

A 50-year Record of Perfluoroalkyl Acids in the High Arctic: Implications for Global and Local Transport

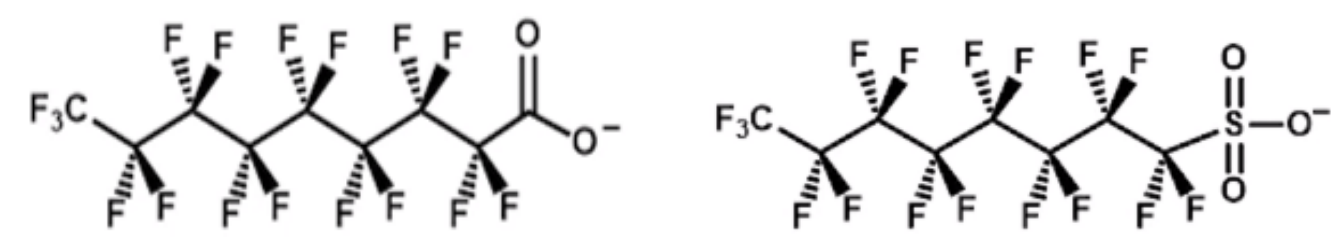
Daniel Persaud¹, Alison S. Criscitiello², Christine Spencer³, Igor Lehnherr⁴, Derek C G. Muir³, Amila O. De Silva³, and Cora J. Young¹

¹Department of Chemistry, York University, Toronto, ON, ²Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada. ³Aquatic Contaminants Research Division, Environmental and Climate Change Canada, Burlington, Ontario, Canada. ⁴Department of Geography, Geomatics and Environment, University of Toronto-Mississauga, Mississauga, Ontario, Canada

Introduction

PFAAs are.....

- A class of anthropogenic compounds containing the highly stable CF₂ bond.
- Predominately used in the “non-stick” and fire suppressant technologies.
- Extremely persistent and distributed ubiquitously in the environment.
- Grouped into classes based on structure and number of carbons.

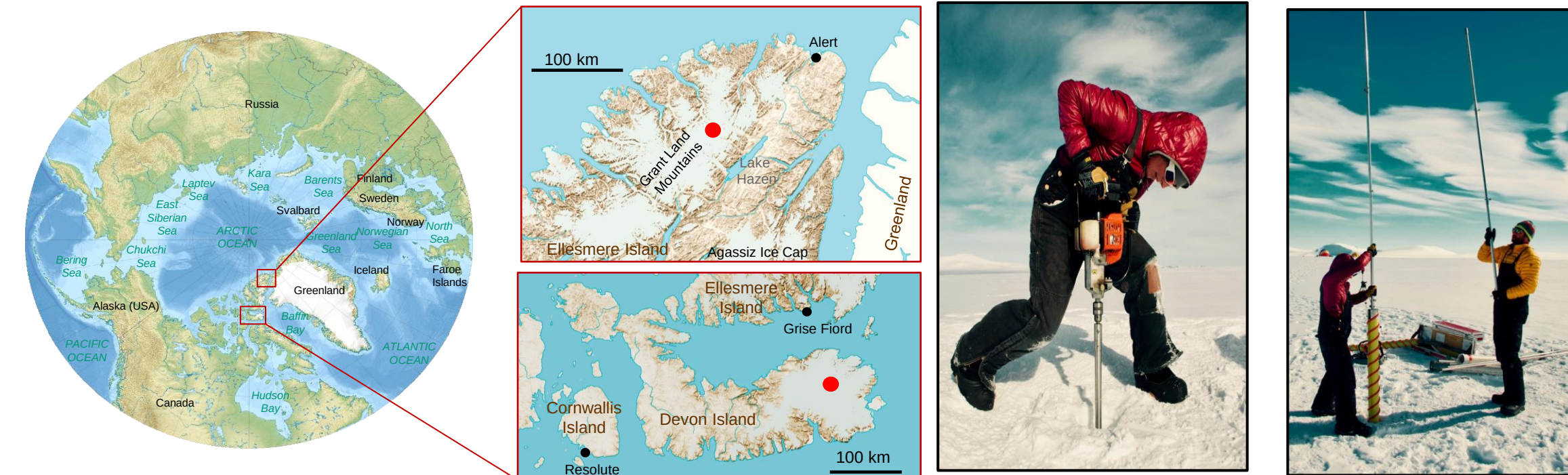


Structure of (A) perfluorononanoic acid, a PFCA and (B) perfluorooctane sulfonic acid, a PFSA.

Motivation and Objectives

- These compounds have been detected frequently in remote locations where local sources are not expected.^{2,3}
- We collected an ice core from the Canadian High Arctic. The core represents 50 years of deposition, which accounts for the **longest deposition record of PFCAs in the Arctic** and the **most extensive record of PFSA globally**.
- We used this extensive PFAA deposition record to examine (i) PFAA deposition profiles (ii) temporal variations; (iii) evidence of indirect and aerosol transport; and (iv) causes of episodic pulses of high deposition.

Methods



A 16 m ice core was collected from Mt. Oxford icefield in May 2017. Previously, a core was collected from Devon Ice Cap (1977 – 2014)², ~800 km south of the current site.

Ice core sectioning



Ice core was sectioned into annual years using MeOH rinsed tools.

Ice core analysis



All samples were concentrated using SPE using Oasis WAX cartridges. Analysis was done using LC-MS/MS.

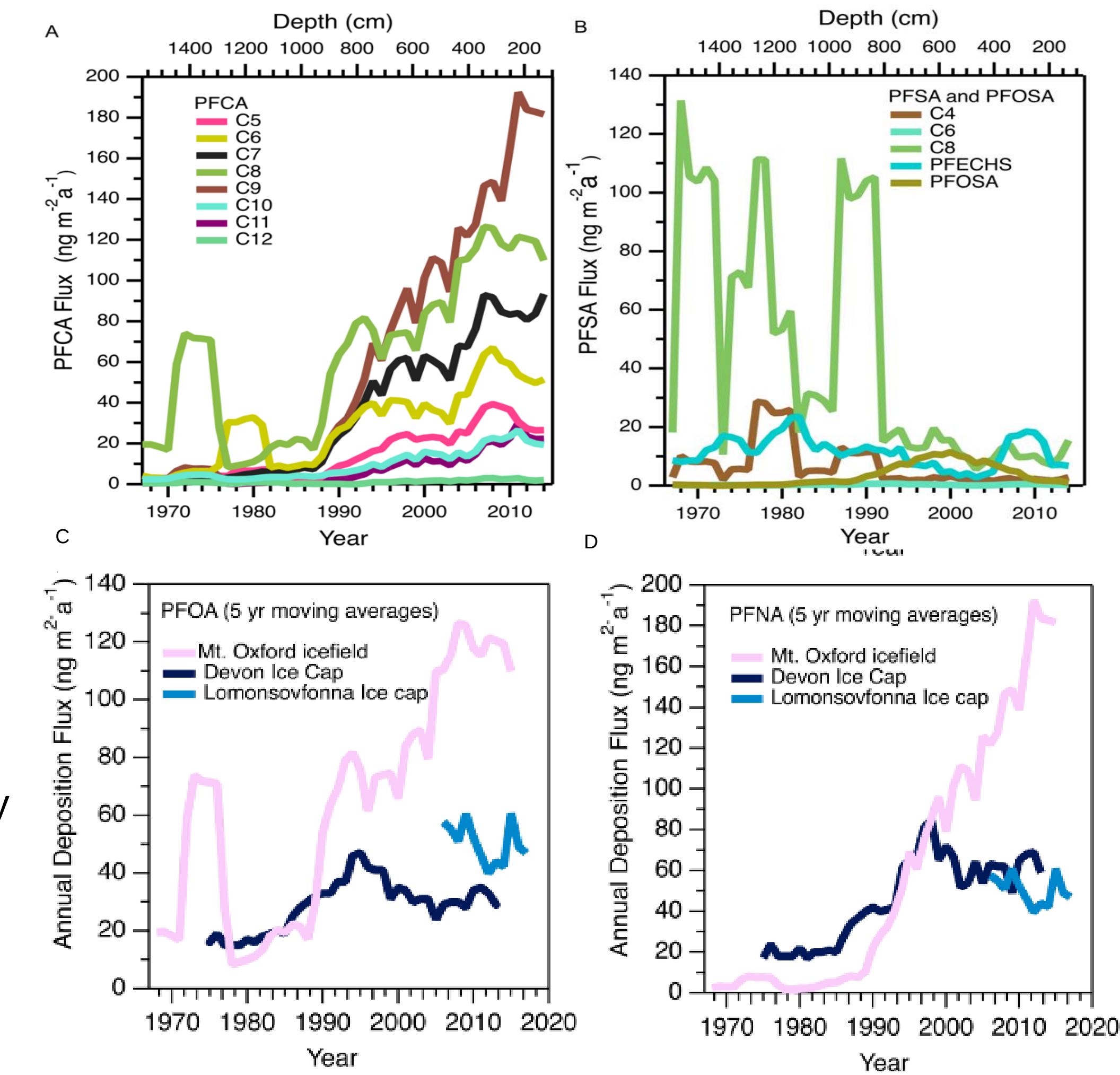
PFAA Deposition on Mt. Oxford icefield

PFCA deposition and temporal trend

- Generally, PFCAs (C5 – C12) have been detected in almost every sample, and depositions have been increasing since the 1990s.
- The PFOA and PFNA homologues were the dominant PFCAs observed at the Mt. Oxford icefield.
- Temporal trend is contrary to observations at the Devon Ice Cap which plateaued and declined after 1995.²
- This may suggest that Devon may be more influenced by the reduction in emissions, while deposition to the more northern Mt. Oxford is affected by continuing global production.
- Elevated levels of C8 – 12 PFCAs was observed in the early 1970s, additionally elevated levels of C6 was also observed in 1980.

PFSA deposition and temporal trend

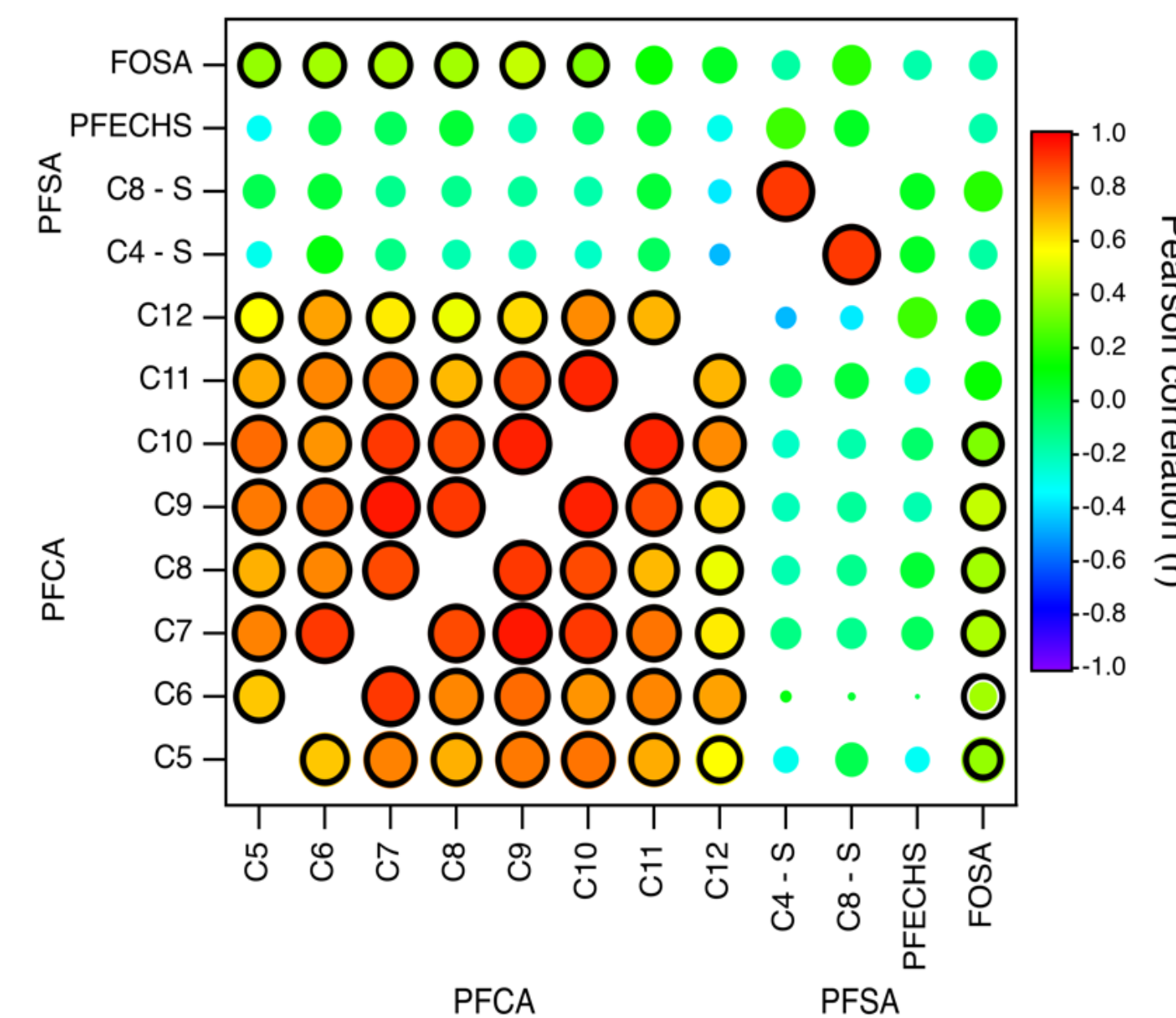
- Fluxes of PFSA do not follow the same trend when compared to PFCAs.
- Fluxes of PFOS peaked in 1970, 1976, 1979 and 1989, suggesting that episodic events may be a major contributor.
- The distribution of PFECHS is not homogeneous in the Arctic and could be attributed to the usage in aircraft hydraulic fluid. No known volatile precursor degrades to PFECHS, suggesting a direct input [2].
- This suggests that Mt. Oxford may be receiving contamination from other sources, particularly continental Asia.



Five year moving averages of PFAAs deposition flux on Mt. Oxford icefield: (A) PFCAs (C5 - C12), (B) PFSA (C4, C6, C8, PFECHS) and FOSA for the period 1967 – 2016, (C) PFOA and (D) PFNA deposition at Mt. Oxford, icefield (1977-2015), Devon Ice Cap² and Lomonosovfonna Ice Cap (2006-2019)⁴

Evidence of Indirect Formation

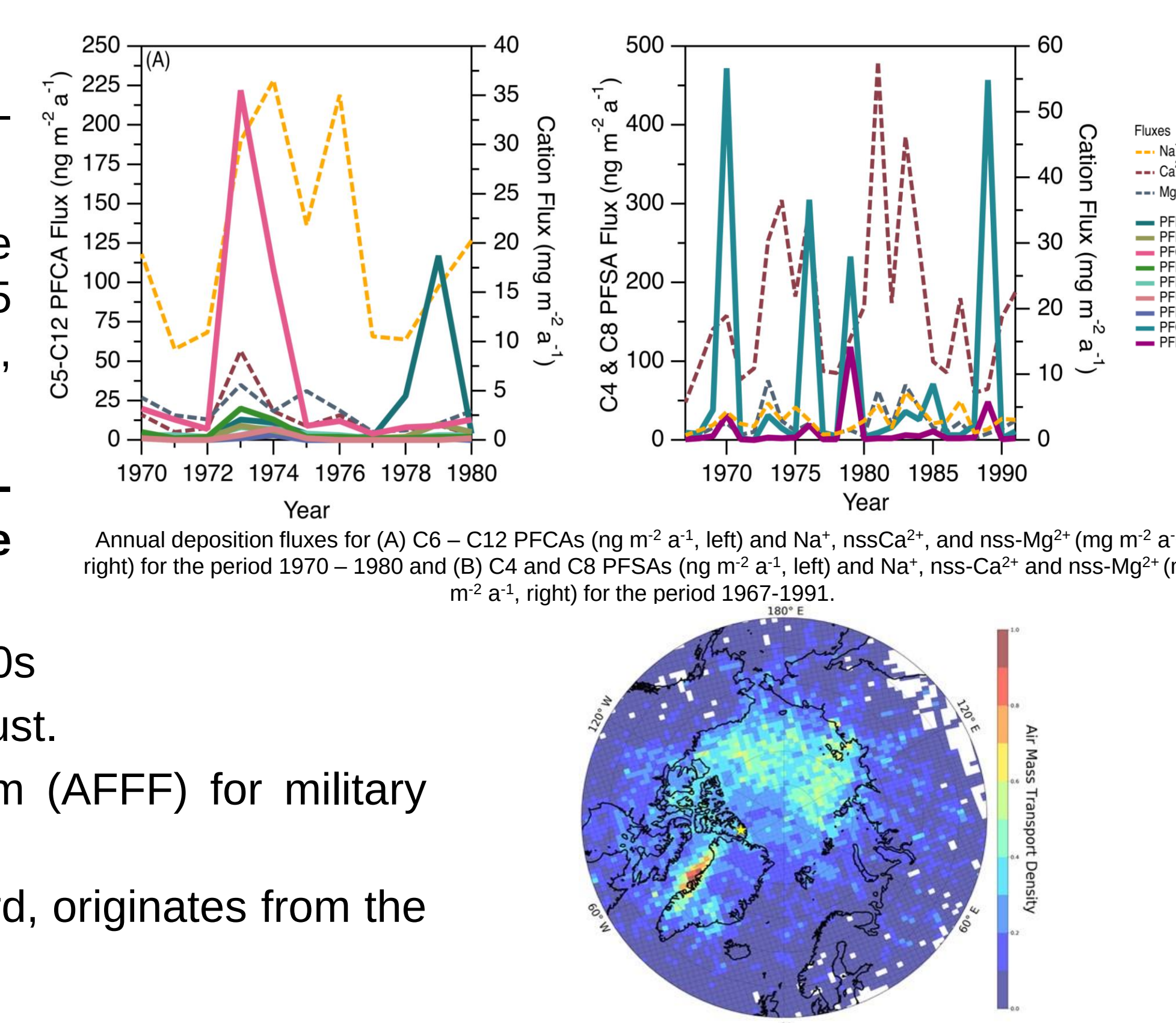
- Volatile and semi-volatile compounds can undergo oxidation in the gas phase to produce PFAAs.
- To assess whether PFAAs can be formed from precursor compounds, we utilized **molar concentration ratios**, **homologue patterns**, and a recent **GEOS – CHEM model**.
- Homologue correlations are used to discern common sources and environmental effects (removal mechanism and post-depositional effects).
- Homologue pairs of C5-C12 were moderately to strongly correlated with each other (r:0.50-0.96, p < 0.05), which suggests a similar source. (figure 5).
- Conversely, most pairs of PFSA were not correlated with each other. An exception was PFOS and PFBS, which were strongly correlated with each other (r²=0.92, p= <0.001).
- Molar concentration ratios and the chemical model also confirm that **oxidation of volatile precursors** is a major source of PFCAs to Mt. Oxford icefield.



Correlation plot of PFCA, PFSA, and FOSA deposition fluxes on Mt. Oxford icefield for the entire sampling period (1967-2016). The strength of the correlation is illustrated by the colour and size of the circle, where larger circles denote a strong correlation. The black outline represents a statistically significant correlation (p-value < 0.05).

Episodic PFAA Transport Pathways

- This ice core uniquely recorded several episodes of elevated deposition of PFAAs.
- In 1973-1974, we observed at least a three-fold increase in deposition of the C6-C12 PFCAs, PFOA showed the most dramatic increase, rising more than 34 times.
- Correlation analysis with tracer ions was done for this period (1967-1979) and we found a statistically significant correlation between C8-C10 PFCAs and Na⁺ (r: 0.55 - 0.70, p < 0.05) and C7 – C10 PFCA were correlated with mineral dust tracers, nss-Ca²⁺ and nss-Mg²⁺ (r: 0.54 - 0.87, p < 0.05).
- Correlations were driven by the co-occurrence of elevated **Na⁺, nss-Ca²⁺, and nss-Mg²⁺ deposition** during the 1973 episode, which may indicate a role for **marine aerosols and/or mineral dust** in the deposition events observed pre-1980.
- We also observed pulses of PFBS and PFOS up to 84 times higher before the 1990s
- **No clear evidence** of indirect formation, transport by marine aerosols or mineral dust.
- Episodic events could be related to known usage of aqueous film forming foam (AFFF) for military activities at CFS Alert and Thule Air Base.
- Air mass back trajectory analysis revealed that some of the air impacting Mt. Oxford, originates from the western coast of Greenland and the Arctic Ocean.



Key Takeaways

1. Deposition fluxes of PFCAs have been increasing since the 1980s.
2. No discernable trend for PFSA.
3. Atmospheric oxidation of volatile precursors are important source of PFCAs.
4. Marine aerosols may be an important source of individual PFAAs.
5. Episodic deposition of PFCAs in the 1970s may be due to marine aerosol or mineral dust transport.
6. Direct release from nearby military activities may be responsible for PFOS and PFBS episodic deposition.

References

1. OECD "Portal on Per and Poly Fluorinated Substances"
2. H. Pickard. et al., 2018 *Atmos Chem Phys*, **18**, 5045–5058.
3. MacInnis, J. J. et al, 2017 *Environ. Sci. Process. Impacts*, **19**, 22–30.,
4. Hartz WF. et al., 2023 *Sci Total Environ*. doi: 10.1016/j.scitoten