue), along with three year moving averages for the 2015 study.



Figure S3. Calculated enrichment factor comparison between the sums of PFAA fluxes for 2001-2006 and 1995-2000, for the three Devon Ice Cap studies (MacInnis et al., 2017; Young et al., 2007).

Concentrations of PFCAs and PFSAs detected on the Devon Ice Cap were compared to a number of other studies in Table S1<u>3</u>2. PFAAs have been detected in a number of other samples including other snow cores, surface snow, precipitation, and lake, river and ocean water.

Matrix (Time)	Site (Reference)	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFOS	FOSA
Ice Core	Devon Ice Cap, Canadian	<10-204	30-280	55-578	82-333	70-755	<13-113	<5.0-218	12-391	<0.2-77
(1977-2015) Snow Core (1996-2008)	Colle Gnifetti, Swiss Alps ⁽¹⁾	<30-400	60-340	40-220	200-630	<120-310	<60-240	<100-180		
Snow Core (1980- 1999, 1996-2007)	Mt. Muztagata and Mt. Zuoqiupu, Tibetan Plateau ⁽²⁾	<25-142	<20-100	<20	38-243	<10-73	8.0-75	<5.0-11	<25-346	
Surface Snow (2006)	Longyearbyen, Svalbard ⁽³⁾	30 ± 4.0	76 ± 40	17 ± 6.0	113 ± 20	51 ± 9.0	22 ± 4.0	<5.0	34 ± 13	
Surface Snow (2004)	Greenland ⁽⁴⁾		<10-35	12-85	51-520	<30-77	110-149		25-137	24-39
Surface Snow (2010)	Lake Namco, Southern Tibetan Plateau ⁽²⁾	95-318	64-140	241-982	68-191	49-91	9.0-36	<5.0-18	25-64	
Surface Snow (2015)	Livingston Island, Antarctica ⁽⁵⁾	<mark>1.5-53</mark>	<mark>2.3-230</mark>	<mark>23-310</mark>	<mark>29-1300</mark>	<mark>14-330</mark>	<mark>3.1-600</mark>	<mark>2.0-150</mark>	<mark>1.3-750</mark>	
Precipitation	Rural U.S.	<100-	<100-	<100-	<100-	<100-				
(1998-1999)	(Ithaca, New York) ⁽⁶⁾	17,000	10,000	11,000	10,000	3,200				
Precipitation (2002)	Remote Canada	<100-1,900	<100-2,300	<100-5,400	<100-3,100	<100-				
(2002) Precipitation	Urban Canada (Toronto	200 1 100	200.000	<100.1700	1 000	5,500	<70.1.000	<70.2 700		
(2003-2004)	Ontario) ⁽⁶⁾	200-1,100	200-900	<100-1,700	11,000	300-9,700	<70-1,000	<70-3,700		
Precipitation (2007, 2008)	Japan (Tsukuba & Kawaguchi) ^(7, 8)	<50-4,970	<250-4,210	150-3,970	110-11,000	160- 17,500	40-2,110	60-2,060	<100- 4,210	<50-250
Precipitation (2007)	U.S.A. (Slingerlands & Downtown Albany) ⁽⁸⁾	<50-2,240	<250-1,110	170-1,130	250-9,420	210-5,390	100-420	<250- 1,910	<100-640	30-310
Lake Water (2004-2010)	The Great Lakes ⁽⁹⁾	120-2,390	244-7,160	47-642	5.0-958	4.0-26	5.0-10		95-9,480	
Lake Water (2003-2005)	Canadian Arctic Lakes (10)	300-49,000	400-16,000	200-6,100	500-29,000	200-5,900	500-2,300		900- 90,000	
River Water (2009)	Switzerland (11)	28-3,070	36-30,300	<28-30,000	<10-5,050	<34-2,560	<51-303		<38- 139,000	
Ocean Water (2005, 2008)	Arctic Ocean ⁽¹²⁾	11-84	7.0-54	3.0-47	2.0-33	0.9-79	1.0-32		9.0-39	1.0-44
Ocean Water (2010)	Arctic Ocean ⁽¹³⁾	<11-240	<20-67	<22-51	<35	<21-24	<9.0		<21-53	<81-260
Ocean Water (2008)	Atlantic Ocean ⁽¹⁴⁾	<3.0-37	< 5.0-223	<3.0-39	<6.0-37	<11-66	<6.0-48		<11-232	<3.0-67

Table S1<u>3</u>2. PFAA Concentration (pg L⁻¹) Comparisons with Other Abiotic Samples.

¹(Kirchgeorg et al., 2013), ²(Wang et al., 2014), ³(Kwok et al., 2013), ⁴(Butt et al., 2010), ⁵(Casal et al., 2017), ⁶(Scott et al., 2006), ⁷(Taniyasu et al., 2008), ⁸(Kwok et al., 2010), ⁹(De Silva et al., 2011), ¹⁰(Stock et al., 2007), ¹¹(Müller et al., 2011), ¹²(Benskin et al., 2012), ¹³(Cai et al., 2012), ¹⁴(Ahrens et al., 2010a)

Section S4. PFAA Deposition and Temporal Trends

The temporal flux trends for the C5 – C13 PFCAs detected on Devon Ice Cap are plotted in Figure S4.



Figure S4. Temporal flux trends for the long-chain PFCAs including PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA. Dotted lines represent annual fluxes and solid lines are the 5-year moving averages of the fluxes.

Table S143. Reproduced EPA's 2014 Report on Percent Reductions in Emissions and Product Content of PFOA, Precursors, and Higher Homologues from U.S. **Operations (cumulative percent reduction from baseline year through end of 2013)** (US EPA, 2014). Percentages in brackets refer to Canadian Percent Reductions (Environment and Climate Change Canada, 2006).

			% Reduction in Emissions	% Reduction in Product Content					
Company	Reduction Year	Chemical Category	% Reductions in total quantity of chemical(s) released from baseline year	Fluoropolymer Dispersions	Other Fluoropolymers	Telomer based products			
Arkema	2013	PFOA, PFOA salts and Higher Homologues	91%	100%	96% (100%)	N/A			
		Precursors		N/A		•			
Asahi	2013	PFOA, PFOA salts and Higher Homologues	100%	100% (100%)	100%	N/A (100%)			
		Precursors		N/A					
Ciba/BASF	2012	PFOA Higher Homologues Precursors		N/A					
Clariant	2013	PFOA and PFOA salts Direct	N/A						
		Precursors		T	T	1			
		PFOA	100%	100%	100%	100%			
Daikin	2013	Precursor and Higher Homologues	100%	N/A	N/A	100%			
		PFOA and PFOA salts	99.8%	00.0% (00.5%)	00.0% (00.5%)	00.09/1 (009/)			
DuPont	2013	Higher Homologues	None Reported	99.9% (99.3%)	99.9% (99.3%)	99.9% (99%)			
		Precursors	CBI	None Reported	None Reported	98% ¹			
3M/Dyneon	2013	PFOA, PFOA salts and Higher Homologues	100%	100%	N/A	No Telomer Production			
		Precursors		No Precursor Prod	uction				
Solvay Solexis	2013	PFOA, PFOA salts and Higher Homologues	>99.999%	>99.999%	>99.999%	N/A			
		Precursors		N/A					

N/A means not available. ¹Global number – regional data are CBI (confidential business information).

Table S154. Reproduced EPA's 2014 Report on Percent Reductions in Emissions and Product Content of PFOA, Precursors, and Higher Homologues from Non-U.S. and Non-Canadian Operations (cumulative percent reduction from baseline year through end of 2013) (US EPA, 2014).

			% Reduction in Emissions	% Redu	% Reduction in Product Content				
Company	Reduction Year	Chemical Category	% Reductions in total quantity of chemical(s) released from baseline year	Fluoropolymer Dispersions	Other Fluoropolymers	Telomer based products			
Arkema	2013	PFOA, PFOA salts and Higher Homologues	СВІ	N/A	CBI	N/A			
		Precursors		N/A	N/A				
Asahi	2013	PFOA, PFOA salts and Higher Homologues	99.8%	100%	99.9%	Negligible as compared to precursors			
		Precursors	100%	N/A	N/A	100%			
Ciba/BASF	2012	PFOA Higher Homologues Precursors	N/A						
Clariant	2013	PFOA and PFOA salts	>80%	None Reported	None Reported	90%			
Clarialit	2015	Direct Precursors	>85%	None Reported	None Reported	94%			
		PFOA							
Daikin	2013	Precursor and Higher Homologues		Not Reported	1				
		PFOA and PFOA salts	99.8%	99.9%	100%	99.9%2			
DuPont	2013	Higher Homologues	None Reported	<i></i>	10070	<i></i>			
		Precursors	CBI	None Reported	None Reported	98% ²			
3M/Dyneon	2013	PFOA, PFOA salts and Higher Homologues	100%	100%	100%	No Telomer Production			
		Precursors		No Precursor Prod	uction				
Solvay Solexis	2013	PFOA, PFOA salts and Higher Homologues	N/A es						
		Precursors		N/A					

N/A means not available. ²Global number reported.

Section S5. PFCA Homologues and Precursors

Pairs of PFCA homologues can be correlated with one another to determine if there are any statistically significant comparisons (Tables S165). Pairs of homologues are useful for determining if precursors play a significant role in LRT of these compounds. Table S1<u>6</u>5. Coefficients of determination (R²) and statistical significance (p) of PFAA homologues and FOSA (n=30). Weak correlations (0.3-0.5) are in green, moderate correlations (0.5-0.7) in blue and strong correlations (0.7-0.99) in red. Statistically significant p-values (p<0.0001) in bold.

	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFBS	PFHpS	PFOS
	$R^2 = 0.668$											
PFHxA	p<0.0001											
	$R^2 = 0.505$	$R^2 = 0.889$										
PFHpA	p<0.0001	p<0.0001										
	$R^2 = 0.298$	$R^2 = 0.437$	$R^2 = 0.527$									
PFOA	p= 0.0005	p<0.0001	p<0.0001									
	$R^2 = 0.095$	$R^2 = 0.186$	$R^2 = 0.334$	$R^2 = 0.708$								
PFNA	p= 0.0633	p= 0.0077	p=0.0002	p<0.0001								
	$R^2 = 0.129$	$R^2 = 0.134$	$R^2 = 0.246$	$R^2 = 0.592$	$R^2 = 0.865$							
PFDA	p= 0.0289	p= 0.0261	p=0.0018	p<0.0001	p<0.0001							
	$R^2 = 0.119$	$R^2 = 0.103$	$R^2 = 0.203$	$R^2 = 0.509$	$R^2 = 0.839$	$R^2 = 0.830$						
PFUnDA	p= 0.0363	p= 0.0527	p= 0.0051	p<0.0001	p<0.0001	p<0.0001						
	$R^2 = 0.130$	$R^2 = 0.064$	$R^2 = 0.114$	$R^2 = 0.208$	$R^2 = 0.477$	$R^2 = 0.511$	$R^2 = 0.554$					
PFDoDA	p= 0.0283	p= 0.1306	p=0.0406	p= 0.0046	p<0.0001	p<0.0001	p<0.0001					
	$R^2 = 0.022$	$R^2 = 0.009$	$R^2 = 0.040$	$R^2 = 0.108$	$R^2 = 0.324$	$R^2 = 0.294$	$R^2 = 0.475$	$R^2 = 0.279$				
PFTrDA	p= 0.3844	p= 0.5782	p=0.2376	p= 0.0474	p= 0.0002	p= 0.0005	p<0.0001	p= 0.0008				
	$R^2 = 0.092$	$R^2 = 0.015$	$R^2 = 0.015$	$R^2 = 0.012$	$R^2 = 7.6e-04$	$R^2 = 1.0e-06$	$R^2 = 0.017$	$R^2 = 0.015$	$R^2 = 0.005$			
PFBS	p= 0.0687	p= 0.4742	p=0.4728	p= 0.5185	p= 0.8711	p= 0.9532	p= 0.4397	p= 0.4651	p= 0.6737			
	$R^2 = 0.080$	$R^2 = 0.003$	$R^2 = 5.1e-05$	$R^2 = 2.4e-04$	$R^2 = 0.018$	$R^2 = 0.042$	$R^2 = 8.2e-06$	$R^2 = 0.013$	$R^2 = 0.004$	$R^2 = 0.229$		
PFHpS	p= 0.0897	p= 0.7328	p= 0.9664	p= 0.9269	p= 0.4289	p= 0.2216	p= 0.9866	p=0.4947	p= 0.6937	p= 0.0027		
	$R^2 = 0.008$	$R^2 = 0.043$	$R^2 = 0.072$	$R^2 = 0.042$	$R^2 = 0.055$	$R^2 = 0.070$	$R^2 = 0.007$	$R^2 = 0.003$	$R^2 = 9.5e-04$	$R^2 = 0.312$	$R^2 = 0.594$	
PFOS	p=0.6042	p= 0.2173	p=0.1095	p=0.2251	p=0.1637	p=0.1132	p= 0.6339	p=0.7302	p= 0.8563	p= 0.0003	p<0.0001	
	$R^2 = 6.9e-04$	$R^2 = 0.025$	$R^2 = 0.066$	$R^2 = 0.011$	$R^2 = 0.014$	$R^2 = 0.027$	$R^2 = 0.014$	$R^2 = 0.016$	$R^2 = 0.041$	$R^2 = 0.049$	$R^2 = 0.043$	$R^2 = 0.037$
FOSA	p= 0.8773	p= 0.3468	p=0.1245	p=0.5286	p= 0.4779	p= 0.3344	p=0.4883	p= 0.4572	p= 0.2323	p= 0.1888	p= 0.2198	p= 0.2517

PFCA molar flux ratio measurements for six pairs of PFPeA to PFUnDA homologues are illustrated in Figure S5. These pairs of PFCAs are most significant for PFHxA:PFHpA, PFHpA:PFOA, PFOA:PFNA, and PFDA:PFUnDA. The PFNA:PFDA homologue is the greatest outlier, and shows that the molar fluxes of PFNA are significantly higher than the fluxes for PFDA, detected on the Devon Ice Cap. This suggests that these two PFCA compounds are not likely coming from the same precursor source. The other pairs of homologues have a correlation close to one suggesting that they are likely coming from similar precursor sources.



Figure S5. Molar flux ratios for six pairs of PFCA homologues ranging from PFPeA to PFUnDA, as a function of depth and year.

Section S6. Long-Range Transport Mechanisms of PFAAs

Concentrations (μ g L⁻¹) of all the anions and cations detected on the Devon Ice Cap with depth and over time, are provided in Tables S1<u>76</u> and S1<u>87</u>, including values <LOD. Some years do not have values due to insufficient volume of sample available for analysis.

			Concentration (µg L ⁻¹)									
Depth	Year	Fluoride	Chloride	Nitrite	Nitrate	Sulfate	Phosphate	Acetate	Propionate	Formate	Butyrate	
19	2015											
78	2014	0.322	57.2	1.20	867	182	8.75	29.8	<4.06	30.4	<1.48	
134	2013	0.467	51.0	1.30	616	181	9.56	<27.2	<4.06	3.68	2.69	
177	2012	0.243	31.9	0.800	249	97.0	7.27	<27.2	<4.06	3.32	2.23	
193	2011											
235	2010	0.341	50.2	1.40	717	229	12.0	58.8	4.65	40.9	1.90	
280	2009	0.327	37.4	1.10	333	139	9.90	<27.2	<4.06	5.97	2.10	
331	2008											
363	2007	0.285	21.7	0.700	156	47.9	7.88	<27.2	<4.06	2.70	<1.48	
390	2006											
429	2005											
454	2004											
487	2003	0.122	26.3	0.800	288	74.4	8.75	101	4.92	50.2	3.67	
547	2002	0.308	39.4	0.800	504	114	6.53	165	4.86	59.9	5.04	
606	2001	0.271	39.6	0.500	414	78.8	6.53	57.0	<4.06	11.3	3.60	
648	2000	0.154	29.2	0.600	320	95.5	<2.86	179	<4.06	3.07	3.67	
684	1999	0.103	51.2	0.900	597	153	<2.86	418	<4.06	29.7	<1.48	
730	1998	< 0.079	60.3	0.600	522	96.0	8.55	<27.2	<4.06	3.15	1.57	
776	1997	0.112	28.4	0.400	224	63.3	7.74	68.0	<4.06	13.4	<1.48	
825	1996	0.201	36.2	0.400	336	107	6.40	70.8	<4.06	20.7	2.23	
857	1995	0.210	42.8	0.800	399	117	7.20	<27.2	<4.06	2.87	4.19	
902	1994	0.210	30.7	0.700	413	131	8.28	<27.2	<4.06	3.07	2.75	
964	1993	0.229	42.5	0.400	530	233	9.42	89.6	4.13	37.7	5.04	
1006	1992	0.243	32.7	0.700	483	218	7.67	63.2	<4.06	66.5	3.41	
1047	1991	0.187	34.7	2.60	335	124	5.52	43.1	<4.06	7.33	3.21	
1088	1990	0.248	36.9	0.600	171	330	7.74	<27.2	<4.06	4.07	2.55	
1144	1989	0.131	32.9	0.700	381	146	6.53	76.3	<4.06	3.57	3.01	
1187	1988	0.182	55.8	0.400	308	163	<2.86	<27.2	<4.06	3.26	2.29	
1216	1987	0.136	25.1	0.500	408	159	6.33	149	<4.06	6.39	2.29	
1251	1986	0.154	50.2	0.400	380	147	7.00	66.2	<4.06	3.43	3.21	
1294	1985	0.164	17.4	0.400	165	106	8.68	<27.2	<4.06	3.12	4.45	
1317	1984	< 0.079	61.3	0.400	420	192	9.09	51.2	<4.06	8.87	4.52	
1358	1983	0.103	41.6	0.400	277	169	9.29	46.0	<4.06	10.7	3.01	
1394	1982	0.187	35.3	0.400	269	176	8.75	<27.2	<4.06	3.88	2.75	
1420	1981											
1458	1980											
1473	1979											
1514	1978	0.107	42.7	0.300	410	198	7.81	<27.2	<4.06	4.94	2.88	
1542	1977	< 0.079	42.0	0.400	220	172	8.89	67.1	<4.06	16.2	2.23	

Table S176. Depth profile (cm) of anion concentrations (µg L⁻¹) on the Devon Ice Cap. Values <LOD are identified in red and years without values were not measured due to lack of sample available.

		Concentration (µg L ⁻¹)									
Depth	Year	Sodium	Potassium	Calcium	Magnesium	Manganese	Aluminum	Iron	Silicon		
19	2015										
78	2014	65.6	35.9	702	25.3	0.984	<2.00	78.3	31.9		
134	2013	60.6	22.6	786	39.7	0.775	14.6	8.34	41.2		
177	2012	49.2	<20.0	742	41.8	1.15	18.4	18.5	25.0		
193	2011										
235	2010	55.4	36.4	772	42.8	1.19	20.1	14.3	25.9		
280	2009	40.3	30.7	592	35.1	1.09	19.9	7.91	26.8		
331	2008										
363	2007	27.1	25.2	380	22.7	0.578	14.0	24.1	24.9		
390	2006										
429	2005										
454	2004										
487	2003	29.9	27.3	294	10.2	0.417	9.32	6.68	27.9		
547	2002	41.2	38.4	344	13.7	< 0.400	14.6	5.40	27.9		
606	2001	40.4	33.4	283	12.5	< 0.400	9.05	3.25	23.6		
648	2000	32.6	22.5	291	9.78	0.934	9.54	3.04	27.0		
684	1999	69.2	31.2	478	23.1	< 0.400	11.2	3.31	20.0		
730	1998	64.4	63.4	363	14.7	< 0.400	17.4	3.60	20.6		
776	1997	24.5	<20.0	229	8.98	< 0.400	9.03	3.16	21.1		
825	1996	33.4	<20.0	266	12.8	< 0.400	8.52	2.85	14.3		
857	1995	43.3	32.4	300	13.8	< 0.400	4.93	2.70	15.3		
902	1994	37.2	21.1	310	15.2	< 0.400	17.2	3.76	31.6		
964	1993	45.7	26.3	409	13.4	< 0.400	12.0	6.15	19.4		
1006	1992	46.8	42.5	354	14.4	2.30	11.1	3.07	17.7		
1047	1991	53.3	39.3	362	14.3	< 0.400	9.89	19.2	31.4		
1088	1990	81.2	<20.0	199	15.8	< 0.400	14.1	2.65	26.0		
1144	1989	24.3	22.5	324	11.2	< 0.400	13.4	13.1	27.8		
1187	1988	47.2	30.2	261	15.1	< 0.400	11.3	<2.00	21.7		
1216	1987	26.3	20.4	330	12.7	< 0.400	16.2	3.23	18.0		
1251	1986	47.7	<20.0	316	10.8	< 0.400	8.88	5.96	17.4		
1294	1985	13.5	<20.0	207	9.21	< 0.400	7.49	2.26	21.1		
1317	1984	67.7	39.6	370	21.8	0.569	26.2	8.24	21.7		
1358	1983	40.8	33.3	290	13.1	< 0.400	11.0	4.14	23.0		
1394	1982	37.1	35.7	251	16.5	0.922	13.0	2.80	35.4		
1420	1981										
1458	1980										
1473	1979										
1514	1978	51.1	23.9	326	13.8	< 0.400	7.38	4.45	22.9		
1542	1977	39.6	<20.0	228	13.6	< 0.400	14.7	21.7	29.4		

Table S187. Depth profile (cm) of cation concentrations (μg L⁻¹) on the Devon Ice Cap. Values <LOD are identified in red and years without values were not measured due to lack of sample available.

The vertical profiles for the anions and cations are plotted in Figures S68-S79. These plots illustrate the depth record in ion concentrations over time, showing that nitrate, sulfate and calcium were some of the ions detected at the highest concentrations over time in the Devon Ice Cap.



Figure S6. Vertical profile of anion concentrations (ng mL⁻¹) on a log scale, per depth in the ice core and by year. Anions detected include F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} .



Figure S7. Vertical profile of cation concentrations (ng mL⁻¹) on a log scale, per depth in the ice core and by year. Cations detected include Na⁺, K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Al³⁺ and Fe³⁺.

The contribution of non-sea salt was calculated for a number of cations and anions that are common ions in marine aerosols, as summarized in Table S198. The average molar concentration of the ions in the core from 1977-2015 was first determined. The average non-sea salt concentrations were then determined by subtracting the individual ion molar concentrations from the sodium molar concentration multiplied by the expected ion to sodium ratio. The ratio values used in the calculations are from (Libes, 2009). The sea salt concentration and percentage of non-sea salt were determined by taking the difference between the total average concentration and the average non-sea salt concentration.

Table S1<u>9</u>8. Non-sea salt and sea salt component concentrations (conc.) (µmol/L) of select ions in the ice core.

	Na ⁺	\mathbf{K}^{+}	Mg^{2+}	Ca ²⁺	Cl	SO ₄ ²⁻	F-
Average molar conc. in ice core (µmol/L)	1.94	0.68	0.74	9.45	10.73	1.54	0.0103
Non-sea salt conc. (µmol/L)		0.64	0.52	9.41	8.39	1.42	0.0100
Sea salt conc. (µmol/L)		0.04	0.22	0.04	2.33	0.12	0.0003
Contribution of non-sea salt component		93.8	70.3	99.5	78.2	92.4	97.2

Figure S8 illustrates the comparison between ice cap and ocean homologue patterns, which is another technique used to assess the influence of marine aerosol deposition of PFAAs to the Devon Ice Cap. Only a few ocean samples had measurements to compare to PFHpS and FOSA that were detected on the ice cap (Benskin et al., 2012) (Cai et al., 2012) (Zhao et al., 2012). Both PFBS and PFHxS were measured in most of the ocean samples but were not detected on the ice cap, therefore no comparisons between these PFSAs could be made (Benskin et al., 2012) (Busch et al., 2010) (Cai et al., 2012) (Ahrens et al., 2010b) (Ahrens et al., 2010a) (Ahrens et al., 2009):



2003), Canadian Artic Arenpeiago (Benskin et al., 2012), Greenhald Sea (Zhao et al., 2012) (Busch et al., 2010), North Sea (Ahrens et al., 2010b), North Atlantic Ocean (Ahrens et al., 2010a) (Ahrens et al., 2009) (Zhao et al., 2012) (Scott et al., 2005), and North Pacific Ocean (Cai et al., 2012) in 1998, 2005, and 2007 to 2010.

The PFAAs were correlated with the cations and anions to determine if there were any statistically significant correlations. The cation and anion correlations are summarized in Tables S2019 and S210, respectively. For the cations, only calcium and magnesium had weak to moderate correlations with statistical significance. For the anions, only fluoride had weak correlations, as well as the organic acid, propionate.

									<mark>Non-Sea Salt</mark>	<mark>Non-Sea Salt</mark>
	Sodium	Potassium	Calcium	Magnesium	Manganese	Aluminum	Iron	Silicon	<mark>Calcium</mark>	Magnesium
	$R^2 = 0.055$	$R^2 = 0.045$	$R^2 = 0.508$	$R^2 = 0.497$	$R^2 = 0.091$	$R^2 = 0.179$	$R^2 = 0.040$	$R^2 = 0.138$	$R^2 = 0.509$	<mark>R²= 0.498</mark>
TFA	p=0.2126	p= 0.2607	p<0.0001	p<0.0001	p=0.1060	p= 0.0198	p= 0.2885	p= 0.0436	<mark>p<0.0001</mark>	<mark>p<0.0001</mark>
	$R^2 = 0.020$	$R^2 = 0.029$	$R^2 = 0.410$	$R^2 = 0.515$	$R^2 = 0.191$	$R^2 = 0.085$	$R^2 = 0.037$	$R^2 = 0.034$	$R^2 = 0.411$	$R^2 = 0.549$
PFPrA	p=0.4585	p= 0.3657	p= 0.0001	p<0.0001	p=0.0158	p= 0.1176	p= 0.3064	p= 0.3316	p = 0.0001	<mark>p<0.0001</mark>
	$R^2 = 0.079$	$R^2 = 0.024$	$R^2 = 0.481$	$R^2 = 0.531$	$R^2 = 0.109$	$R^2 = 0.243$	$R^2 = 0.018$	$R^2 = 0.079$	$R^2 = 0.481$	$R^2 = 0.519$
PFBA	p=0.1335	p= 0.4155	p<0.0001	p<0.0001	p=0.0749	p= 0.0056	p= 0.4740	p= 0.1328	<mark>p<0.0001</mark>	<mark>p<0.0001</mark>
	$R^2 = 0.132$	$R^2 = 0.053$	$R^2 = 0.045$	$R^2 = 0.019$	$R^2 = 0.005$	$R^2 = 0.133$	$R^2 = 0.022$	$R^2 = 0.064$	$R^2 = 0.045$	$R^2 = 0.004$
PFPeA	p=0.0485	p= 0.2228	p= 0.2595	p= 0.4639	p=0.6973	p= 0.0477	p= 0.4295	p= 0.1763	<mark>p=0.2618</mark>	<mark>p= 0.7455</mark>
	$R^2 = 0.218$	$R^2 = 0.061$	$R^2 = 0.372$	$R^2 = 0.297$	$R^2 = 0.069$	$R^2 = 0.276$	$R^2 = 0.003$	$R^2 = 0.133$	$R^2 = 0.371$	$R^2 = 0.226$
PFHxA	p=0.0093	p= 0.1872	p= 0.0003	p= 0.0018	p=0.1598	p= 0.0028	p= 0.7582	p= 0.0477	p= 0.0003	<mark>p= 0.0079</mark>
	$R^2 = 0.161$	$R^2 = 0.015$	$R^2 = 0.465$	$R^2 = 0.471$	$R^2 = 0.058$	$R^2 = 0.251$	$R^2 = 2.6e-04$	$R^2 = 0.125$	<mark>R²= 0.464</mark>	<mark>R²= 0.416</mark>
PFHpA	p=0.0282	p= 0.5194	p<0.0001	p<0.0001	p=0.2006	p= 0.0048	p= 0.9331	p= 0.0548	<mark>p<0.0001</mark> _	p=0.0001
	$R^2 = 0.147$	$R^2 = 0.009$	$R^2 = 0.204$	$R^2 = 0.180$	$R^2 = 3.8e-04$	$R^2 = 0.152$	$R^2 = 0.007$	$R^2 = 0.092$	$R^2 = 0.203$	<mark>R²= 0.134</mark>
PFOA	p=0.0367	p= 0.6272	p= 0.0123	p= 0.0196	p=0.9183	p= 0.0330	p= 0.6504	p= 0.1041	p= 0.0124	<mark>p= 0.0467</mark>
	$R^2 = 0.130$	$R^2 = 0.002$	$R^2 = 0.332$	$R^2 = 0.333$	$R^2 = 0.006$	$R^2 = 0.073$	$R^2 = 9.0e-04$	$R^2 = 0.040$	$R^2 = 0.332$	<mark>R²= 0.289</mark>
PFNA	p=0.0508	p= 0.8080	p= 0.0009	p=0.0008	p=0.6734	p=0.1477	p= 0.8746	p= 0.2900	p= 0.0009	<mark>p= 0.0022</mark>
	$R^2 = 0.166$	$R^2 = 0.024$	$R^2 = 0.302$	$R^2 = 0.241$	$R^2 = 0.005$	$R^2 = 0.086$	$R^2 = 0.004$	$R^2 = 0.112$	$R^2 = 0.302$	<mark>R²= 0.188</mark>
PFDA	p=0.0253	p= 0.4149	p= 0.0016	p= 0.0058	p=0.7170	p= 0.1148	p= 0.7503	p= 0.0703	p= 0.0017	<mark>p= 0.0167</mark>
	$R^2 = 0.037$	$R^2 = 0.003$	$R^2 = 0.210$	$R^2 = 0.193$	$R^2 = 9.8e-04$	$R^2 = 0.086$	$R^2 = 2.2e-04$	$R^2 = 0.034$	$R^2 = 0.211$	<mark>R²= 0.186</mark>
PFUnDA	p=0.3079	p= 0.7756	p= 0.0108	p= 0.0151	p=0.8695	p= 0.1152	p= 0.9380	p= 0.3299	p= 0.0108	<mark>p= 0.0174</mark>
	$R^2 = 0.123$	$R^2 = 0.061$	$R^2 = 0.143$	$R^2 = 0.128$	$R^2 = 3.4e-04$	$R^2 = 0.136$	$R^2 = 6.3e-04$	$R^2 = 0.041$	<mark>R²= 0.142</mark>	<mark>R²= 0.091</mark>
PFDoDA	p=0.0570	p=0.1874	p= 0.0396	p= 0.0526	p=0.9233	p= 0.0448	p= 0.8950	p= 0.2846	<mark>p= 0.0399</mark>	<mark>p= 0.1049</mark>
	$R^2 = 0.010$	$R^2 = 0.086$	$R^2 = 0.064$	$R^2 = 0.114$	$R^2 = 0.043$	$R^2 = 0.007$	$R^2 = 0.010$	$R^2 = 0.008$	<mark>R²= 0.064</mark>	<mark>R²= 0.155</mark>
PFTrDA	p=0.6057	p= 0.1159	p=0.1786	p= 0.0675	p=0.2713	p= 0.6708	p= 0.6073	p= 0.6295	p= 0.1770	<mark>p= 0.0312</mark>
	$R^2 = 0.054$	$R^2 = 5.8e-04$	$R^2 = 0.301$	$R^2 = 0.259$	$R^2 = 0.034$	$R^2 = 0.001$	$R^2 = 0.081$	$R^2 = 0.167$	$R^2 = 0.302$	<mark>R²= 0.247</mark>
PFBS	p=0.2152	p= 0.8995	p= 0.0017	p= 0.0041	p=0.3295	p= 0.8526	p=0.1276	p= 0.0248	p= 0.0017	<mark>p= 0.0052</mark>
	$R^2 = 0.053$	$R^2 = 2.0e-06$	$R^2 = 0.300$	$R^2 = 0.211$	$R^2 = 0.046$	$R^2 = 0.039$	$R^2 = 0.329$	$R^2 = 0.118$	$R^2 = 0.300$	<mark>R²= 0.196</mark>
PFHpS	p=0.2212	p= 0.9940	p= 0.0017	p= 0.0107	p=0.2545	p=0.2937	p= 0.0009	p= 0.0628	p= 0.0017	<mark>p= 0.0142</mark>
	$R^2 = 0.064$	$R^2 = 1.5e-04$	$R^2 = 0.353$	$R^2 = 0.329$	$R^2 = 0.038$	$R^2 = 0.018$	$R^2 = 0.019$	$R^2 = 0.214$	$R^2 = 0.353$	$R^2 = 0.316$
PFOS	p=0.1758	p= 0.9495	p= 0.0005	p= 0.0009	p=0.3010	p= 0.4797	p= 0.4676	p= 0.0100	p = 0.0005	p = 0.0012
	$R^2 = 8.3e-05$	$R^2 = 5.4e-04$	$R^2 = 0.061$	$R^2 = 0.112$	$R^2 = 0.098$	$R^2 = 0.012$	$R^2 = 0.056$	$R^2 = 4.4e-05$	$R^2 = 0.061$	<mark>R²= 0.134</mark>
FOSA	p= 0.9618	p= 0.9034	p=0.1879	p= 0.0703	p=0.0922	p= 0.5677	p= 0.2083	p= 0.9723	p= 0.1870	<mark>р= 0.0466</mark>

Table S2019. Coefficients of determination (R²) and statistical significance (p) of PFAA homologues, as well as FOSA, cations, and metals (n=25). Weak correlations (R²=0.3-0.5) shown in green and moderate correlations (R²=0.5-0.7) in blue. Statistically significant p-values (p<0.0001) in bold.

	Fluoride	Chloride	Nitrite	Nitrate	Sulfate	Phosphate	Acetate	Propionate	Formate	Butyrate
	$R^2 = 0.455$	$R^2 = 0.041$	$R^2 = 0.126$	$R^2 = 0.204$	$R^2 = 6.1e-06$	$R^2 = 0.066$	$R^2 = 0.034$	$R^2 = 0.320$	$R^2 = 0.246$	$R^2 = 0.051$
TFA	p<0.0001	p= 0.2813	p = 0.0547	p = 0.0122	p= 0.9897	p = 0.1712	p= 0.3283	p = 0.0011	p= 0.0054	p= 0.2317
	$\hat{R}^2 = 0.311$	$R^2 = 0.015$	$R^2 = 0.094$	$R^2 = 0.113$	$R^2 = 2.7e-04$	$R^2 = 0.067$	$R^2 = 0.003$	$R^2 = 0.055$	$R^2 = 0.051$	$R^2 = 2.2e-04$
PFPrA	p = 0.0014	p= 0.5167	p=0.0994	p= 0.0695	p=0.9319	p= 0.1657	p=0.7880	p= 0.2166	p= 0.2287	p= 0.9373
	$R^2 = 0.306$	$R^2 = 0.026$	$R^2 = 0.145$	$R^2 = 0.125$	$R^2 = 0.007$	$R^2 = 0.043$	$R^2 = 0.043$	$R^2 = 0.286$	$R^2 = 0.215$	$R^2 = 0.033$
PFBA	p= 0.0015	p= 0.3905	p=0.0382	p=0.0554	p= 0.6690	p = 0.2740	p=0.2709	p= 0.0023	p= 0.0098	p= 0.3386
	$R^2 = 0.162$	$R^2 = 0.076$	$R^2 = 0.040$	$R^2 = 0.059$	$R^2 = 0.051$	$R^2 = 4.6e-04$	$R^2 = 0.095$	$R^2 = 0.324$	$R^2 = 0.226$	$R^2 = 0.350$
PFPeA	p= 0.0273	p= 0.1410	p=0.2891	p=0.1972	p=0.2292	p= 0.9108	p= 0.0977	p= 0.0010	p= 0.0079	p= 0.0006
	$R^2 = 0.383$	$R^2 = 0.194$	$R^2 = 0.095$	$R^2 = 0.244$	$R^2 = 0.141$	$R^2 = 0.081$	$R^2 = 0.071$	$R^2 = 0.422$	$R^2 = 0.292$	$R^2 = 0.297$
PFHxA	p= 0.0003	p= 0.0147	p=0.0970	p= 0.0056	p= 0.0408	p= 0.1262	p= 0.1558	p= 0.0001	p= 0.0020	p= 0.0018
	$R^2 = 0.376$	$R^2 = 0.142$	$R^2 = 0.094$	$R^2 = 0.166$	$R^2 = 0.047$	$R^2 = 0.043$	$R^2 = 0.060$	$R^2 = 0.308$	$R^2 = 0.169$	$R^2 = 0.130$
PFHpA	p= 0.0003	p= 0.0400	p=0.1000	p=0.0256	p=0.2515	p=0.2724	p=0.1920	p= 0.0014	p= 0.0239	p= 0.0505
	$R^2 = 0.286$	$R^2 = 0.191$	$R^2 = 0.072$	$R^2 = 0.159$	$R^2 = 0.034$	$R^2 = 0.016$	$R^2 = 0.074$	$R^2 = 0.189$	$R^2 = 0.101$	$R^2 = 0.074$
PFOA	p= 0.0023	p= 0.0158	p= 0.1522	p= 0.0290	p=0.3289	p= 0.5063	p= 0.1460	p= 0.0163	p= 0.0867	p= 0.1455
	$R^2 = 0.166$	$R^2 = 0.121$	$R^2 = 0.077$	$R^2 = 0.160$	$R^2 = 1.7e-04$	$R^2 = 0.008$	$R^2 = 0.205$	$R^2 = 0.072$	$R^2 = 0.069$	$R^2 = 9.4e-04$
PFNA	p= 0.0253	p= 0.0600	p=0.1364	p=0.0284	p= 0.9454	p= 0.6431	p= 0.0119	p= 0.1527	p= 0.1612	p= 0.8725
	$R^2 = 0.278$	$R^2 = 0.164$	$R^2 = 0.115$	$R^2 = 0.218$	$R^2 = 1.8e-04$	$R^2 = 0.011$	$R^2 = 0.238$	$R^2 = 0.156$	$R^2 = 0.127$	$R^2 = 0.020$
PFDA	p= 0.0028	p= 0.0264	p= 0.0674	p= 0.0092	p= 0.9441	p= 0.5795	p= 0.0062	p= 0.0306	p= 0.0532	p= 0.4534
	$R^2 = 0.133$	$R^2 = 0.030$	$R^2 = 0.068$	$R^2 = 0.073$	$R^2 = 0.037$	$R^2 = 0.027$	$R^2 = 0.201$	$R^2 = 0.111$	$R^2 = 0.074$	$R^2 = 0.003$
PFUnDA	p= 0.0479	p= 0.3591	p=0.1647	p=0.1496	p= 0.3061	p= 0.3858	p= 0.0129	p= 0.0720	p= 0.1459	p= 0.7628
	$R^2 = 0.049$	$R^2 = 0.076$	$R^2 = 0.038$	$R^2 = 0.114$	$R^2 = 0.002$	$R^2 = 0.028$	$R^2 = 0.492$	$R^2 = 0.180$	$R^2 = 0.216$	$R^2 = 0.026$
PFDoDA	p= 0.2388	p= 0.1401	p=0.3044	p=0.0687	p= 0.7997	p= 0.3759	p<0.0001	p= 0.0194	p= 0.0096	p= 0.3903
	$R^2 = 0.002$	$R^2 = 0.067$	$R^2 = 0.001$	$R^2 = 0.058$	$R^2 = 0.066$	$R^2 = 0.006$	$R^2 = 0.012$	$R^2 = 5.9e-04$	$R^2 = 0.002$	$R^2 = 0.012$
PFTrDA	p=0.8204	p= 0.1684	p= 0.8661	p= 0.1993	p=0.1704	p= 0.6739	p= 0.5577	p= 0.8989	p= 0.7987	p= 0.5645
	$R^2 = 0.245$	$R^2 = 0.048$	$R^2 = 0.085$	$R^2 = 0.118$	$R^2 = 0.009$	$R^2 = 0.031$	$R^2 = 0.018$	$R^2 = 0.005$	$R^2 = 0.006$	$R^2 = 0.008$
PFBS	p= 0.0054	p= 0.2469	p= 0.1179	p=0.0631	p= 0.6197	p= 0.3556	p=0.4785	p= 0.6987	p= 0.6842	p= 0.6391
	$R^2 = 0.204$	$R^2 = 0.048$	$R^2 = 0.086$	$R^2 = 0.169$	$R^2 = 0.006$	$R^2 = 0.022$	$R^2 = 0.022$	$R^2 = 0.009$	$R^2 = 7.0e-04$	$R^2 = 0.031$
PFHpS	p= 0.0122	p= 0.2472	p=0.1161	p=0.0241	p=0.6749	p= 0.4392	p= 0.4389	p= 0.6229	p= 0.8896	p= 0.3502
	$R^2 = 0.289$	$R^2 = 0.057$	$R^2 = 0.101$	$R^2 = 0.119$	$R^2 = 0.012$	$R^2 = 0.045$	$R^2 = 0.010$	$R^2 = 1.6e-05$	$R^2 = 0.002$	$R^2 = 5.2e-05$
PFOS	p= 0.0022	p= 0.2047	p=0.0868	p= 0.0620	p= 0.5680	p= 0.2580	p= 0.6075	p= 0.9835	p= 0.8009	p= 0.9697
	$R^2 = 0.023$	$R^2 = 0.007$	$R^2 = 3.0e-04$	$R^2 = 9.5e-04$	$R^2 = 0.028$	$R^2 = 0.013$	$R^2 = 0.008$	$R^2 = 3.5e-05$	$R^2 = 0.012$	$R^2 = 0.018$
FOSA	p=0.4283	p= 0.3286	p=0.9276	p=0.8713	p=0.3760	p= 0.5445	p= 0.6362	p=0.9754	p=0.5658	p=0.4771

Table S210. Coefficients of determination (R²) and statistical significance (p) of PFAA homologues, as well as FOSA, anions, and organic acids (n=27). Weak correlations (R²=0.3-0.5) are shown in green. Statistically significant p-values (p<0.0001) in bold.

Table S22. Coefficients of determination (R²) and statistical significance (p) between PFAS deposition and Arctic sea ice extent and area. Sea ice time series are based on SMMR/ SMM/I satellite observations. The slope sign is indicated as either positive (+) or negative (-) for each PFAA compound. Correlations are ranked in terms of significance by purple>blue>orange, but in general, the correlations are not very significant between PFASs and sea ice minimum.

Table S21. Coefficients of determination (R²) and statistical significance (p) between PFAS deposition and Arctic sca ice extent and area. The slope sign is indicated as either positive (+) or negative (-) for each PFAA compound. Correlations are ranked in terms of significance by purple>blue>orange, but in general, the correlations are not very significant between PFASs and sea ice minimum.

	<mark>Sea Ice Extent</mark>	<mark>Sea Ice Area</mark>	<mark>Slope Sign (+/-)</mark>
	$R^2 = 0.047$	$R^2 = 0.050$	
<mark>PFPeA</mark>	p=0.2088	p=0.1959	+
	$R^2 = 0.217$	$R^2 = 0.215$	
PFHxA	<mark>p=0.0048</mark>	<mark>p=0.0050</mark>	+
	$R^2 = 0.295$	$R^2 = 0.295$	
<mark>PFHpA</mark>	<mark>p=0.0007</mark>	<mark>p=0.0007</mark>	+
	$R^2 = 0.106$	$R^2 = 0.114$	
PFOA	<mark>р=0.0559</mark>	<mark>р=0.0470</mark>	+
	$R^2 = 0.183$	<mark>R²= 0.199</mark>	
PFNA	p=0.0104	<mark>p=0.0073</mark>	+
	$R^2 = 0.129$	$R^2 = 0.142$	
<mark>PFDA</mark>	<mark>p=0.0339</mark>	<mark>p=0.0258</mark>	+
	$R^2 = 0.161$	$R^2 = 0.169$	
PFUnDA	<mark>p=0.0168</mark>	<mark>p=0.0140</mark>	+
	$R^2 = 0.058$	$R^2 = 0.067$	
<mark>PFD0DA</mark>	<mark>p=0.1648</mark>	<mark>p=0.1334</mark>	+
	$R^2 = 0.030$	$R^2 = 0.033$	
<mark>PFTrDA</mark>	p=0.3172	<mark>p=0.2938</mark>	+
	$R^2 = 0.007$	$R^2 = 0.017$	
<mark>PFOcDA</mark>	p=0.6437	<mark>p=0.4618</mark>	-
	$R^2 = 0.113$	$R^2 = 0.116$	
<mark>PFBS</mark>	p=0.0485	p=0.0451	+
	$R^2 = 0.055$	$R^2 = 0.049$	
<mark>PFHpS</mark>	p=0.1735	p=0.2000	+
	$R^2 = 0.099$	$R^2 = 0.085$	
PFOS	p=0.0659	p=0.0887	+
FOSA	$R^2 = 0.266$	$R^2 = 0.261$	



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