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Key Points:
- First report of multidecadal deposition for short-chain perfluorocarboxylic acids collected from two Arctic ice caps
- Deposited short-chain perfluorocarboxylic acids increased with time starting in 1990
- Chlorofluorocarbon replacements introduced as a result of the Montreal Protocol likely a major source of trifluoroacetic acid to the Arctic

Supporting Information:
- Supporting Information S1

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Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations

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Abstract Short chain perfluoroalkylcarboxylic acids (scPFCAs, $C_xF_{2x+1}COOH$, $x \leq 3$) are persistent compounds formed from atmospheric oxidation of fluorotelomer compounds and chlorofluorocarbon (CFC) replacements introduced as a result of the Montreal Protocol. Understanding sources and impacts of scPFCAs has been limited by observational data. We report multidecadal depositional fluxes for trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), and perfluorobutanoic acid (PFBA) from two Arctic ice cores. Fluxes of all three scPFCAs increase starting around 1990. Through comparison with chemical transport models and assessment of temporal trends, we observe the importance of CFC replacements in the increased deposition of TFA. Fluorotelomer degradation may contribute to the deposition of PFBA but is insignificant for TFA and PFPrA. Deposition of TFA is expected to increase as new CFC replacement compounds are phased in. This work demonstrates the increased environmental burden of persistent and potentially toxic scPFCAs as a result of global regulation.

Plain Language Summary Measurements of persistent compounds were made in two Arctic ice cores. The multidecadal records allow us to better understand the sources and deposition of these chemicals to remote areas. We observed that amounts deposited to the Arctic increased with time starting around 1990. Our results suggest that global regulation and replacement of other environmentally harmful chemicals contributed to the increase of these compounds in the Arctic, illustrating that regulations can have important unanticipated consequences.

1. Introduction

Perfluoroalkylcarboxylic acids (PFCAs, $C_xF_{2x+1}COOH$) are characterized by resistance to environmental degradation and potential adverse impacts on human and environmental health (Buck et al., 2011), each a hallmark of persistent organic pollutants. Widely used for the production of fluoropolymers and in surfactant and polymer products since the 1960s, PFCAs are accumulating in the global environment, including remote regions such as the Arctic (Muir et al., 2019). The fate and impact of PFCAs with carbon chain lengths ≥7 has been widely studied over the past two decades. This is linked to interest in the fate of commercial products with these chain lengths and the fact that PFCA bioaccumulation potential increases with chain length. One outcome of these studies was that PFCAs can be formed through atmospheric oxidation of volatile fluorotelomer compounds (i.e., substances possessing $F(CF_2)_xCH_2CH_2R$), which are used as synthetic precursors to commercial products (Ellis et al., 2004; Young & Mabury, 2010). Atmospheric degradation of fluorotelomer compounds has been shown to contribute to PFCA contamination in remote regions (Benskin et al., 2012; Pickard et al., 2018).

Less attention has been paid by the scientific community to short-chain PFCAs (scPFCAs). Here, we will define scPFCAs as PFCAs with carbon chain lengths ≤4, of which there are three compounds: trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), and perfluorobutanoic acid (PFBA). Although these

compounds have never been shown to have predator-prey bioaccumulation factors >1, Pérez et al. (2013) observed that mean PFBA concentrations were more than six times higher than any other measured perfluoroalkyl substance (PFAS) in the kidney and lung tissue of human cadavers. Recently, the first measurements of TFA and PFPrA in human serum were reported, where TFA concentrations were higher than all other PFAS except for perfluorooctanoic acid and perfluorooctane sulfonic acid (Duan et al., 2020). Accumulation of scPFCAs has also been demonstrated in plants, including crops for human consumption (Felizeter et al., 2012; Krippner et al., 2014; Likens et al., 1997; Liu et al., 2019). The toxicity of TFA to plants is well established (Solomon et al., 2016). Acute effects to a freshwater invertebrate increased with decreasing PFCA chain length, with lethal concentrations of 70 mg L^{-1} for TFA, 80 mg L^{-1} for PFPrA, and 110–140 mg L^{-1} for PFBA (Wang et al., 2014). Like longer-chain PFCAs, scPFCAs are persistent in the aqueous environment and may accumulate in sensitive ecosystems, such as wetlands (Tromp et al., 1995).

Atmospheric oxidation of volatile precursors forms scPFCAs. There are several precursors that can form scPFCAs, including fluorotelomer compounds and chlorofluorocarbon (CFC) replacement compounds (Young & Mabury, 2010). The propensity of CFCs to deplete stratospheric ozone led to their regulation through the Montreal Protocol. This international agreement entered into force in 1989 and mandated replacement of CFCs with hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and other substances with lower ozone depleting potentials (UNEP, 2019). From 1990–1999, several amendments were made to the Montreal Protocol to regulate HCFCs, and in 2016, an amendment was made to regulate HFCs. The Montreal Protocol has reduced the impact of ozone-depleting substances (ODSs) on the stratospheric ozone layer (Morgenstern et al., 2008; Shepherd et al., 2014; Solomon et al., 2016). Many ODSs are also long-lived greenhouse gases, and thus, the Montreal Protocol concurrently decreased anthropogenic radiative forcing (Morgenstern et al., 2008; Velders et al., 2007). Despite these clear benefits, increased production and consumption of CFC replacement compounds may increase the environmental burden of scPFCAs.

Better understanding of the global burden of scPFCAs from precursor oxidation requires atmospheric deposition measurements, with those made in remote regions providing an opportunity to assess impacts without interferences from local sources. Similarly, temporal trends of deposition that overlap with known production changes can aid in source elucidation. To date, there are limited atmospheric deposition measurements of scPFCAs, with only a handful made in remote regions. Temporal trend data for scPFCAs in the environment are extremely limited. The objective of this work was to measure deposition records of scPFCAs in ice cores from the Canadian high Arctic. We use these first multidecadal records of scPFCAs to elucidate precursor chemical sources of these persistent chemicals to remote regions.

2. Methods

2.1. Ice Core Collection and Dating

Ice cores were sampled from two locations in the High Arctic of Canada. A 15.5 m ice core was collected from the summit of Devon Ice Cap, Nunavut (75.2°N, 82.7°W, 2,175 m above sea level) in May 2015 using a 4-inch (9 cm) diameter aluminum and stainless-steel Kovacs ice drill. A 16.5 m ice core was collected from the summit of the Mt. Oxford icefield, Nunavut (82.19°N, 72.96°W, 1,784 m above sea level) in May 2017 using a 3-inch (7.7 cm) diameter aluminum and stainless-steel Kovacs ice drill. Samples were shipped frozen to the Canada Center for Inland Waters, Burlington, Ontario. Samples were kept frozen (−35°C) prior to sectioning. Ice cores were sectioned into discrete samples corresponding to individual years in a refrigerated vestibule using stainless steel tools. Annual sections were stored in pre-cleaned 4 L polyethylene containers. Age-depth scales for each site were created using $\delta^{18}O$ and ion chemistry, using 2 cm depth resolution, measured in colocated cores (Criscitiello et al., 2014; McConnell et al., 2002). Elemental analysis was conducted by inductively coupled plasma mass spectrometry in a continuous melt-flow analyzer. The $\delta^{18}O$ time series was used to establish an age-depth relationship by matching the $\delta^{18}O$ core record with local summer and winter solstice dates (linearly interpolating between solstices). Where $\delta^{18}O$ records were ambiguous, we additionally used the non sea salt sulfur/sodium and hydrogen peroxide summer peaks to ascertain the annual $\delta^{18}O$ maxima. We counted annual peaks in other major ionic species to confirm the accuracy of the age assignment. The ice cores for Devon Ice Cap and Mt. Oxford icefield were dated from 1977–2015 and 1967–2017, respectively. The total dating error is ±1 year. Further details are in Section S1 in the

supporting information. Data for the partial years of sample collection (2015 for Devon Ice Cap and 2017 for Mt. Oxford icefield) were not included in our analysis.

2.2. Chemical Analysis

Samples from Devon Ice Cap (500 ml for PFBA and PFPrA and 100 ml for TFA) were concentrated to 0.5 ml by solid phase extraction using a weak anion exchange sorbent. Isotopically labeled ^{13}C-TFA and $^{13}C_{1,2,3,4}$-PFBA were used as surrogate standards to correct for recovery and matrix effects in quantitation. Extracted analytes were separated by ultra-performance liquid chromatography (Waters Acquity UPLC I) and detected by electrospray negative ionization tandem mass spectrometry (Waters Xevo® TQ-S, MS/MS) with conditions shown in Tables S1 and S2. Analytes were separated using a Shodex RSPak column (2.0 × 150 mm, 5 μm). Samples from Mt. Oxford icefield were processed using analogous methods but with a 500 ml sample volume for all analytes. Mt. Oxford icefield extracts were analyzed using the same instrument but using a nanopolymer silica hybrid column (Acclaim™ Trinity™ P1, 2.1 × 100 mm, 3 μm). Additional details for extraction, analysis, and QA/QC are presented in Sections S2 and S3.

2.3. Calculation of Pseudo Production Rates of scPFCAs

Pseudo production rates for TFA and PFPrA for each long lived, CFC replacement precursor compound, were calculated as follows:

$$\text{Pseudo production rate} = \frac{1}{\tau_{OH}} \times [\text{precursor}] \times \text{scPFCA yield},$$

where τ_{OH} is the lifetime of the precursor compound with respect to reaction with OH in years (the predominant fate in the troposphere, Carpenter et al. (2014)), [precursor] is the number density in molecules cm^{-3} of the precursor compound (Kloss et al., 2014; Krummel et al., 2006; Laube et al., 2014; Montzka et al., 2015; Prinn et al., 2019; Vollmer et al., 2015), and scPFCA molar yield is the fraction of each mol of precursor that forms the scPFCA through oxidation initiated by OH (Calvert et al., 2008). Data used for the calculations are shown in Tables S5 and S6. Production of TFA from five precursors: HCFC-123, HCFC-124, HCFC-133a, HFC-134a, and HFC-227 could be calculated. Data were available to calculate the pseudo production rate of PFPrA from a single precursor: HCFC-225ca. The total pseudo production rates for TFA and PFPrA were determined by summing the pseudo production rates for each precursor.

3. Results and Discussion

3.1. Concentrations and Fluxes of scPFCAs to the Arctic

Observed concentrations in both ice cores were highest for TFA, which was found above the method detection limit in every sample from Devon Ice Cap and 96% of Mt. Oxford icefield samples. Concentrations of TFA on Devon Ice Cap ranged from 4.24 to 129 ng L^{-1}, while those on Mt. Oxford icefield ranged from <0.37 to 148 ng L^{-1} (Table S7). Concentrations of PFPrA were above the detection limit in every sample from Devon Ice Cap and Mt. Oxford icefield, ranging from 3.14 to 192 ng L^{-1} and 0.30 to 73 ng L^{-1}, respectively. Concentrations of PFBA were much lower than both TFA and PFPrA. PFBA was detected in 68% of samples from the Devon Ice Cap and 74% of samples from the Mt. Oxford icefield. Concentrations of PFBA ranged from <0.040 to 1.34 ng L^{-1} on the Devon Ice Cap and 0.003 to 1.90 ng L^{-1} on the Mt. Oxford icefield.

Measurements of scPFCA concentrations in precipitation have been previously reported (Table S8). Measurements of TFA concentrations in precipitation have been made in several locations across North America, Europe, Asia and some polar locations, while measurements of PFPrA have been limited to only a few studies in North America and Asia. Measurements of PFBA in precipitation are much more common, since they are measured along with longer-chain PFCAs. Unfortunately, concentrations in precipitation cannot be meaningfully compared because of strong spatial variations in precipitation rates. Flux measurements allow comparison of deposition between samples collected at different locations and times. Therefore, measured scPFCA ice core concentrations in our study were converted to annual deposition fluxes. Devon Ice Cap fluxes ranged from 0.471 to 21.5 μg m^{-2} a^{-1} for TFA, 0.494 to 29.0 μg m^{-2} a^{-1} for PFPrA, and 0.002 to 0.171 μg m^{-2} a^{-1} for PFBA (Table S7). Mt. Oxford icefield fluxes ranged from 0.029 to 20.1 μg m^{-2} a^{-1} for TFA, 0.038 to 6.7 μg m^{-2} a^{-1} for PFPrA, and 0.0005 to 0.303 μg m^{-2} a^{-1} for PFBA (Table S7). Few

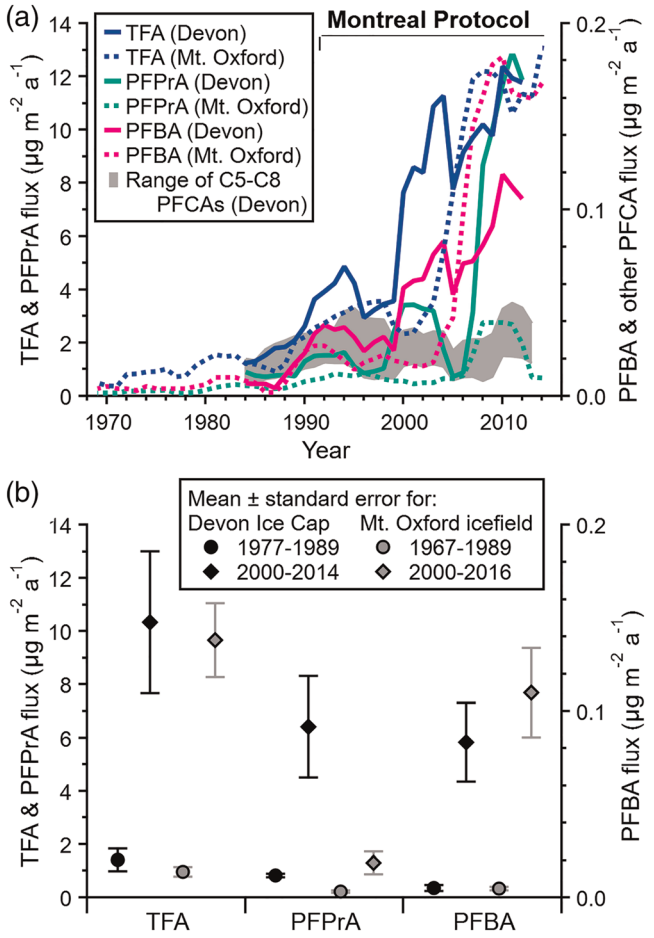

Figure 1. (a) Five-year moving average deposition fluxes of TFA, PFPrA, and PFBA from Devon Ice Cap (solid lines) and Mt. Oxford icefield (dashed lines) ice cores; rapidly increasing flux is noted during the Montreal protocol post-1989 regulating CFCs, HFCs, and HCFCs; (b) comparison of mean fluxes up to Montreal protocol 1989 (circles) and after 2000 (diamonds) for Devon Ice Cap (black) and Mt. Oxford icefield (gray), with error bars representing standard error of the mean. All fluxes from 2000 onward are significantly higher than fluxes up to 1989 (t test, $p < 0.015$).

previous studies have reported fluxes of scPFCAs (Table S9). Those that have been reported generally do not provide continuous temporal flux data and represent semiquantitative estimates of total deposition flux. Estimates of TFA flux in rainwater were made in the late 1990s (Berg et al., 2000; Scott et al., 2000, Scott, Spencer, et al., 2005), with three made more recently (Chen et al., 2019; Wang et al., 2014; Zhai et al., 2015). Only two studies have reported fluxes of PFPrA in rainwater (Chen et al., 2019; Kwok et al., 2010), while measured PFBA fluxes have been reported in rainwater, firn, and snow in several studies (e.g., Dreyer et al., 2010; Kirchgeorg et al., 2016). In general, our fluxes of TFA to the Arctic are several times lower than fluxes from the same year to lower latitude regions (Table S9). Similarly, fluxes of PFBA are higher at lower latitudes. This suggests that TFA and PFBA have short-lived atmospheric sources that cause levels to be elevated near population centers. In contrast, PFPrA deposition fluxes are comparable at lower and higher latitudes. Although data are limited, this could suggest that PFPrA sources are more consistent globally.

3.2. Temporal Trends

Temporal trend analysis using ice cores can elucidate source and precursor contributions to scPFCAs. The integrity of ice core temporal records relies on minimal postdepositional processes. Changes in ice core concentrations of semivolatile compounds, including volatilization after deposition, are well documented (e.g., Grannas et al., 2013). The only postdepositional effect likely to affect highly water soluble scPFCAs (Table S3) is melting. Melting effects can significantly alter records in areas where meltwater percolation is common, such as low-latitude ice cores (Kirchgeorg et al., 2016). In areas where temperatures rarely exceed 0°C, including the highest, most central regions of Canadian High Arctic ice caps, postdepositional processes of scPFCA concentrations in ice cores are expected to be small (MacInnis et al., 2017; Wang et al., 2014). We represent ice core temporal trends as 5-year moving averages of annual data to reduce the influence of dating errors (±1 year) and possible melting effects (±1 year; MacInnis et al., 2017). From our earliest measurements through the 1980s, scPFCAs were consistently detected at low levels (Figure 1a) in both the Devon Ice Cap and Mt. Oxford icefield records. Starting in ~1990, just after the Montreal Protocol entered into force (1989), fluxes of scPFCAs increased in both ice cores. In the Devon Ice Cap, mean fluxes of TFA rose almost an order of magnitude between pre-1990 (1977–1989, 1.4 µg m^{-2} a^{-1}) and post-2000 (2001–2014, 10.3 µg m^{-2} a^{-1}). A similar increase was observed on the Mt. Oxford icefield. Increases of PFPrA and PFBA were also observed over the same time period. Comparing the fluxes pre-1990, prior to the Montreal Protocol, to those post-2000, after amendments were made to the Protocol to regulate some CFC replacements, significant increases are shown (t test, $p < 0.015$) for all three scPFCAs in both ice cores (Figure 1b).

Our measurements represent the first multiyear temporal trends of deposition fluxes for TFA and PFPrA. Some temporal trends have been reported for PFBA from firn or snow cores from glaciers in low latitude regions (Kirchgeorg et al., 2013, 2016; Wang, Halsall, et al., 2014). Unfortunately, trends for PFBA from our ice cores cannot be compared to these data because of melting effects reported in firn samples or absence of reported annual deposition fluxes. Furthermore, these low latitude locations are in greater proximity to pollution sources and anthropogenic activity. Environment and Climate Change Canada has continuously monitored PFBA and other PFAS in the air at the northern tip of Ellesmere Island (Alert, Nunavut, Canada) since 2006 (Wong et al., 2018). Similar to our findings, Wong et al. report an increase in PFBA between 2007 and 2014. Although PFBA was the shortest PFCA measured in that study, levels of PFBA

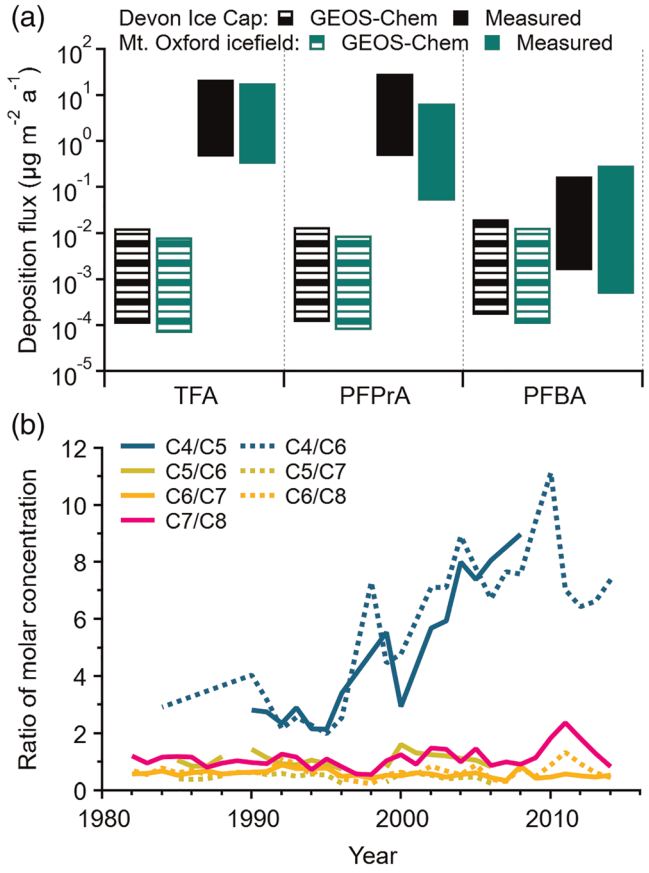

Figure 2. (a) Comparison between GEOS-Chem modeled (Thackray et al., 2020) and measured deposition ranges from 1978–2014 (Devon Ice Cap, black) and 1978–2015 (Mt. Oxford icefield, green); (b) measured molar ratios of PFCAs of different chain lengths from the Devon Ice Cap (C5 to C8 PFCA deposition from Pickard et al. (2018)).

were 1 to 2 orders of magnitude higher than other PFAS such as perfluorooctanoic acid in combined gas-phase and particle sampling media. The lack of appropriate temporal measurements of deposition fluxes for not only TFA and PFPrA but also PFBA emphasizes the novelty of this study and that ice cores can be extremely useful for monitoring multidecadal deposition of contaminants.

3.3. Arctic Source Implications

Deposition on high-altitude ice caps is solely atmospheric. Emission to the atmosphere could occur through industrial production of scPFCAs. Prior to 1998, PFBA was directly produced by 3M (Wang et al., 2014). Direct production of PFBA and its methyl ester were reported by Miteni (Wang, Cousins, et al., 2014), which would have ended with the bankruptcy of the company in late 2018 (Hogue, 2019). Little information is available concerning current direct production of scPFCAs. Measurements of atmospheric TFA, PFPrA, and PFBA near fluorochemical manufacturing facilities suggest direct emissions are occurring (Chen et al., 2018), although the method could not distinguish between gas and aerosol phase scPFCAs. Production of scPFCAs can also occur during thermolysis of fluorinated polymers (Ellis et al., 2001), which was estimated to release up to 200 t a^{-1} TFA in Europe in the late 1990s (Jordan & Frank, 1999). However, directly emitted scPFCAs are unlikely to act as a large source to remote regions. These compounds have short atmospheric lifetimes that are assumed to be on the order of a few days, dominated by wet and dry deposition, analogous to other strong acids, such as nitric acid (Kotamarthi et al., 1998; Wu et al., 2014). Other fates of scPFCAs are possible, including slow reaction with OH (lifetimes <100 days, Hurley et al. (2004)) and rapid reaction with Criegee intermediates in large forested regions where these reactive species are abundant (Chhantyal-Pun et al., 2018).

Several volatile precursors form scPFCAs through atmospheric oxidation (Table S10). All three scPFCAs are known to be formed from the degradation of fluoropolymer precursors (Ellis et al., 2004; Young & Mabury, 2010). By comparing to a chemical transport model and examining homologue trends, we can assess the importance of this source to our observed scPFCA deposition. A recent GEOS-Chem model (Thackray et al., 2020) predicted global deposition of longer-chain PFCAs from the atmospheric oxidation of fluorotelomer substances. Comparing this model output to our measured fluxes demonstrates that this model underpredicts deposition (Figure 2a, Figures S7, S8, and Table S11). Fluorotelomer oxidation only accounts for a small fraction of scPFCAs measured on the ice caps, shown in Figure 2a as the difference between the bars representing range in deposition flux outputted from the GEOS-Chem model and the measurements. The upper limit of the modeled deposition range accounts for <1% and <2.5% of observed annual deposition of TFA and PFPrA, respectively, in both ice cores. This suggests that fluorotelomer oxidation plays a minor role in the deposition of TFA and PFPrA in the Canadian Arctic. Fluorotelomer degradation can account for a greater fraction of deposited PFBA. On the Devon Ice Cap, the model can account for all the PFBA deposited in a single year for 3 years, the latest of which was 1997. Similarly, the model can account for all PFBA deposited in 6 years prior to 1995 on Mt. Oxford icefield. In both ice cores, the maximum deposition predicted by the model could account for less than one-third of the observed PFBA deposition in most years (Table S11). This suggests that fluorotelomer degradation is an important source of PFBA to the ice core sites but not the only source. Evidence for an additional source of PFBA comes from ratios of PFBA to other PFCA homologues (Figure 2b). Homologue ratios are commonly used to assess the role of atmospheric oxidation of fluorotelomers to PFCA levels. Fluorotelomer degradation leads to deposited PFCAs with ratios that are reasonably consistent with time. Pickard et al. (2018) observed that all PFCAs with carbon chain lengths ≥5 have similar deposition trends through time to the same Devon Ice Cap ice

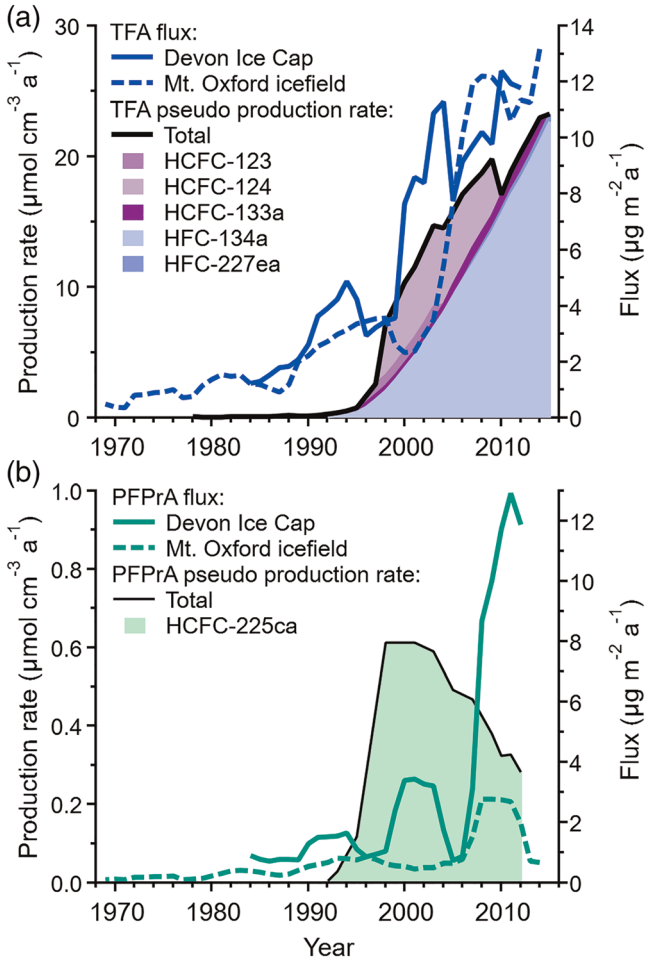

Figure 3. Pseudo production rates (shaded area, with sum as solid black line) and measured deposition fluxes from Devon Ice Cap (solid colored line) and Mt. Oxford icefield (dashed colored line) for (a) TFA and (b) PFPrA.

core. Ratios among PFCAs with five to eight carbons are reproduced in Figure 2b and demonstrate the difference in deposition trends for PFBA. The deposition of PFBA appears to follow a similar trend as the other PFCAs through the mid-1990s. Starting around the year 1995, deposition of PFBA increased relative to other PFCAs. This suggests that an additional, nonfluorotelomer source of PFBA, is needed to explain the observed deposition.

It is well-established that atmospheric oxidation of CFC replacements leads to the formation of TFA (e.g., Wallington et al., 1992; Tuazon & Atkinson, 1993; Hayman et al., 1994). There are six HCFC and HFC compounds that have been shown to produce TFA as a product with yield >10% and three others that are suspected to form TFA as a major product, based on analogous mechanisms (Young & Mabury, 2010). The pseudo-production rate, calculated for five major CFC replacement precursors of TFA, shows a similar temporal profile to the observed ice core TFA deposition (Figure 3a). Our deposition measurements can also be compared to models that predict the impact of CFC replacements on TFA deposition. Kanakidou et al. (1995) predicted <342 µg m^{-2} TFA would be deposited to the Arctic between 1990 and 2020. We observed 187 µg m^{-2} TFA on the Devon Ice Cap (cumulative for the period 1990–2014) and 106 µg m^{-2} on Mt. Oxford icefield (1990–2016). Kotamarthi et al. (1998) predicted <1,100 µg m^{-2} TFA deposition in the northern hemisphere region including the Canadian High Arctic from 1985–2010. During this same period, we observed 155 µg m^{-2} and 118 µg m^{-2} deposited to Devon Ice Cap and Mt. Oxford icefield, respectively. Modeled depositions are higher than our ice core measurements. Both models overestimate TFA produced from HFC-134a by up to a factor of two, because they used a TFA yield that does not account for decomposition of excited alkoxy radicals (Wallington et al., 1996). Despite these uncertainties, the models suggest CFC replacements could account for most to all TFA deposition in our ice cores. At lower latitudes, a few studies have examined sources of measured environmental TFA. Two studies found that CFC replacements did not account for the full measured loading of TFA (considering HFC-134a, HCFC-123, and HCFC-124 (Jordan & Frank, 1999) and considering HFC-134a only (Wu et al., 2014)), while another determined they were the dominant source (considering HFC-134a, HCFC-123, and HCFC-124 (Wang, Wang, & Ding, 2014)). In our study, we provide significant support for CFC-replacements as important sources of TFA using a homologous suite of scPFCAs, as opposed to only TFA, and by examining the temporal profile in scPFCA deposition instead of a single time point.

Replacements for CFCs also act as sources for PFPrA. One precursor produces PFPrA as a major source, HCFC-225ca (Tuazon & Atkinson, 1994). An additional precursor detected globally in the atmosphere (Arnold et al., 2014), HFC-43-10-mee, is suspected to act as a major source based on comparison to analogous mechanisms. Several additional precursors produce PFPrA as a minor product (Jackson et al., 2011; Young & Mabury, 2010). We observed pulses represented by 5–10 year increases in PFPrA deposition to ice cores beginning in about 1990. Three pulses were observed to the Devon Ice Cap, while only one (the most recent) was observed to Mt. Oxford icefield. Timing of the onset of pulses suggests the involvement of CFC replacements as precursors. We have only enough data to calculate a PFPrA pseudo production rate for HCFC-225ca (Figure 3b). Emissions of relatively short-lived HCFC-225ca peaked in 1999 and may be responsible for the peak observed in the Devon Ice Cap ice core around the year 2000. The nature of the pulses and the disagreement between the two ice cores suggests that relatively short-lived precursors may be involved in the formation of PFPrA. More work is needed to understand atmospheric sources of PFPrA to the Arctic.

Several CFC replacement compounds have been identified as precursors to PFBA, all of which form PFBA as a minor product (Wang, Cousins, et al., 2014). We cannot calculate pseudo production rates for PFBA from these precursors, because the yield of PFBA is complex and driven by local atmospheric conditions (e.g., NO_x/HO_x ratio). The similarity in temporal trends between PFBA and TFA and their relationship to the timing of Montreal Protocol regulation in both ice cores suggests the importance of CFC replacement compounds as precursors of this compound in the Arctic. We note that direct emission of PFBA cannot be eliminated as a potential source but cannot be constrained because of negligible information on PFBA industrial production. More work is needed to fully elucidate sources of PFBA.

3.4. Implications of Ongoing Regulations

Ongoing amendments to the Montreal Protocol are likely to impact deposition of scPFCAs. Replacement of HFC-134a with the short-lived hydrofluoroolefin (HFO) HFO-1234yf as the coolant in mobile air conditioners will lead to an increase in TFA deposition. The yield of TFA from HFC-134a is <0.2, while the yield from HFO-1234yf is 1. One model estimates replacement of HFC-134a with HFO-1234yf will result in annual TFA wet deposition of 160–240 $\mu g\ m^{-2}$ in continental North America (Luecken et al., 2010), which is higher than the cumulative deposition during the last decade of record for each ice core (Devon Ice Cap, 110 $\mu g\ m^{-2}$ (2005–2014); Mt. Oxford icefield, 127 $\mu g\ m^{-2}$ (2007–2016)). Another model predicts annual TFA deposition of 42.3 $\mu g\ m^{-2}$ to the area including the Devon Ice Cap (Wang et al., 2018). This represents an increase compared to our observed annual TFA fluxes from 2001 to 2014, which ranged from 3.9 to 21.5 $\mu g\ m^{-2}\ a^{-1}$. Both models suggest a large future increase in TFA deposition in the Arctic compared to our measurements from 1970 to 2015.

4. Summary and Conclusions

We report here the first multidecadal records of scPFCA deposition. The deposition of all three scPFCAs increased starting around 1990. Through comparison to a model and homologue ratios, we determined that fluorotelomer sources are of minor importance to TFA and PFPrA deposition but could contribute to PFBA deposition. Temporal trends and comparison to models indicate that CFC replacements introduced as a result of the Montreal Protocol are likely the major source of TFA to the Arctic. Temporal trends suggest CFC replacements could be important to the deposition of PFPrA and PFBA, but more work is needed. The Montreal Protocol will undoubtedly continue to positively impact stratospheric ozone and climate and represents an unparalleled achievement in global environmental stewardship. However, this study emphasizes that even the most successful regulations can result in unintended environmental impacts. Persistent and mobile scPFCAs can circulate in the water cycle and cause irreversible contamination (Brendel et al., 2018). They accumulate in edible plants and are not removed by current drinking water treatment technologies, allowing for multiple pathways of human exposure. For these reasons and more, persistence and mobility should be taken into consideration when replacing one class of performance chemicals with another (Cousins et al., 2019), since this can often lead to unanticipated environmental effects that persist for the foreseeable future.

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