

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 “long-range 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 longer-chain 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 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.” (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 Chemical Economics Handbook 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<sup>-2</sup> yr<sup>-1</sup> 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<sup>-2</sup> yr<sup>-1</sup> 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 source 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 re-entering 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 PFSA, **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.
- Armitage, J. M., Macleod, M. and Cousins, I. T.: Comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources, *Environ. Sci. Technol.*, 43(15), 5830–5836, 2009a.
- Armitage, J. M., Macleod, M. and Cousins, I. T.: Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model, *Environ. Sci. Technol.*, 43, 1134–1140, 2009b.
- Benskin, J. P., Muir, D. C. G., Scott, B. F., Spencer, C., De Silva, A. O., Kylin, H., Martin, J. W., Morris, A., Lohmann, R., Tomy, G., Rosenberg, B., Taniyasu, S. and Yamashita, N.: Perfluoroalkyl Acids in the Atlantic and Canadian Arctic Oceans, *Environ. Sci. Technol.*, 46(11), 5815–5823, doi:10.1021/es300578x, 2012.
- Braune, B. M. and Letcher, R. J.: Perfluorinated Sulfonate and Carboxylate Compounds in Eggs of Seabirds Breeding in the Canadian Arctic: Temporal Trends (1975–2011) and Interspecies Comparison, *Environ. Sci. Technol.*, 47, 616–624, doi:10.1021/es303733d, 2013.
- Cai, M., Xie, Z., Möller, A., Yin, Z., Huang, P., Cai, M., Yang, H., Sturm, R., He, J. and Ebinghaus, R.: Polyfluorinated compounds in the atmosphere along a cruise pathway from the Japan Sea to the Arctic Ocean, *Chemosphere*, 87(9), 989–997, doi:10.1016/j.chemosphere.2011.11.010, 2012a.
- Cai, M., Zhao, Z., Yin, Z., Ahrens, L., Huang, P., Cai, M., Yang, H., He, J., Sturm, R., Ebinghaus, R. and Xie, Z.: SI: Occurrence of Perfluoroalkyl Compounds in Surface Waters from the North Pacific to the Arctic Ocean, *Environ. Sci. Technol.*, 46(2), 661–668, doi:10.1021/es2026278, 2012b.
- Calafat, A. M., Kuklanyik, Z., Reidy, J. A., Caudill, S. P., Tully, J. S. and Needham, L. L.: Serum Concentrations of 11 Polyfluoroalkyl Compounds in the U.S. Population: Data from the National Health and Nutrition Examination Survey (NHANES) 1999–2000, *Environ. Sci. Technol.*, 41(7), 2237–2242, doi:10.1021/es062686m, 2007.
- Cheng, J., Psillakis, E., Hoffman, M. R. and Colussi, A. J.: Acid dissociation versus molecular association of perfluoroalkyl oxoacids: Environmental implications, *J. Phys. Chem. A*, 113, 8152–8156, 2009.
- D’eon, J. C., Hurley, M. D., Wallington, T. J. and Mabury, S. A.: Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>N(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OH: Kinetics and mechanism of reaction with OH, *Environ. Sci. Technol.*, 40(6), 1862–1868, 2006.
- Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P. and Wallington, T. J.: Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids, *Environ. Sci. Technol.*, 38(12), 3316–3321, 2004.
- Gawor, A., Shunthirasingham, C., Hayward, S. J., Lei, Y. D., Gouin, T., Mmerek, B. T.,

- Masamba, W., Ruepert, C., Castillo, L. E., Shoeib, M., Lee, S. C., Harner, T. and Wania, F.: Neutral polyfluoroalkyl substances in the global Atmosphere, *Environ. Sci. Process. Impacts*, 16(3), 404–413, doi:10.1039/C3EM00499F, 2014.
- Gewurtz, S. B., Martin, P. A., Letcher, R. J., Burgess, N. M., Champoux, L., Elliott, J. E. and Weseloh, D. V. C.: Spatio-temporal trends and monitoring design of perfluoroalkyl acids in the eggs of gull (*Larid*) species from across Canada and parts of the United States, *Sci. Total Environ.*, 565, 440–450, doi:10.1016/j.scitotenv.2016.04.149, 2016.
- Lewis, E. R. and Schwartz, S. E.: *Sea Salt Aerosol Production: Mechanisms, Methods, Measurements and Models - A Critical Review*, Geophys. Monogr. Ser., vol. 152, AGU, Washington, D. C., 2004.
- McMurdo, C. J., Ellis, D. A., Webster, E., Butler, J., Christensen, R. D. and Reid, L. K.: Aerosol Enrichment of the Surfactant PFO and Mediation of the Water–Air Transport of Gaseous PFOA, *Environ. Sci. Technol.*, 42(11), 3969–3974, doi:10.1021/es7032026, 2008.
- Olsen, G. W., Church, T. R., Miller, J. P., Burris, J. M., Hansen, K. J., Lundberg, J. K., Armitage, J. B., Herron, R. M., Medhdizadehkashi, Z., Nobilette, J. B., O’Neill, E. M., Mandel, J. H. and Zobel, L. R.: Perfluorooctanesulfonate and Other Fluorochemicals in the Serum of American Red Cross Adult Blood Donors, *Environ. Health Perspect.*, 111(16), 1892–1901, doi:10.1289/ehp.6316, 2003.
- Plassmann, M. M., Meyer, T., Lei, Y. D., Wania, F., McLachlan, M. S. and Berger, U.: Laboratory Studies on the Fate of Perfluoroalkyl Carboxylates and Sulfonates during Snowmelt, *Environ. Sci. Technol.*, 45(16), 6872–6878, doi:10.1021/es201249d, 2011.
- Prevedouros, K., Cousins, I. T., Buck, R. C. and Korzeniowski, S. H.: Sources, Fate and Transport of Perfluorocarboxylates, *Environ. Sci. Technol.*, 40(1), 32–44, doi:10.1021/es0512475, 2006.
- Thackray, C. P. and Selin, N. E.: Uncertainty and variability in atmospheric formation of PFCAs, *Atmos. Chem. Phys. Discuss.*, (August), 1–18, doi:10.5194/acp-2016-679, 2016.
- Wallington, T. J., Hurley, M. D., Xia, J., Wuebbles, D. J., Sillman, S., Ito, A., Penner, J. E., Ellis, D. A., Martin, J., Mabury, S. A., Nielsen, O. J. and Sulbaek Andersen, M. P.: Formation of C7F15COOH (PFOA) and Other Perfluorocarboxylic Acids during the Atmospheric Oxidation of 8:2 Fluorotelomer Alcohol, *Environ. Sci. Technol.*, 40(3), 924–930, doi:10.1021/es051858x, 2006.
- Young, C. J. and Mabury, S. A.: *Atmospheric Perfluorinated Acid Precursors: Chemistry, Occurrence, and Impacts*, edited by D. M. Whitacre, Springer New York, New York, NY., 2010.
- Zhao, Z., Xie, Z., Möller, A., Sturm, R., Tang, J., Zhang, G. and Ebinghaus, R.: Distribution and long-range transport of polyfluoroalkyl substances in the Arctic, Atlantic Ocean and Antarctic coast, *Environ. Pollut.*, 170, 71–77, doi:10.1016/j.envpol.2012.06.004, 2012.