Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1009-RC1, 2017

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Continuous Non-Marine Inputs of Per- and Polyfluoroalkyl Substances to the High Arctic: A Multi-Decadal Temporal Record" *by* Heidi M. Pickard et al.

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Received and published: 14 December 2017

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.

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Discussion paper

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

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

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".

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

P1, L18: Typo – "perfluorooctane"

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.

P1, L20: I would replace "emission and use" by "manufacture, use and emission".

P2, L3: After "(PFAAs)" insert ", a sub-group of PFASs,"

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.

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

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).

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.

P2, L20: See comment above on marine aerosols.

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.

P4, L27 and 29: To avoid any confusion, the use of the terms “long-chain” and “short-chain” 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.

P6, L23: Typo – Longyearbyen (also in Table S12).

P6, L24: What is meant here by “short-chain PFCAs”?

P7, L14: What was “unusual”? The PFAA concentrations, fluxes, or homologue profiles?

P8, L3: Replace “more than” by “at least”.

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.

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 co-workers).

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.

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/fluoropolymers-chemical-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.

P10, L1 and 2: Use “PFASs” as the plural of “PFAS”.

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.

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.

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?

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”?

P12, L28, 29, 30 and 31: “2013” or “2012”?

P13, L6: Change acronyms for NAFSEs and NAFSEs.

P13, L17: Typo – Longyearbyen

P13, L31: Replace “compound” by “homologue”.

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.

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?

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?

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

P15, L11: Typo – Arctic

P15, L13 and 14: Change “concentrations” to “fractions” or “proportions”?

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?

P15, Figure 5: Are the Devon Ice Cap values taken solely from the present study, or are previous measurements included (for 2005, at least)?

P16, L8: See previous comment on “heat transfer fluids”.

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”?

P17, L16: After “PFAAs” insert “in the atmosphere”.

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.

P21, L28: Typo – Kallenborn

P24, L5-6: This paper has now been published in Atmospheric Chemistry and Physics,

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so the citation should be replaced by that of the final published version.

P24, L7: It would be useful to provide a web-link, as in the Supplementary Information.

Specific comments on the Supplementary Information

P8, Table S4: The concentration units should be indicated.

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”.

P17, penultimate line: “albeit with some subtle differences”.

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.

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

P23, Table S13 and P24, Table S14: Does N/A mean “not available” or “not applicable”? In Table S14, does “non-US” include Canada?

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

P33, 2nd Kwok reference: Typo – Kallenborn

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