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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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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 $\delta^{18}O$ of water samples is ≤0.1%). Sample isotope ratios were standardized using three working standards calibrated against the IAEA standards VSMOW and SLAP. Final $\delta^{18}O$ values are on the VSMOW/SLAP scale. 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) (Criscitiello et al., 2014). Elemental, ion, and H_2O_2 analyses were performed on an ICP-MS (McConnell et al., 2002). Where $\delta^{18}O$ records were ambiguous, we additionally used the non-sea salt sulfur/sodium (nssS/Na) summer peak (indicative of summer solstice) as well as H_2O_2 to ascertain the annual $\delta^{18}O$ 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^+, H_2O_2, Mg^{2+}, Cl^-, and Ca^{2+}. 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 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.

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 Transition (m/z)	Internal Standard	Instrument 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 different ion transitions (m/z). Samples (500 mL) were spiked with internal standard (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 blanks.

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

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

Table S5. Method detection limit (ng/L) based on 3x the standard deviation of the blanks.

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

[*]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).

Table S6. Instrument limit of detection (LOD) and quantitation (LOQ) for PFAAs.

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
	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

[1]LOD is concentration corresponding to signal-to-noise (S/N) ratios of 3. [2]LOQ is concentration corresponding to S/N of 10. [3]Reproducibility 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 S7. The inlet and mass spectrometric conditions for this analysis are summarized in Table S8. For the second analysis, the short**er**-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% H_2O and 80% MeOH. The inlet and mass spectrometric conditions for this analysis were the same as the first (Table S8), except for column temperature, which was 40°C.

Table S7. Summary of chromatographic conditions.

Time (minutes)	**Flow rate (mL min^{-1})**	**% H_2O**	**% 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 S8. 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 (Dionex™ IonPac™ 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) HNO_3 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, **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.

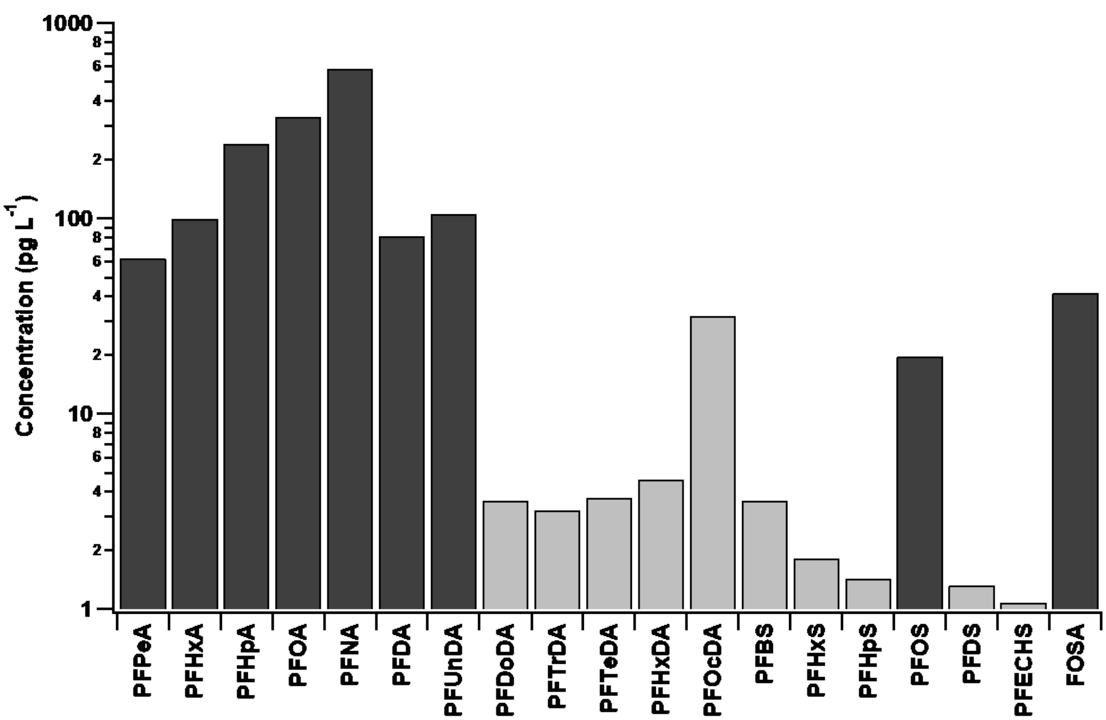


Figure S1. Concentrations of detected PFAS analytes (excluding C2 – C4 PFCAs) for the year 1996, as a single representative year. Light grey bars represent the LOD for measurements <LOD.

Concentrations (pg L^{-1}) of all the PFCA analytes detected on the Devon Ice Cap with depth and over time, are given in Table S9, including values below the LOD and LOQ. PFSA and FOSA concentrations are given in Table S10. 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 S11-S12.

Table S9. 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**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTrDA**
19	2015	<10.4	43.0	55.0	102	140	17.0	<15.7	<3.61	<3.21
78	2014	<10.4	42.8	94.4	129	284	54.0	41.1	<3.61	<3.21
134	2013	<10.4	95.2	235	207	440	72.3	66.8	<3.61	<3.21
177	2012	<10.4	193	438	275	596	84.2	145	<12.0	<3.21
193	2011	<10.4	280	578	278	382	47.6	53.8	<3.61	<3.21
235	2010	<10.4	130	317	195	427	43.0	62.4	<3.61	<3.21
280	2009	<10.4	63.7	173	173	262	43.3	53.8	<3.61	<3.21
331	2008	73.8	104	144	181	319	49.8	75.2	<3.61	<3.21
363	2007	<10.4	38.7	135	156	274	29.0	70.1	<3.61	<3.21
390	2006	51.3	73.4	196	258	755	113	218	<12.0	4.96
429	2005	108	122	231	180	403	65.6	128	<5.12	<3.21
454	2004	88.8	94.9	198	226	443	69.2	75.4	<3.61	<3.21
487	2003	74.0	73.5	183	144	274	41.7	68.6	<3.61	<3.25
547	2002	126	120	241	185	302	70.8	88.6	5.71	<3.21
606	2001	54.2	48.9	93.1	116	159	31.0	29.3	<3.61	<3.21
648	2000	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	1998	<10.4	29.2	80.1	166	385	56.0	88.7	<3.61	<3.21
776	1997	<34.7	42.7	91.9	181	299	38.8	74.4	<3.61	<3.21
825	1996	62.9	101	243	333	584	81.8	106	<3.61	<3.21
857	1995	95.0	122	180	186	225	24.2	52.6	<3.61	<3.21
902	1994	81.0	90.8	140	221	241	37.1	45.2	<3.61	<3.21
964	1993	79.9	107	162	159	173	24.9	30.2	<3.61	<3.21
1006	1992	87.1	112	145	129	147	18.1	<15.7	<3.61	<3.21
1047	1991	79.4	82.0	145	178	213	37.8	41.9	<3.61	<3.21
1088	1990	81.4	67.5	124	145	163	28.5	25.7	<3.61	<3.21
1144	1989	<34.7	49.7	95.1	105	162	18.7	35.2	<3.61	<3.21
1187	1988	87.1	87.1	174	209	262	39.4	41.2	<3.61	<3.21
1216	1987	35.4	50.0	86.5	122	138	25.8	18.9	<3.61	<3.21
1251	1986	46.1	65.2	124	122	125	35.0	<15.7	<3.61	<3.21
1294	1985	39.2	44.2	98.3	93.8	101	<12.5	17.9	<3.61	<3.21
1317	1984	<34.7	67.1	115	112	117	16.4	16.4	<3.61	<3.21
1358	1983	<34.7	34.6	68.1	82.2	81.0	<12.5	<4.72	<3.61	<3.21
1394	1982	<34.7	56.2	113	107	133	19.9	<15.7	<3.61	<3.21
1420	1981									
1458	1980									
1473	1979	<34.7	40.4	85.5	82.5	70.4	<12.5	<4.72	<3.61	<3.21
1514	1978	<34.7	54.8	130	96.6	137	16.5	<15.7	<3.61	<3.21

1542	1977	<34.7	47.2	86.7	107	110	12.6	<4.72	<3.61	<3.21

Table S10. 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.

		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 S11. Depth profile (cm) of PFCA fluxes (ng m^{-2} yr^{-1}) on the Devon Ice Cap. Values <LOD are identified in red and values <LOQ are identified in blue.

Depth (cm)	Year	Flux (ng m^{-2} yr^{-1}) PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA
19	2015	<LOD	4.58	5.86	10.9	15.0	1.81	0.84	<LOD	<LOD
78	2014	<LOD	6.91	15.2	20.8	45.8	8.70	6.63	<LOD	<LOD
134	2013	<LOD	19.6	48.4	42.6	90.5	14.9	13.7	<LOD	<LOD
177	2012	33.9	38.2	86.7	54.5	118	16.7	28.6	1.19	<LOD
193	2011	13.7	18.8	38.7	18.6	25.6	3.19	3.60	<LOD	<LOD
235	2010	<LOD	19.6	48.0	29.4	64.6	6.50	9.43	<LOD	<LOD
280	2009	<LOD	10.5	28.5	28.4	43.1	7.11	8.85	<LOD	<LOD
331	2008	16.7	23.6	32.6	40.9	72.1	11.3	17.0	<LOD	<LOD
363	2007	<LOD	5.50	19.2	22.1	38.9	4.12	10.0	<LOD	<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
454	2004	9.19	9.82	20.5	23.4	45.9	7.16	7.81	<LOD	<LOD
487	2003	8.01	7.96	19.8	15.6	29.7	4.52	7.43	<LOD	0.176
547	2002	37.0	35.4	71.0	54.5	88.9	20.8	26.1	1.68	<LOD
606	2001	13.8	12.4	23.7	29.6	40.5	7.87	7.44	<LOD	<LOD
648	2000	16.7	12.3	27.9	25.5	55.1	13.1	18.3	<LOD	<LOD
684	1999	12.0	17.8	39.2	43.0	122	16.0	21.6	1.51	<LOD
730	1998	<LOD	4.00	11.0	22.7	52.7	7.65	12.1	<LOD	<LOD
776	1997	3.15	7.76	16.7	32.9	54.4	7.06	13.5	<LOD	<LOD
825	1996	15.2	24.3	58.7	80.5	141	19.8	25.7	<LOD	<LOD
857	1995	14.2	18.3	27.0	27.8	33.7	3.62	7.86	<LOD	<LOD
902	1994	17.1	19.2	29.6	46.7	50.9	7.83	9.55	<LOD	<LOD
964	1993	24.1	32.2	48.8	48.1	52.3	7.53	9.10	<LOD	<LOD
1006	1992	16.9	21.6	28.2	25.1	28.6	3.51	1.53	<LOD	<LOD
1047	1991	15.9	16.4	28.9	35.6	42.6	7.57	8.38	<LOD	<LOD
1088	1990	16.4	13.6	25.0	29.2	32.8	5.73	5.16	<LOD	<LOD
1144	1989	4.80	13.8	26.3	29.0	44.9	5.17	9.73	<LOD	<LOD
1187	1988	19.7	19.7	39.4	47.3	59.2	8.90	9.32	<LOD	<LOD
1216	1987	5.44	7.67	13.3	18.7	21.2	3.96	2.89	<LOD	<LOD
1251	1986	9.23	13.1	24.8	24.5	25.1	7.02	1.58	<LOD	<LOD
1294	1985	8.33	9.41	20.9	20.0	21.4	1.33	3.81	<LOD	<LOD
1317	1984	2.21	8.57	14.7	14.3	14.9	2.09	2.09	<LOD	<LOD
1358	1983	3.79	7.56	14.9	18.0	17.7	1.37	<LOD	<LOD	<LOD
1394	1982	3.56	11.6	23.3	22.0	27.4	4.08	1.62	<LOD	<LOD
1420	1981									
1458	1980									
1473	1979	1.38	3.21	6.79	6.56	5.59	0.50	<LOD	<LOD	<LOD
1514	1978	4.03	12.7	30.2	22.5	31.9	3.83	1.83	<LOD	<LOD
1542	1977	2.65	7.22	13.3	16.3	16.9	1.93	<LOD	<LOD	<LOD

Table S12. Depth profile (cm) of PFSA fluxes (ng m^{-2} yr^{-1}) on the Devon Ice Cap. Values <LOD are identified in red.

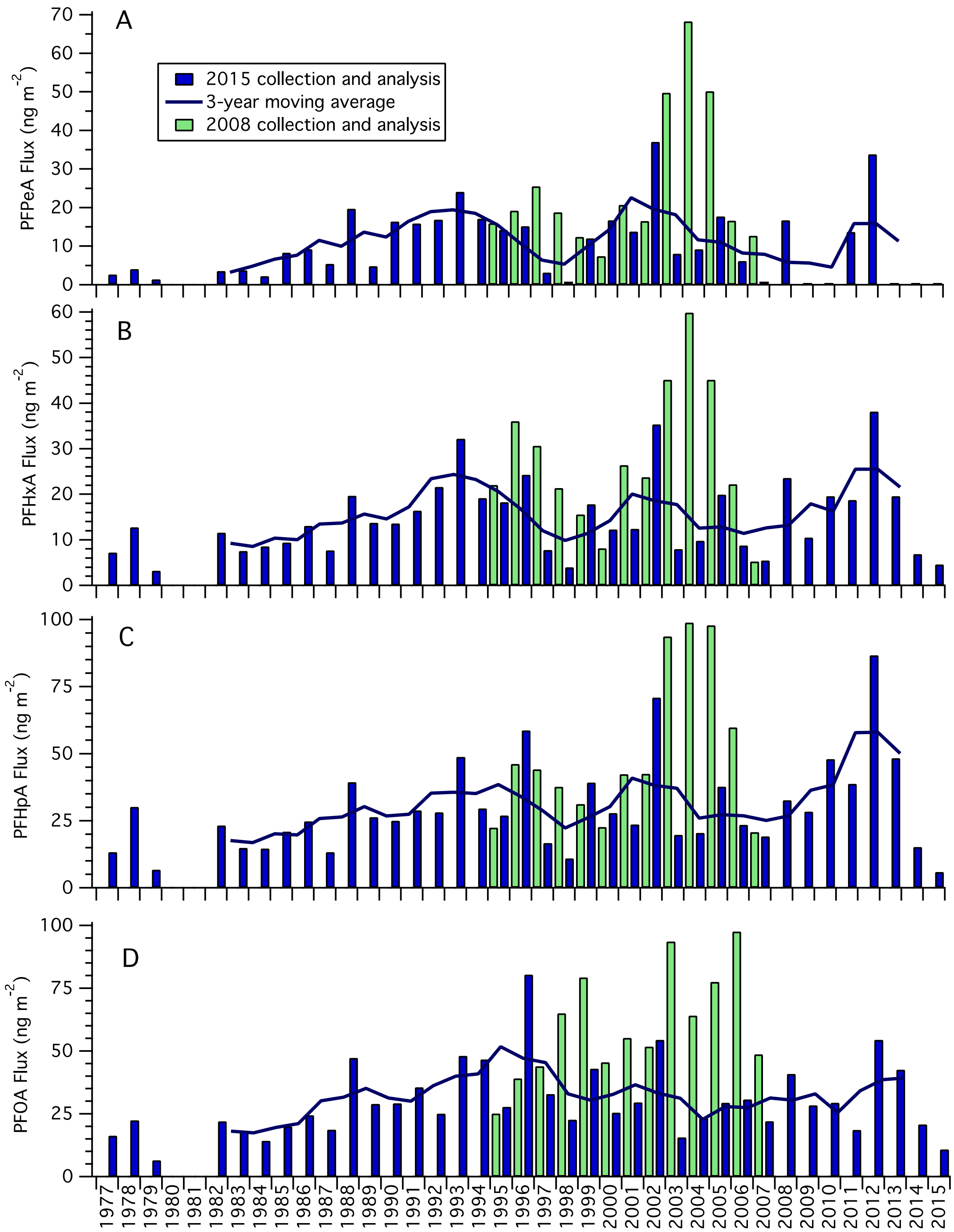
		Flux (ng m^{-2} yr^{-1})			
Depth (cm)	**Year**	**PFBS**	**PFHpS**	**PFOS**	**FOSA**
19	2015	0.725	<LOD	5.57	<LOD
78	2014	<LOD	1.50	15.3	<LOD
134	2013	0.861	1.80	80.3	<LOD
177	2012	<LOD	<LOD	10.1	0.297
193	2011	<LOD	<LOD	6.88	<LOD
235	2010	<LOD	<LOD	4.84	<LOD
280	2009	<LOD	<LOD	4.56	<LOD
331	2008	<LOD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

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

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

$$(\text{Area} = \pi \text{r}^2 \text{ where r} = 4.5\text{cm})$$

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.


A
B
C
D
2015 collection and analysis
3-year moving average
2008 collection and analysis
PFPeA Flux (ng m^{-2})
PFHxA Flux (ng m^{-2})
PFHpA Flux (ng m^{-2})
PFOA Flux (ng m^{-2})
1977 1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015

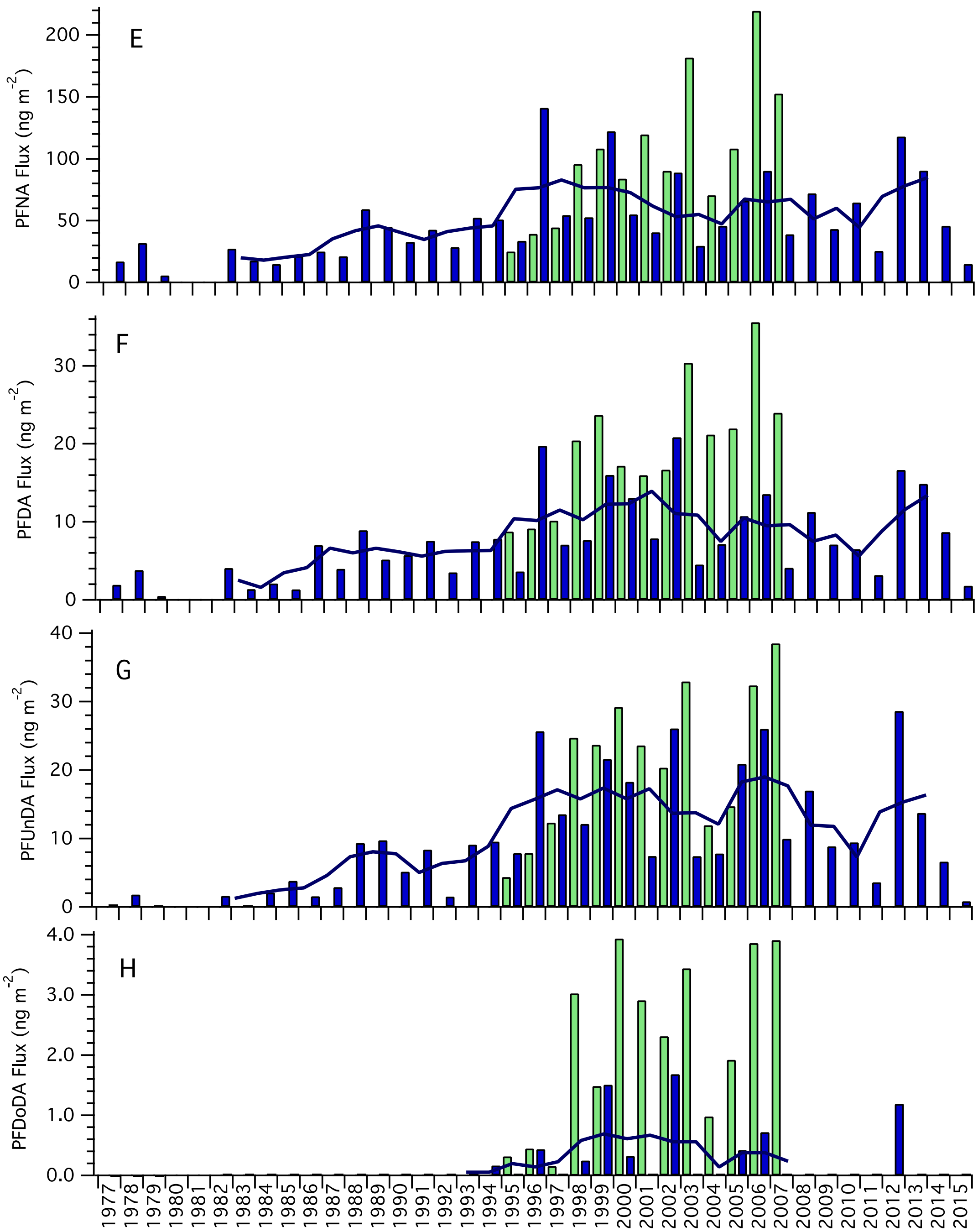


Figure S2. Temporal flux trends for a) PFPeA, b) PFHxA, c) PFHpA, d) PFOA, e) PFNA, f) PFDA, g) PFUnDA, and h) PFDoDA calculated from samples collected in 2008 (green) and 2015 (blue), along with three year moving averages for the 2015 study.

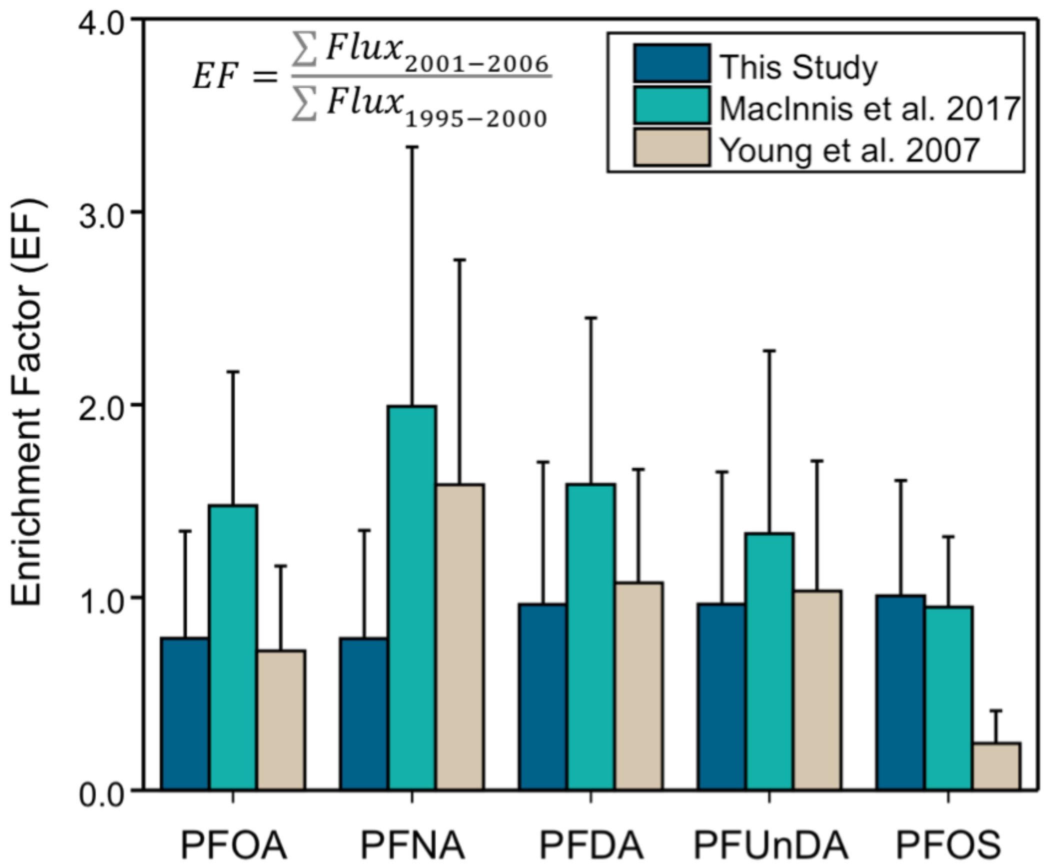


Figure S3. Calculated enrichment factor comparison between the sums of PFAA fluxes for 2001-2006 and 1995-2000, for the three Devon Ice Cap studies (MacInnis et al., 2017; Young et al., 2007).

Concentrations of PFCAs and PFSAs detected on the Devon Ice Cap were compared to a number of other studies in Table S13. PFAAs have been detected in a number of other samples including other snow cores, surface snow, precipitation, and lake, river and ocean water.

Table S13. PFAA Concentration (pg L^{-1}) Comparisons with Other Abiotic Samples.

Matrix (Time)	Site (Reference)	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFOS	FOSA
Ice Core (1977-2015)	Devon Ice Cap, Canadian Arctic (this study)	<10-204	30-280	55-578	82-333	70-755	<13-113	<5.0-218	12-391	<0.2-77
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)	1.5-53	2.3-230	23-310	29-1300	14-330	3.1-600	2.0-150	1.3-750	
Precipitation (1998-1999)	Rural U.S. (Ithaca, New York) (6)	<100-17,000	<100-10,000	<100-11,000	<100-10,000	<100-3,200				
Precipitation (2002)	Remote Canada (Kejimkujik, Nova Scotia) (6)	<100-1,900	<100-2,300	<100-5,400	<100-3,100	<100-3,300				
Precipitation (2003-2004)	Urban Canada (Toronto, Ontario) (6)	200-1,100	200-900	<100-1,700	1,000-11,000	500-9,700	<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

[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.

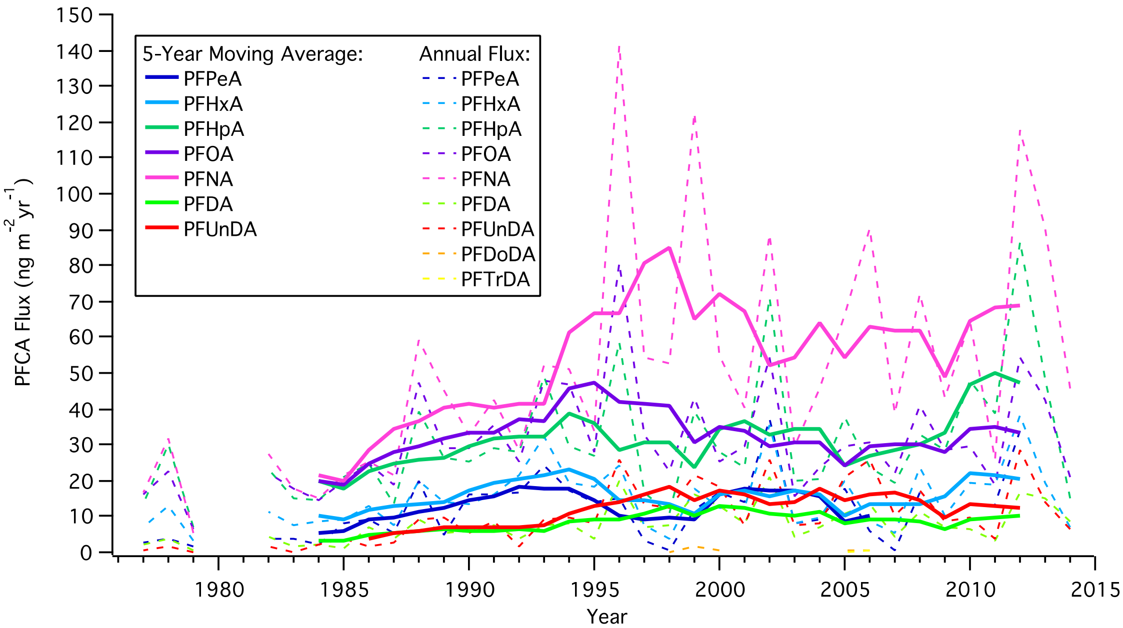


Figure S4. Temporal flux trends for the long-chain PFCAs including PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA. Dotted lines represent annual fluxes and solid lines are the 5-year moving averages of the fluxes.

Table S14. 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).

<table>
<tr><th colspan="3"></th><th>% Reduction in Emissions</th><th colspan="3">% Reduction in Product Content</th></tr>
<tr><th>Company</th><th>Reduction Year</th><th>Chemical Category</th><th>% Reductions in total quantity of chemical(s) released from baseline year</th><th>Fluoropolymer Dispersions</th><th>Other Fluoropolymers</th><th>Telomer based products</th></tr>
<tr><td rowspan="2">Arkema</td><td rowspan="2">2013</td><td>PFOA, PFOA salts and Higher Homologues</td><td>91%</td><td>100%</td><td>96% (100%)</td><td>N/A</td></tr>
<tr><td>Precursors</td><td colspan="4">N/A</td></tr>
<tr><td rowspan="2">Asahi</td><td rowspan="2">2013</td><td>PFOA, PFOA salts and Higher Homologues</td><td>100%</td><td>100% (100%)</td><td>100%</td><td>N/A (100%)</td></tr>
<tr><td>Precursors</td><td colspan="4">N/A</td></tr>
<tr><td rowspan="3">Ciba/BASF</td><td rowspan="3">2012</td><td>PFOA</td><td colspan="4" rowspan="3">N/A</td></tr>
<tr><td>Higher Homologues</td></tr>
<tr><td>Precursors</td></tr>
<tr><td rowspan="2">Clariant</td><td rowspan="2">2013</td><td>PFOA and PFOA salts</td><td colspan="4" rowspan="2">N/A</td></tr>
<tr><td>Direct Precursors</td></tr>
<tr><td rowspan="2">Daikin</td><td rowspan="2">2013</td><td>PFOA</td><td>100%</td><td>100%</td><td>100%</td><td>100%</td></tr>
<tr><td>Precursor and Higher Homologues</td><td>100%</td><td>N/A</td><td>N/A</td><td>100%</td></tr>
<tr><td rowspan="3">DuPont</td><td rowspan="3">2013</td><td>PFOA and PFOA salts</td><td>99.8%</td><td rowspan="2">99.9% (99.5%)</td><td rowspan="2">99.9% (99.5%)</td><td rowspan="2">99.9%[1] (99%)</td></tr>
<tr><td>Higher Homologues</td><td>None Reported</td></tr>
<tr><td>Precursors</td><td>CBI</td><td>None Reported</td><td>None Reported</td><td>98%[1]</td></tr>
<tr><td rowspan="2">3M/Dyneon</td><td rowspan="2">2013</td><td>PFOA, PFOA salts and Higher Homologues</td><td>100%</td><td>100%</td><td>N/A</td><td>No Telomer Production</td></tr>
<tr><td>Precursors</td><td colspan="4">No Precursor Production</td></tr>
<tr><td rowspan="2">Solvay Solexis</td><td rowspan="2">2013</td><td>PFOA, PFOA salts and Higher Homologues</td><td>>99.999%</td><td>>99.999%</td><td>>99.999%</td><td>N/A</td></tr>
<tr><td>Precursors</td><td colspan="4">N/A</td></tr>
</table>

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

Table S15. 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	**% 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	CBI	N/A	CBI	N/A
		Precursors	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	N/A			
		Higher Homologues				
		Precursors				
Clariant	2013	PFOA and PFOA salts	>80%	None Reported	None Reported	90%
		Direct Precursors	>85%	None Reported	None Reported	94%
Daikin	2013	PFOA	Not Reported			
		Precursor and Higher Homologues				
DuPont	2013	PFOA and PFOA salts	99.8%	99.9%	100%	99.9%[2]
		Higher Homologues	None Reported			
		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 Production			
Solvay Solexis	2013	PFOA, PFOA salts and Higher Homologues	N/A			
		Precursors	N/A			

N/A means not available.
[2]Global 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 S16). Pairs of homologues are useful for determining if precursors play a significant role in LRT of these compounds.

Table S16. Coefficients of determination (R^2) 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
PFHxA	**R^2= 0.668**											
	p<0.0001											
PFHpA	**R^2= 0.505**	**R^2= 0.889**										
	p<0.0001	**p<0.0001**										
PFOA	R^2= 0.298	**R^2= 0.437**	**R^2= 0.527**									
	p= 0.0005	**p<0.0001**	**p<0.0001**									
PFNA	R^2= 0.095	R^2= 0.186	R^2= 0.334	**R^2= 0.708**								
	p= 0.0633	p= 0.0077	p= 0.0002	**p<0.0001**								
PFDA	R^2= 0.129	R^2= 0.134	R^2= 0.246	**R^2= 0.592**	**R^2= 0.865**							
	p= 0.0289	p= 0.0261	p= 0.0018	**p<0.0001**	**p<0.0001**							
PFUnDA	R^2= 0.119	R^2= 0.103	R^2= 0.203	**R^2= 0.509**	**R^2= 0.839**	**R^2= 0.830**						
	p= 0.0363	p= 0.0527	p= 0.0051	**p<0.0001**	**p<0.0001**	**p<0.0001**						
PFDoDA	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**					
	p= 0.0283	p= 0.1306	p= 0.0406	p= 0.0046	**p<0.0001**	**p<0.0001**	**p<0.0001**					
PFTrDA	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				
	p= 0.3844	p= 0.5782	p= 0.2376	p= 0.0474	p= 0.0002	p= 0.0005	**p<0.0001**	p= 0.0008				
PFBS	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			
	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			
PFHpS	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		
	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		
PFOS	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**	
	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**	
FOSA	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
	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.

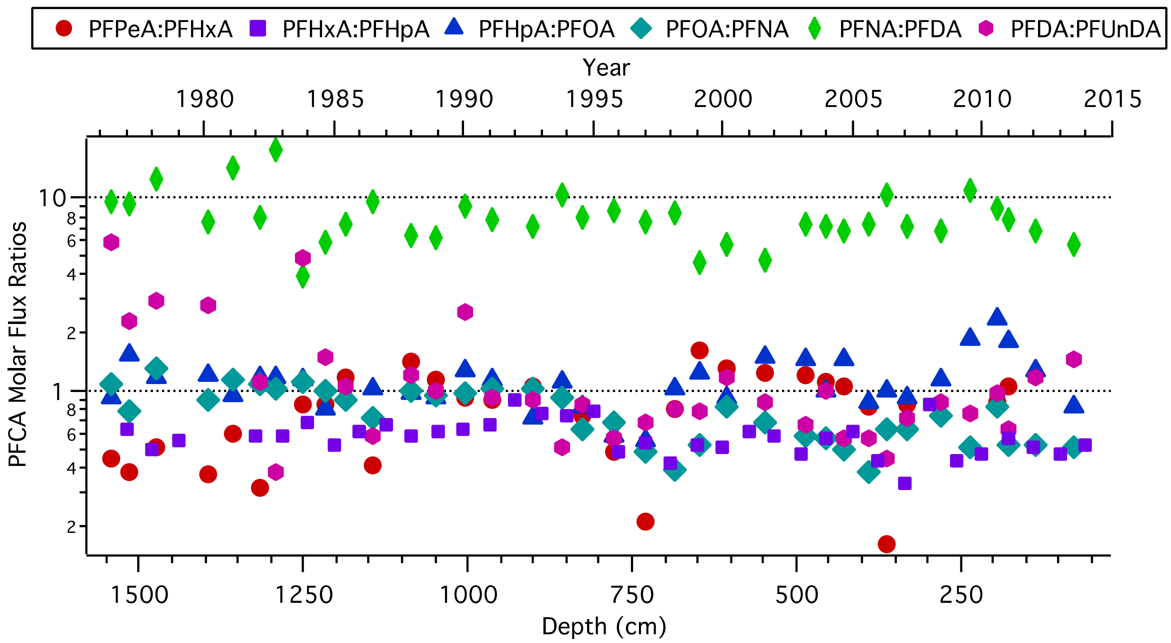


Figure S5. Molar flux ratios for six pairs of PFCA homologues ranging from PFPeA to PFUnDA, as a function of depth and year.

Section S6. Long-Range Transport Mechanisms of PFAAs

Concentrations (μg L^{-1}) of all the anions and cations detected on the Devon Ice Cap with depth and over time, are provided in Tables S17 and S18, including values <LOD. Some years do not have values due to insufficient volume of sample available for analysis.

Table S17. 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**	**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 S18. 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.

		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

The vertical profiles for the anions and cations are plotted in Figures S6-S7. 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.

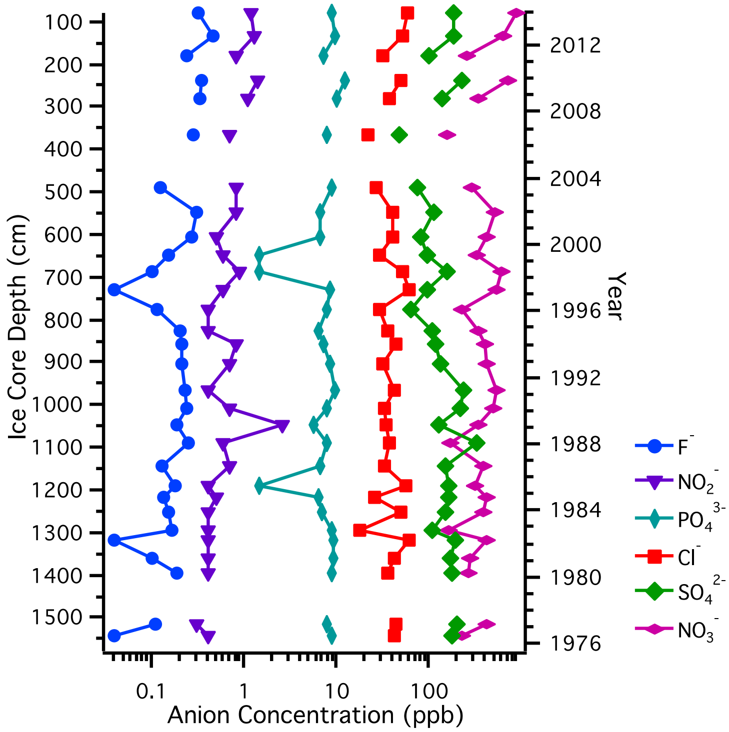


Figure S6. Vertical profile of anion concentrations (ng mL^{-1}) on a log scale, per depth in the ice core and by year. Anions detected include F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}.

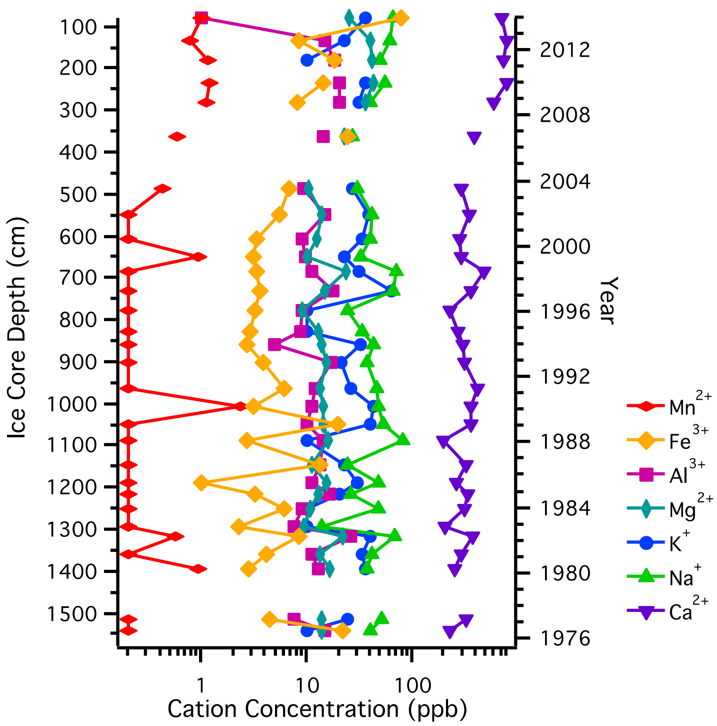


Figure S7. Vertical profile of cation concentrations (ng mL^{-1}) on a log scale, per depth in the ice core and by year. Cations detected include Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+} and Fe^{3+}.

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 S19. 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 S19. Non-sea salt and sea salt component concentrations (conc.) (μmol/L) of select ions in the ice core.

	Na^+	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).

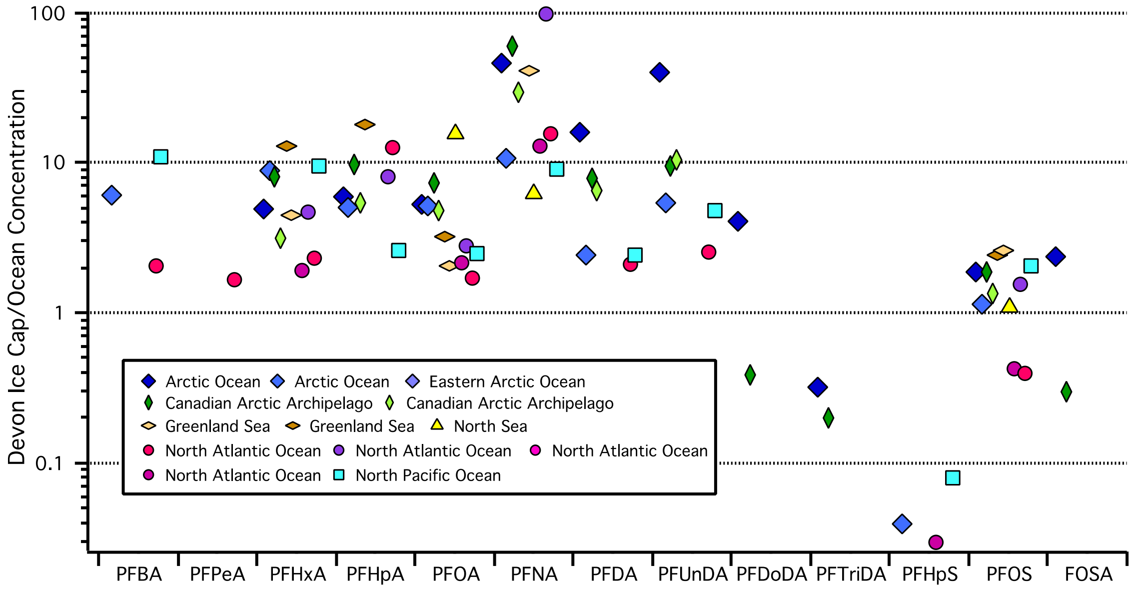


Figure S8. Ratios of observed concentrations in the Devon Ice Cap compared to levels in the Arctic Ocean (Benskin et al., 2012) (Cai et al., 2012), Eastern Arctic Ocean (Scott et al., 2005), Canadian Artic Archipelago (Benskin et al., 2012), Greenland Sea (Zhao et al., 2012) (Busch et al., 2010), North Sea (Ahrens et al., 2010b), North Atlantic Ocean (Ahrens et al., 2010a) (Ahrens et al., 2009) (Zhao et al., 2012) (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 S20 and S21, 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.

Table S20. Coefficients of determination (R^2) and statistical significance (p) of PFAA homologues, as well as FOSA, cations, and metals (n=25). Weak correlations (R^2=0.3-0.5) shown in green and moderate correlations (R^2=0.5-0.7) in blue. Statistically significant p-values (p<0.0001) in bold.

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

Table S21. Coefficients of determination (R^2) and statistical significance (p) of PFAA homologues, as well as FOSA, anions, and organic acids (n=27). Weak correlations (R^2=0.3-0.5) are shown in green. Statistically significant p-values (p<0.0001) in bold.

	Fluoride	Chloride	Nitrite	Nitrate	Sulfate	Phosphate	Acetate	Propionate	Formate	Butyrate
TFA	**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
	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
PFPrA	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
	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
PFBA	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
	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
PFPeA	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
	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
PFHxA	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
	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
PFHpA	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
	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
PFOA	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
	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
PFNA	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
	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
PFDA	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
	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
PFUnDA	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
	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
PFDoDA	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
	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
PFTrDA	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
	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
PFBS	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
	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
PFHpS	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
	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
PFOS	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
	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
FOSA	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
	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 S22. Coefficients of determination (R^2) 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 (+/-)
PFPeA	R^2= 0.047 p=0.2088	R^2= 0.050 p=0.1959	+
PFHxA	R^2= 0.217 p=0.0048	R^2= 0.215 p=0.0050	+
PFHpA	R^2= 0.295 p=0.0007	R^2= 0.295 p=0.0007	+
PFOA	R^2= 0.106 p=0.0559	R^2= 0.114 p=0.0470	+
PFNA	R^2= 0.183 p=0.0104	R^2= 0.199 p=0.0073	+
PFDA	R^2= 0.129 p=0.0339	R^2= 0.142 p=0.0258	+
PFUnDA	R^2= 0.161 p=0.0168	R^2= 0.169 p=0.0140	+
PFDoDA	R^2= 0.058 p=0.1648	R^2= 0.067 p=0.1334	+
PFTrDA	R^2= 0.030 p=0.3172	R^2= 0.033 p=0.2938	+
PFOcDA	R^2= 0.007 p=0.6437	R^2= 0.017 p=0.4618	-
PFBS	R^2= 0.113 p=0.0485	R^2= 0.116 p=0.0451	+
PFHpS	R^2= 0.055 p=0.1735	R^2= 0.049 p=0.2000	+
PFOS	R^2= 0.099 p=0.0659	R^2= 0.085 p=0.0887	+
FOSA	R^2= 0.266 p=0.0015	R^2= 0.261 p=0.0017	-

References

Ahrens, L., Barber, J. L., Xie, Z. and Ebinghaus, R.: Longitudinal and Latitudinal Distribution of Perfluoroalkyl Compounds in the Surface Water of the Atlantic Ocean, Environ. Sci. Technol., 43(9), 3122–3127, doi:10.1021/es803507p, 2009.

Ahrens, L., Xie, Z. and Ebinghaus, R.: Distribution of perfluoroalkyl compounds in seawater from Northern Europe, Atlantic Ocean, and Southern Ocean, Chemosphere, 78(8), 1011–1016, doi:10.1016/j.chemosphere.2009.11.038, 2010a.

Ahrens, L., Gerwinski, W., Theobald, N. and Ebinghaus, R.: Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: Evidence from their spatial distribution in surface water, Mar. Pollut. Bull., 60(2), 255–260, doi:10.1016/j.marpolbul.2009.09.013, 2010b.

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.

Busch, J., Ahrens, L., Xie, Z., Sturm, R. and Ebinghaus, R.: Polyfluoroalkyl compounds in the East Greenland Arctic Ocean, J. Environ. Monit., 12(6), 1242, doi:10.1039/c002242j, 2010.

Butt, C. M., Berger, U., Bossi, R. and Tomy, G. T.: Levels and trends of poly- and perfluorinated compounds in the arctic environment, Sci. Total Environ., 408(15), 2936–2965, doi:10.1016/j.scitotenv.2010.03.015, 2010.

Cai, M., Zhao, Z., Yin, Z., Ahrens, L., Huang, P., Cai, M., Yang, H., He, J., Sturm, R., Ebinghaus, R. and Xie, Z.: 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, 2012.

Casal, P., Zhang, Y., Martin, J. W., Pizarro, M., Jiménez, B. and Dachs, J.: Role of Snow Deposition of Perfluoroalkylated Substances at Coastal Livingston Island (Maritime Antarctica), Environ. Sci. Technol., 51(15), 8460–8470, doi:10.1021/acs.est.7b02521, 2017.

Criscitiello, A. S., Das, S. B., Karnauskas, K. B., Evans, M. J., Frey, K. E., Joughin, I., Steig, E. J., McConnell, J. R. and Medley, B.: Tropical Pacific Influence on the Source and Transport of Marine Aerosols to West Antarctica, J. Clim., 27(3), 1343–1363, doi:10.1175/JCLI-D-13-00148.1, 2014.

Environment and Climate Change Canada: Environmental Performance Agreement, [online] Available from: http://ec.gc.ca/epe-epa/default.asp?lang=En&n=AE06B51E-1, 2006.

Kirchgeorg, T., Dreyer, A., Gabrieli, J., Kehrwald, N., Sigl, M., Schwikowski, M., Boutron, C., Gambaro, A., Barbante, C. and Ebinghaus, R.: Temporal variations of perfluoroalkyl substances and polybrominated diphenyl ethers in alpine snow, Environ. Pollut., 178, 367–374, doi:10.1016/j.envpol.2013.03.043, 2013.

Kwok, K. Y., Taniyasu, S., Yeung, L. W. Y., Murphy, M. B., Lam, P. K. S., Horii, Y., Kannan, K., Petrick, G., Sinha, R. K. and Yamashita, N.: Flux of Perfluorinated Chemicals through Wet Deposition in Japan, the United States, And Several Other Countries, Environ. Sci. Technol., 44(18), 7043–7049, doi:10.1021/es101170c, 2010.

Kwok, K. Y., Yamazaki, E., Yamashita, N., Taniyasu, S., Murphy, M. B., Horii, Y., Petrick, G., Kallenborn, R., Kannan, K., Murano, K. and Lam, P. K. S.: Transport of Perfluoroalkyl substances (PFAS) from an arctic glacier to downstream locations: Implications for sources, Sci. Total Environ., 447, 46–55, doi:10.1016/j.scitotenv.2012.10.091, 2013.

Libes, S. M.: Introduction to Marine Biogeochemistry, Second., Elsevier., 2009.

MacInnis, J. J., French, K., Muir, D. C. G., Spencer, C., Criscitiello, A., De Silva, A. O. and Young, C. J.: A 14-year depositional ice record of perfluoroalkyl substances in the High Arctic, Environ. Sci. Process. Impacts, 19(1), 22–30, doi:10.1039/C6EM00593D, 2017.

McConnell, J. R., Lamorey, G. W., Lambert, S. W. and Taylor, K. C.: Continuous Ice-Core Chemical Analyses Using Inductively Coupled Plasma Mass Spectrometry, Environ. Sci. Technol., 36(1), 7–11, doi:10.1021/es011088z, 2002.

Müller, C. E., Gerecke, A. C., Alder, A. C., Scheringer, M. and Hungerbühler, K.: Identification of perfluoroalkyl acid sources in Swiss surface waters with the help of the artificial sweetener acesulfame, Environ. Pollut., 159, 1419–1426, doi:10.1016/j.envpol.2010.12.035, 2011.

Scott, B. F., Macdonald, R. W., Kannan, K., Fisk, A., Witter, A., Yamashita, N., Durham, L., Spencer, C. and Muir, D. C. G.: Trifluoroacetate Profiles in the Arctic, Atlantic, and Pacific Oceans, Environ. Sci. Technol., 39(17), 6555–6560, doi:10.1021/es047975u, 2005.

Scott, B. F., Spencer, C., Mabury, S. A. and Muir, D. C. G.: Poly and Perfluorinated Carboxylates in North American Precipitation, Environ. Sci. Technol., 40(23), 7167–7174, doi:10.1021/es061403n, 2006.

De Silva, A. O., Spencer, C., Scott, B. F., Backus, S. and Muir, D. C. G.: Detection of a Cyclic Perfluorinated Acid, Perfluoroethylcyclohexane Sulfonate, in the Great Lakes of North America, Environ. Sci. Technol., 45(19), 8060–8066, doi:10.1021/es200135c, 2011.

Stock, N. L., Furdui, V. I., Muir, D. C. G. and Mabury, S. A.: Perfluoroalkyl Contaminants in the Canadian Arctic: Evidence of Atmospheric Transport and Local Contamination, Environ. Sci. Technol., 41(10), 3529–3536, doi:10.1021/es062709x, 2007.

US EPA: 2010/2015 PFOA Stewardship Program - 2014 Annual Progress Reports, [online] Available from: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/20102015-pfoa-stewardship-program-2014-annual-progress, 2014.

Wang, X., Halsall, C., Codling, G., Xie, Z., Xu, B., Zhao, Z., Xue, Y., Ebinghaus, R. and Jones, K. C.: Accumulation of Perfluoroalkyl Compounds in Tibetan Mountain Snow: Temporal Patterns from 1980 to 2010, Environ. Sci. Technol., 48(1), 173–181, doi:10.1021/es4044775, 2014.

Young, C. J., Furdui, V. I., Franklin, J., Koerner, R. M., Muir, D. C. G. and Mabury, S. a.: Perfluorinated Acids in Arctic Snow: New Evidence for Atmospheric Formation, Environ. Sci. Technol., 41(10), 3455–3461, doi:10.1021/es0626234, 2007.

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.