A 14-year depositional ice record of perfluoroalkyl acids in the High Arctic

John J. MacInnis[†], Katherine French[‡], Derek C.G. Muir[‡], Christine Spencer[‡], Alison Criscitiello[•], Amila O. De Silva[‡*], Cora J. Young[†*]

[†]Department of Chemistry, Memorial University, St. John's, NL, Canada A1B 3X7
[‡]Aquatic Contaminants Research Division, Environment and Climate Change Canada, Burlington, ON, Canada L7S 1A1
[•]Department of Geography, University of Calgary, Calgary AB, Canada T2N 1N4

*Corresponding Authors amila.desilva@canada.ca, cora.young@mun.ca

S1.1 Sample preparation and analysis

Samples were defrosted the night before extraction, and 500 mL of melted sample was used. Melted samples were spiked with 30 μL of a surrogate mixture (Table S2), which acted as the internal standard to monitor recovery. Covered samples were shaken and sonicated for ten minutes and were placed in the lab for 30 minutes to equilibrate at room temperature. Samples were concentrated using an OASIS® weak anion exchange (WAX) solid phase extraction (SPE) cartridge (6 cm^3, 150 mg, 30 μm). Two elution fractions were collected: the first fraction was eluted with 6 mL of methanol for FOSA, while the second fraction was eluted with 8 mL of 0.1% ammonia in methanol for PFAAs. Both fractions were evaporated to dryness using nitrogen and reconstituted in 0.25 mL of water pre-cleaned using SPE and 0.25 mL methanol (Fisher Brand HPLC Grade, ThermoFisher). Contamination was rarely observed in cartridge blanks; however, where contamination was observed, it was generally lower than the LOQ. Method recoveries for PFAAs ranged from 95 - 113 %, with the exception of PFOcDA ranging from 35 - 70 %. Method recoveries demonstrate negative biases resulting from subsampling and storage were not significant in this study. Recoveries for PFOcDA are reflective of the analytical limitations of the method. Recovery of internal standards and instrument performance standards in sample extracts are listed below (Tables S3 – S4). Due to the common presence of trace PFAAs in purchased reagent water, water (Fisher Brand HPLC Grade, ThermoFisher) used in the mobile phase was subjected to additional cleaning through OASIS WAX SPE.

S1.2 Data Analysis

Years of deposition were based on snow density, ion chemistry, and annual snow accumulation data as described in detail by Meyer et al.[1] Net deposition fluxes for each analyte were calculated by multiplying the ng L^{-1} concentration by the annual accumulation of water equivalent (L cm^{-2} yr^{-1}):

$$\left(\frac{ng_{PFAA}}{L_{H_2O}}\right) x \left(\frac{L_{H_2O}}{1000\ cm^3{}_{H_2O}}\right) x \left(\frac{cm^3{}_{H_2O}}{cm^3{}_{snow}}\right) x \left(\frac{25\ cm_{snow}}{year}\right) x \left(\frac{10{,}000\ cm^2_{snow}}{m^2_{snow}}\right) = ng_{PFAA}\ m^{-2}_{snow}\ year^{-1}$$

S1.3 Even-even PFCA homologue trends

To further validate fluorotelomer precursor oxidation as a major source of PFCA deposition at the Devon Ice Cap, even-even homologue relationships were determined for PFBA to PFDoDA. A correlation between PFHxA and PFOA ($R^2 = 0.17$, $p = 0.0311$) concentrations was weak, moderate among PFHxA and PFBA ($R^2 = 0.32$, $p = 0.0016$) and PFDA and PFDoDA ($R^2 = 0.54$, $p<0.0001$), and strong between PFOA and PFDA ($R^2 = 0.79$, $p<0.0001$). Molar PFCA flux ratios for even-even homologues were determined (Figure 2b). Unlike the even-odd flux ratios, only 17% of the measurements were within a factor of two and only 56% of the measurements were within a factor of 5. It is interesting that most flux ratios of PFOA: PFHxA, and PFDA: PFOA, are within factors of 2 and 5, respectively. These observations are consistent with our knowledge of the fugitive emissions of different FTOHs from fluoropolymer products.[3] In the work of Dinglasan-Panlilio and Mabury, 8:2 FTOH was the dominant residual impurity in marketed fluorinated products, followed by 6:2 and 10:2 FTOH.[3] Elevated proportions of residual volatile precursors in fluoropolymer products may suggest the presence of PFHxA, PFOA, and PFDA on the Devon Ice Cap are partially derived from common fugitive emission sources.

Table S1. Comparison of PFAA concentration (ng L^{-1}) in field, stay, and method blanks.

Perfluoroalkyl Substance	Stay Blank (500 mL HPLC grade water)	Field Blank A (500 mL HPLC grade water)	Field Blank B (500 mL HPLC grade water)	Method Blanks
PFBA	<LOD	<LOD	<LOD	0.042-0.058
PFPeA	<LOD	<LOD	<LOD	<LOD
PFHxA	0.476	0.265	0.255	<LOD
PFHpA	0.037	0.046	0.045	<LOD
PFOA	0.332	0.36	0.342	0.002-0.005
PFNA	0.061	0.063	0.061	<LOD
PFDA	0.158	0.151	0.157	<LOD
PFUnDA	0.016	0.012	0.019	<LOD
PFDoDA	0.028	0.026	0.030	<LOD
PFTrDA	<LOD	<LOD	<LOD	<LOD
PFTeDA	<LOD	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD
PFOcDA	<LOD	<LOD	<LOD	<LOD
PFECHS	<LOD	<LOD	<LOD	<LOD
PFBS	0.002	0.003	0.002	<LOD
PFHxS	<LOD	<LOD	<LOD	<LOD
PFHpS	<LOD	<LOD	<LOD	<LOD
PFOS	0.018	0.014	0.018	<LOD
PFDS	<LOD	<LOD	<LOD	<LOD
FOSA	<LOD	<LOD	<LOD	0.022-0.025

Table S2. Analyte 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	Internal Standard	Instrument Performance Standard
PFBA	$^{13}C_4$ PFBA (217/172)	$^{13}C_3$ PFBA (216/172)
PFPeA	$^{13}C_5$ PFPeA (268/223)	$^{13}C_3$ PFPeA (266/222)
PFHxA	$^{13}C_2$ PFHxA (315/270)	$^{13}C_5$ PFHxA (318/273)
PFHpA	$^{13}C_4$ PFHpA (367/322)	
PFOA	$^{13}C_4$ PFOA (417/372)	$^{13}C_2$ PFOA (415/370)
PFNA	$^{13}C_5$ PFNA (468/423)	$^{13}C_9$ PFNA (472/427)
PFDA	$^{13}C_2$ PFDA (515/470)	$^{13}C_6$ PFDA (519/474)
PFUnDA	$^{13}C_2$ PFUnDA (565/520)	$^{13}C_7$ PFUnDA (570/525)
PFDoDA	$^{13}C_2$ PFDoDA (615/570)	
PFTrDA	$^{13}C_2$ PFDoDA (615/570)	
PFTeDA	$^{13}C_2$ PFTeDA (715/670)	
PFHxDA	$^{13}C_2$ PFHxDA (815/770)	
PFOcDA	$^{13}C_2$ PFHxDA (815/770)	
PFBS	$^{18}O_2$ PFHxS (403/84)	
PFHxS	$^{18}O_2$ PFHxS (403/103)	$^{13}C_3$ PFHxS (402/99)
PFHpS	$^{18}O_2$ PFHxS (403/84)	
PFOS	$^{13}C_4$ PFOS (503/80)	$^{13}C_8$ PFOS (507/99)
PFDS	$^{13}C_4$ PFOS (503/80)	
PFECHS	$^{18}O_2$ PFHxS (403/84)	
FOSA	$^{13}C_8$ FOSA (506/78)	

Table S3. Recovery of IS in sample extracts. 500 mL of sample was spiked with 0.125 ng of internal standard prior to extraction. Recovery is based on peak area comparison to solvent standard. Mean (standard error) recovery reported for n=18 samples from the Devon Ice Cap.

IS	Recovery (%)
$^{13}C_4$ PFBA	64 (3)
$^{13}C_5$ PFPeA	71 (4)
$^{13}C_2$ PFHxA	73 (3)
$^{13}C_4$ PFHpA	74 (3)
$^{13}C_4$ PFOA	89 (3)
$^{13}C_5$ PFNA	86 (3)
$^{13}C_2$ PFDA	83 (2)
$^{13}C_7$ PFUnDA	99 (1)
$^{13}C_2$ PFDoDA	74 (1)
$^{13}C_2$ PFTeDA	50 (3)
$^{13}C_2$ PFHxDA	98 (9)
$^{13}C_4$ PFOS 99	98 (1)
$^{13}C_4$ PFOS 80	97 (1)
$^{18}O_2$ PFHxS 103	102 (1)
$^{18}O_2$ PFHxS 84	103 (1)

Table S4. Recovery of IP standard in sample extracts. 500 mL of sample was spiked with 0.125 ng of performance standard after extraction. Recovery is based on peak area comparison to solvent standard. Mean (standard error) recovery reported for n=18 samples from the Devon Ice Cap.

IP	Recovery (%)
$^{13}C_3$ PFBA	98 (3)
$^{13}C_3$ PFPeA	98 (1)
$^{13}C_5$ PFHxA	100 (1)
$^{13}C_2$ PFOA	105 (1)
$^{13}C_9$ PFNA	97 (1)
$^{13}C_6$ PFDA	95 (1)
$^{13}C_2$ PFUnDA	86 (1)
$^{13}C_8$ PFOS 99	100 (1)
$^{13}C_8$ PFOS 80	101 (1)
$^{13}C_3$ PFHxS 99	104 (1)

Table S5. 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	0.000	75	25

*Mobile phases buffered with 0.1 mM ammonium acetate.

Table S6. Summary of inlet and mass spectrometric conditions.

Capillary Voltage (kV)	0.5
Source Temperature (°C)	150
Desolvation Gas Temperature (°C)	450
Cone Gas Flow (L hr^{-1})	150
Desolvation Gas Flow (L hr^{-1})	650
Collision Gas Flow (mL min^{-1})	0.15
Nebulizer Pressure (bar)	7
Column Temperature (°C)	50
Injection Volume (μL)	9

Table S7. Summary of PFAA elution order, retention time, and ion transitions.

Elution Order	PFAA	Retention Time (min)	Quantifier Ion Transition (m/z)	Qualifier Ion Transition (m/z)
1	PFBA	0.91	213 > 169	
2	PFPeA	2.11	263 > 219	
3	PFBS	2.38	299 > 80	299 > 99
4	PFHxA	3.07	313 > 269	313 > 119
5	PFHpA	3.68	363 > 319	363 > 119,169
6	PFHxS	3.74	399 > 80	399 > 99
7	PFECHS	4.08	461 > 381	461 > 99
8	PFOA	4.12	413 > 369	413 > 169
9	PFHpS	4.16	449 > 80	449 > 99
10	PFNA	4.48	463 > 419	463 > 219
11	PFOS	4.50	499 > 80	499 > 99
12	PFDA	4.78	513 > 469	513 > 219
13	PFUnDA	5.03	563 > 519	563 > 319,269
14	PFDS	5.03	599 > 80	599 > 99
15	FOSA	5.13	498 > 78	
16	PFDoDA	5.24	613 > 569	613 > 169
17	PFTrDA	5.42	663 > 619	663 > 169
18	PFTeDA	5.58	713 > 669	713 > 169
19	PFHxDA	5.82	813 > 769	813 > 169
20	PFOcDA	5.95	913 > 869	913 > 169

Table S8. Instrument limit of detection and quantitation for PFAAs.

Perfluoroalkyl Substance	LOD (pg L^{-1})	LOQ (pg L^{-1})
PFBA	10	50
PFPeA	7	20
PFHxA	1	4
PFHpA	2	5
PFOA	2	6
PFNA	2	6
PFDA	1	4
PFUnDA	1	5
PFDoDA	1	4
PFTrDA	1	4
PFTeDA	2	5
PFHxDA	6	20
PFOcDA	10	40
PFECHS	0.3	1
PFBS	4	10
PFHxS	1	4
PFHpS	1	4
PFOS	1	4
PFDS	2	7
FOSA	1	3

Table S9. Depth profile (cm) of PFAA concentrations (ng L^{-1}) on the Devon Ice Cap. Values <LOQ are identified in blue.

LOD	0.010	0.007	0.001	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.002	0.004	0.001	0.002	0.0003	0.001
LOQ	**0.050**	**0.020**	**0.004**	**0.005**	**0.006**	**0.006**	**0.004**	**0.005**	**0.004**	**0.004**	**0.005**	**0.010**	**0.004**	**0.007**	**0.001**	**0.003**
Avg Depth	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**	**C4-S**	**C8-S**	**C10-S**	**PFECHS**	**FOSA**
12.5	0.260	0.060	<LOD	<LOD	0.079	0.035	0.013	0.014	0.011	<LOD	<LOD	0.095	<LOD	<LOD	0.020	<LOD
37.5	0.166	0.055	<LOD	0.052	0.069	0.112	0.017	0.027	<LOD	<LOD	<LOD	0.054	<LOD	<LOD	0.019	<LOD
62.5	0.120	0.042	0.052	0.167	0.371	1.395	0.214	0.348	0.031	0.026	<LOD	0.065	0.014	<LOD	0.009	0.020
87.5	0.171	0.056	0.079	0.200	0.340	0.850	0.136	0.147	0.009	0.005	<LOD	0.086	0.017	<LOD	0.005	0.010
112.5	0.230	0.117	0.152	0.424	0.677	1.424	0.232	0.185	0.032	0.019	0.002	0.070	0.019	<LOD	0.007	0.013
137.5	0.467	0.245	0.183	0.505	0.505	0.878	0.143	0.121	0.017	0.006	<LOD	0.066	0.016	0.002	0.011	0.021
162.5	0.889	0.292	0.297	0.544	0.335	0.307	0.095	0.040	0.004	0.008	<LOD	0.105	0.016	<LOD	0.009	0.013
187.5	1.630	0.457	0.412	0.693	0.458	0.569	0.169	0.083	0.008	0.001	<LOD	0.120	0.013	<LOD	0.003	0.008
212.5	0.848	0.236	0.192	0.301	0.185	0.118	0.038	0.038	0.002	<LOD	<LOD	0.196	0.013	<LOD	<LOD	0.007
237.5	0.154	0.110	0.130	0.296	0.348	0.707	0.111	0.151	0.023	0.009	<LOD	0.152	0.017	<LOD	0.007	0.014
262.5	1.084	0.217	0.191	0.367	0.350	0.686	0.106	0.109	0.006	<LOD	0.002	0.132	0.002	<LOD	0.000	0.009
287.5	0.566	0.139	0.103	0.221	0.190	0.332	0.071	0.055	0.005	0.001	<LOD	0.088	0.009	<LOD	0.000	0.014
312.5	0.331	0.066	0.092	0.141	0.190	0.312	0.065	0.079	0.007	0.007	<LOD	0.113	0.010	<LOD	0.004	0.040
337.5	0.322	0.091	0.135	0.267	0.304	0.552	0.094	0.114	0.015	0.006	<LOD	0.092	0.010	<LOD	0.013	0.034
362.5	0.121	0.079	0.107	0.172	0.223	0.537	0.070	0.088	0.011	0.010	<LOD	0.103	0.014	<LOD	0.007	0.093
387.5	0.163	0.090	0.107	0.173	0.226	0.425	0.059	0.105	0.013	0.010	<LOD	0.109	0.015	<LOD	0.009	0.072
412.5	1.103	0.042	0.064	0.116	0.220	0.371	0.059	0.111	0.011	0.006	<LOD	0.089	0.011	<LOD	0.009	0.061
437.5	1.071	0.034	0.024	0.112	0.235	0.457	0.106	0.172	0.026	0.023	0.008	0.128	0.004	<LOD	0.009	0.082
462.5	0.138	0.065	0.071	0.154	0.437	0.541	0.121	0.104	0.007	0.012	0.003	0.177	0.016	<LOD	0.011	0.043
487.5	0.145	0.046	0.068	0.126	0.272	0.426	0.091	0.107	0.006	0.005	<LOD	0.175	0.019	<LOD	0.014	0.060
512.5	0.119	0.038	0.067	0.104	0.234	0.324	0.057	0.056	0.003	0.004	<LOD	0.141	0.016	<LOD	0.014	0.065
537.5	0.139	0.127	0.122	0.228	0.340	0.521	0.123	0.161	0.023	0.010	<LOD	0.159	0.017	0.009	0.012	0.129
562.5	0.366	0.152	0.171	0.257	0.211	0.211	0.045	0.055	<LOD	0.004	<LOD	0.216	0.016	<LOD	0.012	0.042
587.5	0.176	0.116	0.152	0.208	0.254	0.258	0.062	0.075	0.002	0.007	<LOD	0.226	0.015	<LOD	0.012	0.048
612.5	2.023	0.123	0.270	0.369	0.343	0.340	0.072	0.067	0.005	0.003	<LOD	0.154	0.015	<LOD	0.013	0.038
637.5	0.599	0.109	0.153	0.166	0.101	0.106	0.034	0.022	<LOD	<LOD	<LOD	<LOD	0.017	<LOD	0.015	0.021
662.5	0.212	0.130	0.150	0.173	0.157	0.157	0.039	0.026	<LOD	0.001	<LOD	<LOD	0.019	0.005	0.011	0.035
687.5	1.710	0.077	0.130	0.116	0.159	0.158	0.067	0.028	0.004	0.001	<LOD	<LOD	0.027	0.007	0.015	0.036

Table S10. PFAA flux to the Devon Ice Cap expressed in ng m^{-2} yr^{-1}. Estimated PFAA flux (red) is calculated from homologue LOD.

Year	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C16	C18	C4-S	C6-S	C7-S	C8-S	C10-S	PFECHS	FOSA
2007	43.66	12.70	5.40	20.97	48.72	152.65	23.98	38.49	3.98	2.82	<0.50	<1.50	<2.49	17.57	<0.25	<0.25	1.53	<0.50	3.76	2.07
2006	38.97	16.61	22.22	59.77	97.66	219.58	35.57	32.37	3.86	2.20	0.39	<1.18	<1.97	15.39	<0.20	<0.20	3.53	<0.39	1.13	2.19
2005	127.91	50.19	45.13	97.82	77.56	108.23	21.98	14.72	1.92	1.33	<0.37	<1.12	<1.86	16.08	<0.19	<0.19	2.92	0.37	1.82	3.09
2004	243.87	68.28	59.87	98.89	64.15	70.48	21.18	11.93	0.98	0.19	<0.38	<1.13	<1.89	28.92	<0.19	<0.19	2.43	<0.38	0.39	1.42
2003	136.34	35.09	34.22	70.29	73.51	146.45	22.84	27.05	2.89	0.98	0.42	<1.26	<2.11	29.78	<0.21	<0.21	1.85	<0.42	0.73	2.45
2002	97.41	22.15	21.21	39.31	41.50	70.36	14.83	14.81	1.34	0.89	<0.44	<1.31	<2.19	22.07	<0.22	<0.22	2.06	<0.44	0.53	5.99
2001	48.37	19.63	27.69	49.46	60.02	126.72	18.71	23.14	2.98	1.89	<0.47	<1.40	<2.33	22.88	<0.23	<0.23	2.83	<0.47	2.24	15.74
2000	110.05	13.68	17.44	29.14	43.91	78.91	11.60	21.10	2.34	1.60	<0.39	<1.18	<1.96	19.69	<0.20	<0.20	2.67	<0.39	1.78	13.27
1999	139.81	11.13	10.74	30.14	75.87	113.28	25.71	31.58	3.84	4.07	1.23	<1.36	<2.27	34.61	<0.23	<0.23	2.19	<0.45	2.27	14.37
1998	29.49	9.34	15.05	25.59	56.56	83.73	16.55	18.30	1.03	1.07	<0.45	<1.34	<2.23	35.24	<0.22	<0.22	3.94	<0.45	3.11	13.94
1997	51.03	29.20	30.42	50.85	59.38	80.33	18.50	23.78	2.70	1.62	<0.42	<1.27	<2.11	38.98	<0.21	<0.21	3.47	1.19	2.58	18.86
1996	204.97	22.36	39.38	53.91	55.74	55.94	12.49	13.34	0.61	0.90	<0.37	<1.12	<1.87	35.58	<0.19	<0.19	2.77	<0.37	2.37	8.06
1995	42.66	7.79	10.89	11.84	7.22	7.53	2.44	1.58	<0.07	<0.07	<0.14	<0.43	<0.71	<0.28	<0.07	<0.07	1.23	<0.14	1.04	1.51
1994	14.71	9.01	10.41	12.04	10.93	10.93	2.73	1.80	<0.07	0.06	<0.14	<0.42	<0.69	<0.28	<0.07	<0.07	1.34	0.35	0.76	2.45
1993	153.28	6.93	11.63	10.39	14.25	14.13	6.01	2.55	0.32	0.08	<0.18	<0.54	<0.90	<0.36	<0.09	<0.09	2.39	0.64	1.31	3.19

Table S11. Coefficients of determination (R^2) and statistical significance (p) of PFAA homologues (n=28).

	Na^+	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C4-S	C8-S	PFECHS
C4	R^2= 1.6e-03 p= 0.9553													
C5	R^2= 0.02 p= 0.4316	R^2= 0.19 p= 0.0217												
C6	R^2= 0.03 p= 0.3444	R^2= 0.32 p= 0.0016	R^2= 0.79 p<0.0001											
C7	R^2= 0.07 p= 0.1874	R^2= 0.16 p= 0.0345	R^2= 0.79 p<0.0001	R^2= 0.81 p<0.0001										
C8	R^2= 0.10 p= 0.1057	R^2= 1.1e-03 p= 0.8627	R^2= 0.13 p= 0.0625	R^2= 0.17 p= 0.0311	R^2= 0.46 p<0.0001									
C9	R^2= 0.06 p= 0.1935	R^2= 0.04 p= 0.3056	R^2= 2.3e-04 p= 0.9387	R^2= 7.7e-04 p= 0.8882	R^2= 0.12 p= 0.0667	R^2=0.67 p<0.0001								
C10	R^2= 0.08 p= 0.1408	R^2= 3.6e-04 p= 0.9235	R^2= 0.05 p= 0.2537	R^2= 0.05 p= 0.2331	R^2= 0.27 p= 0.0048	R^2= 0.79 p<0.0001	R^2= 0.87 p<0.0001							
C11	R^2= 1.9e-03 p= 0.8232	R^2= 0.05 p= 0.2454	R^2= 0.04 p= 0.3138	R^2= 0.03 p= 0.3423	R^2= 5.9e-03 p= 0.6974	R^2= 0.32 p= 0.0016	R^2= 0.75 p<0.0001	R^2=0.64 p<0.0001						
C12	R^2= 2.2e-04 p= 0.9407	R^2= 0.04 p= 0.3356	R^2= 0.03 p= 0.4025	R^2= 0.04 p= 0.3168	R^2= 0.01 p= 0.5853	R^2= 0.33 p= 0.0013	R^2= 0.61 p <0.0001	R^2= 0.54 p<0.0001	R^2= 0.71 p<0.0001					
C13	R^2= 0.02 p= 0.5222	R^2= 0.07 p= 0.1875	R^2= 0.09 p= 0.1132	R^2= 0.07 p= 0.1749	R^2=1.1e-03 p=0.8614	R^2= 0.22 p= 0.0113	R^2= 0.47 p<0.0001	R^2= 0.43 p=0.0002	R^2= 0.70 p<0.0001	R^2=0.66 p<0.0001				
C4-S	R^2= 2.8e-03 p= 0.7883	R^2= 7.6e-03 p= 0.6587	R^2= 0.01 p= 0.5940	R^2= 0.01 p= 0.5371	R^2= 0.01 p= 0.5689	R^2= 0.02 p= 0.4254	R^2= 5.3e-03 p= 0.7115	R^2= 7.2e-04 p= 0.8925	R^2= 2.6e-03 p= 0.7947	R^2= 3.6e-03 p= 0.7607	R^2=5.6e-03 p= 0.7044			
C8-S	R^2= 0.03 p= 0.3675	R^2= 4.9e-04 p= 0.9112	R^2= 2.2e-03 p= 0.8145	R^2= 0.09 p= 0.1269	R^2= 0.04 p= 0.3298	R^2= 0.09 p= 0.1233	R^2= 0.03 p= 0.3970	R^2= 0.06 p= 0.1942	R^2= 4.2e-03 p= 0.7435	R^2= 2.6e-06 p= 0.9935	R^2= 6.6e-03 p= 0.6814	R^2= 6.9e-03 p= 0.6749		
PFECHS	R^2= 4.6e-03 p= 0.7314	R^2= 0.03 p= 0.3987	R^2= 0.19 p= 0.0205	R^2= 0.14 p= 0.0531	R^2= 0.21 p= 0.0142	R^2= 0.11 p= 0.0863	R^2= 0.11 p= 0.0905	R^2= 0.12 p= 0.0682	R^2= 0.05 p= 0.2383	R^2= 0.01 p= 0.5490	R^2= 6.3e-03 p= 0.6868	R^2= 0.04 p= 0.3357	R^2= 1.3e-03 p= 0.8566	
FOSA	R^2= 9.1e-05 p= 0.9616	R^2= 0.03 p= 0.3487	R^2= 0.05 p= 0.2303	R^2=0.03 p= 0.3620	R^2= 0.05 p= 0.2723	R^2= 6.1e-04 p= 0.9010	R^2= 2.1e-03 p= 0.8152	R^2= 7.8E-04 p= 0.8880	R^2= 0.02 p= 0.4710	R^2= 1.8e-04 p= 0.9460	R^2= 0.01 p= 0.5976	R^2= 0.15 p= 0.0406	R^2= 0.01 p= 0.5886	R^2= 1.3e-03 p= 0.8542

Table S12. First order elimination kinetics for PFOS flux, 1998-2004 using 2006 and 2008 data sets (corresponds to Fig S10)

	2006 data	2008 data
First order elimination rate, K_e (y^{-1})	0.3197±0.1333	0.0731±0.0400
p-value	0.0617	0.127
R^2 on ln flux versus year regression	0.535	0.401
Degrees of freedom	5	5
Half life, $T_{1/2}$ (y) based on ln2/k_e	2.2 ± 5.2	9.5 ± 17

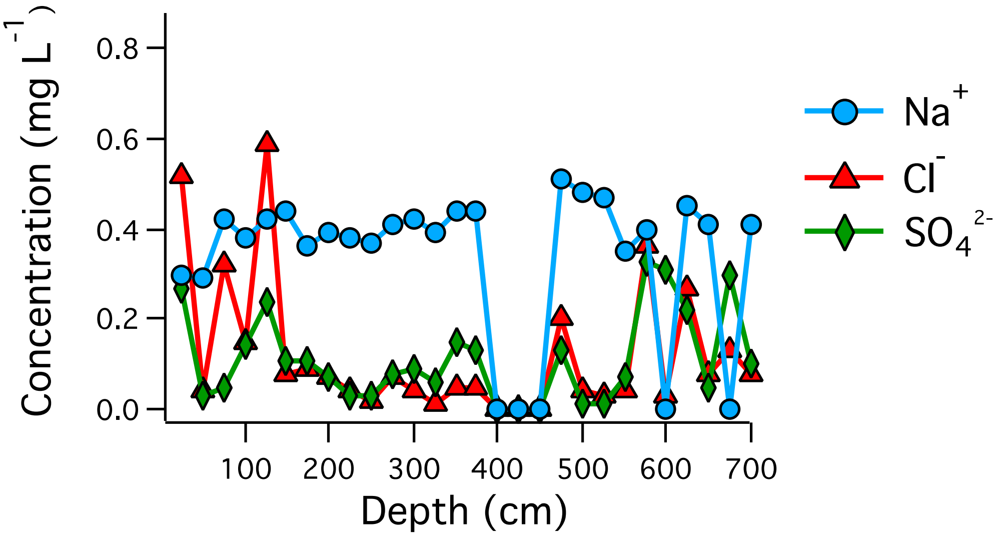


Figure S1. Depth profile of inorganic ions on the Devon Ice Cap.

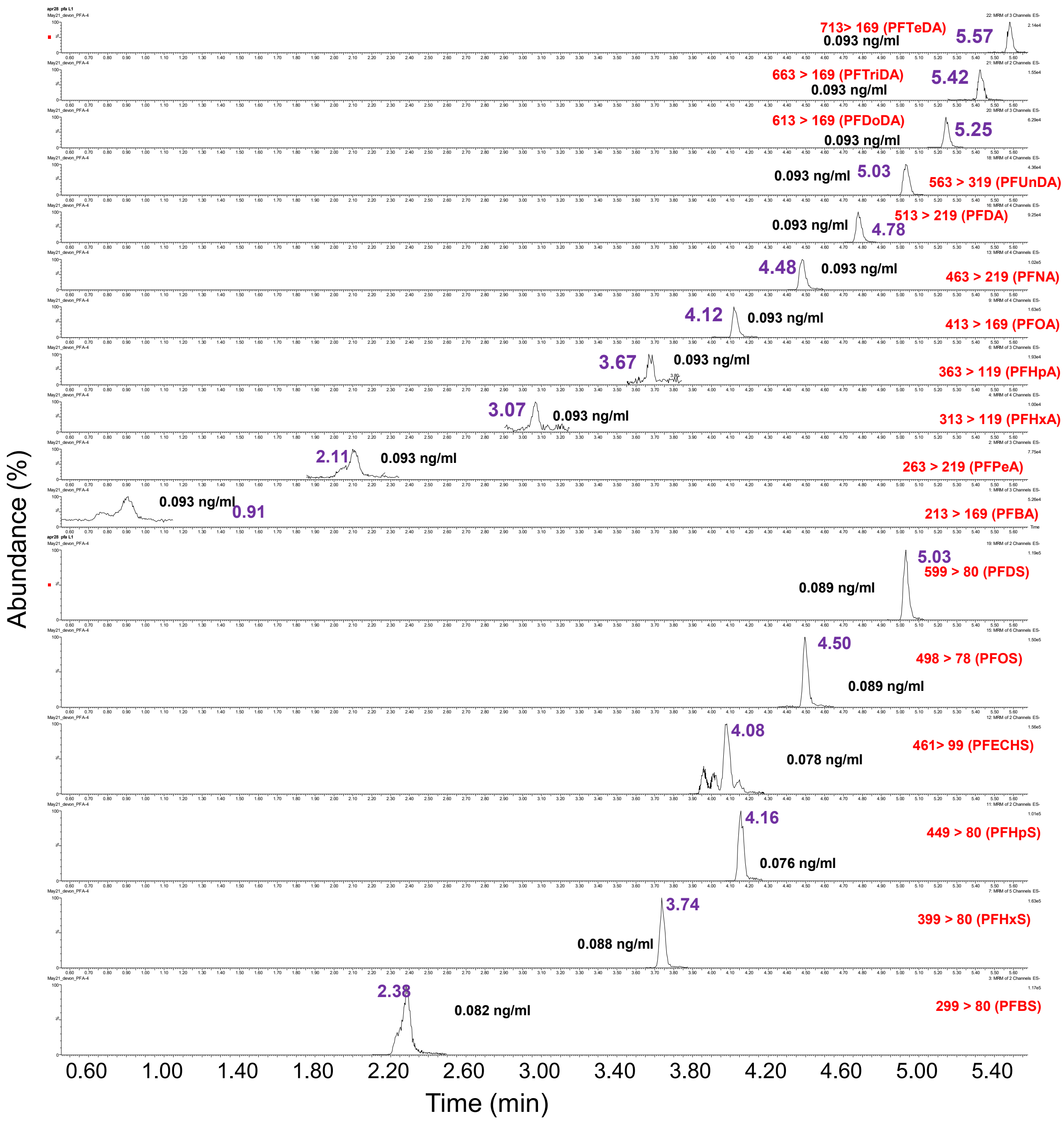


Figure S2. Chromatogram of PFAAs in a low-level (~ 0.1 ng mL^{-1}) standard. Chromatograms have not been smoothed. Precursor-product ion transition is shown in red for analytes. Peaks are annotated with retention time and standard concentration.

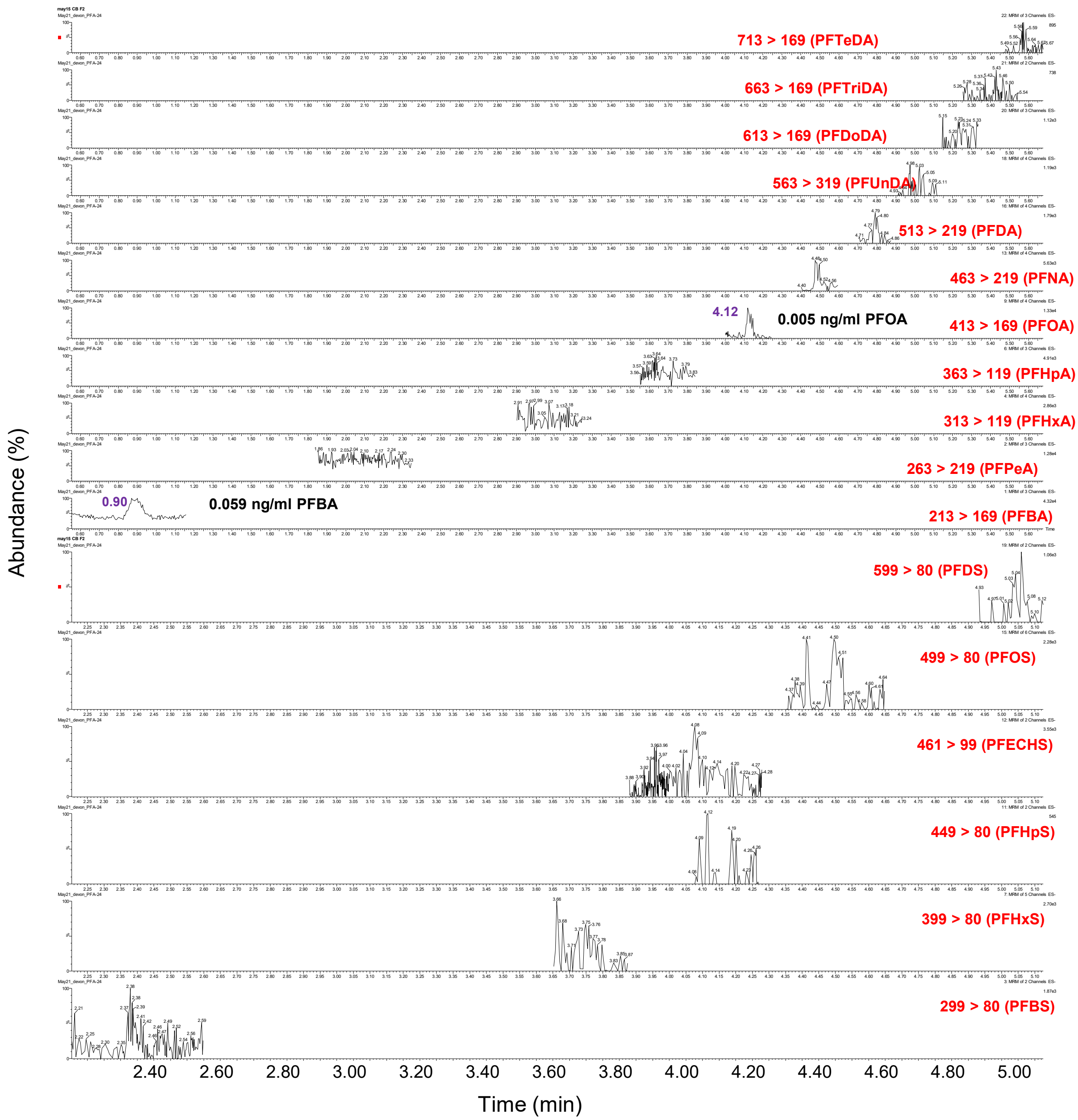


Figure S3. Chromatogram of PFAAs in extracted blank. Chromatograms have not been smoothed. Precursor-product ion transition is shown in red for analytes. Retention times are annotated for detected peaks.

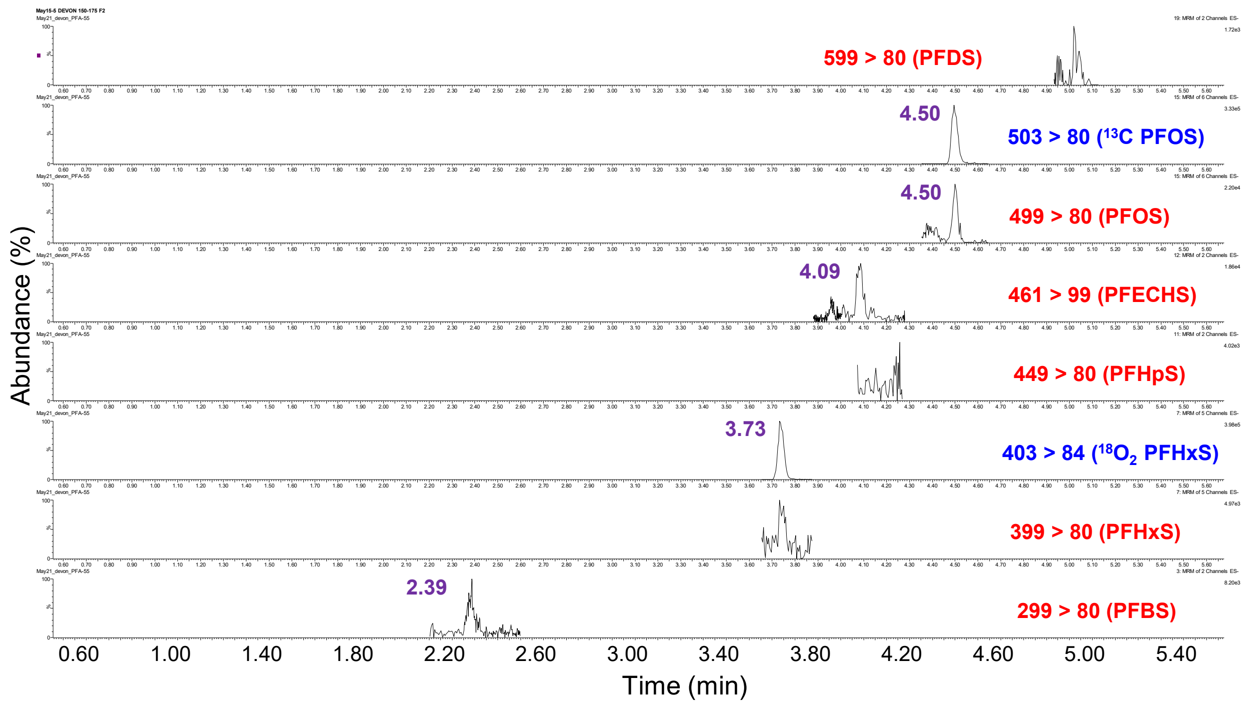


Figure S4. Chromatogram of PFSAs and internal standards in Devon Ice Cap extract. Chromatograms have not been smoothed. Precursor-product ion transition is shown in red for analytes and blue for internal standards. Retention times for detected peaks are in purple. This sample contained 0.105 ng L^{-1} PFBS, 0.016 ng L^{-1} PFOS, and 0.0088 ng L^{-1} PFECHS. PFHxS, PFHpS, PFDS, were < LOD.

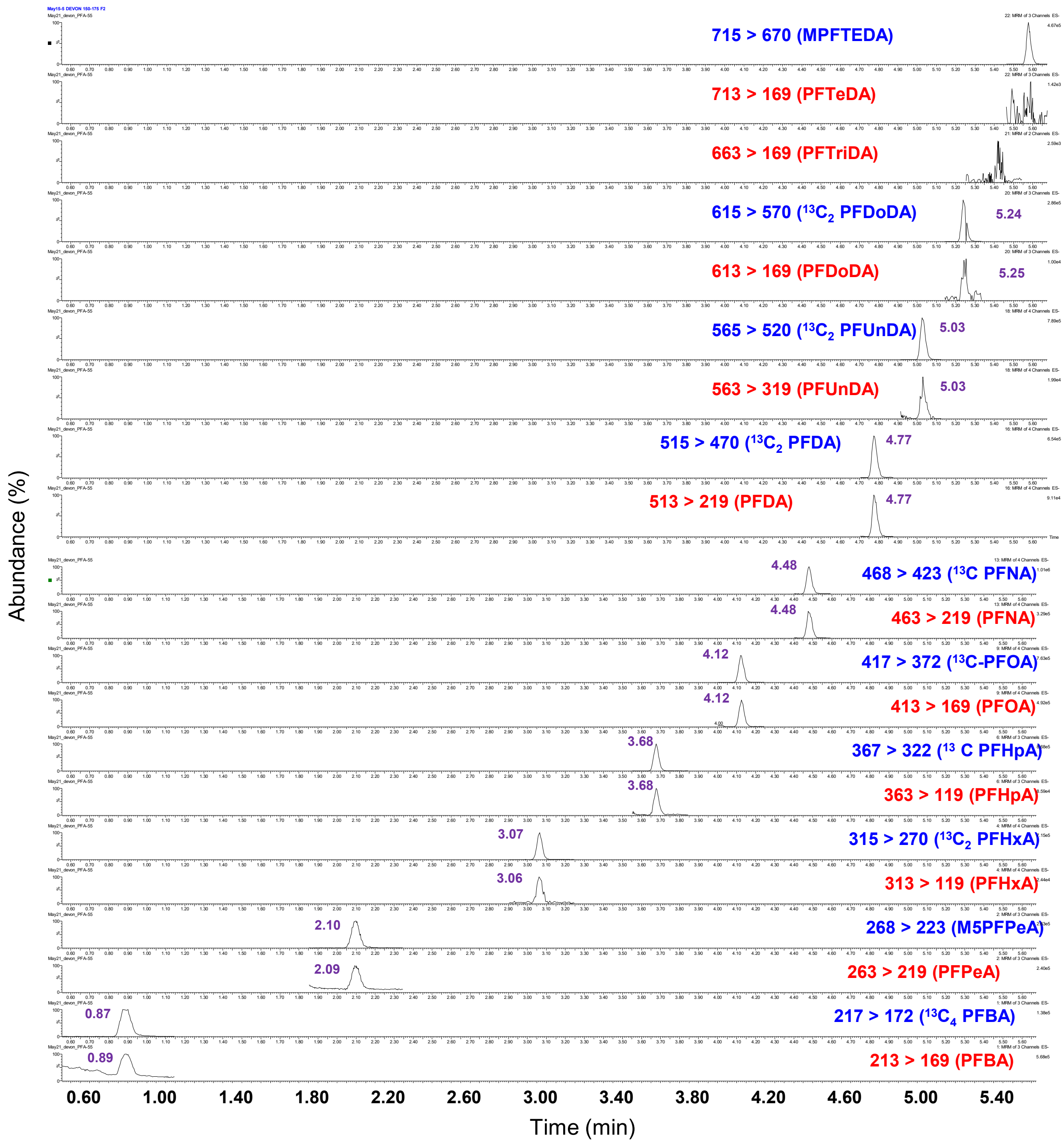


Figure S5. Chromatogram of PFCAs and internal standards in Devon Ice Cap extract. Chromatograms have not been smoothed. Precursor-product ion transition is shown in red for analytes and blue for internal standards. Retention times for detected peaks are in purple. This sample contained 0.89 ng L^{-1} PFBA, 0.29 ng L^{-1} PFPeA, 0.30 ng L^{-1} PFHxA, 0.54 ng L^{-1} PFHpA, 0.34 ng L^{-1} PFOA, 0.31 ng L^{-1} PFNA, 0.095 ng L^{-1} PFDA, 0.040 ng L^{-1} PFUnDA, 0.044 ng L^{-1} PFDoDA, 0.0083 ng L^{-1} PFTrDA. PFTeDA was <LOD.

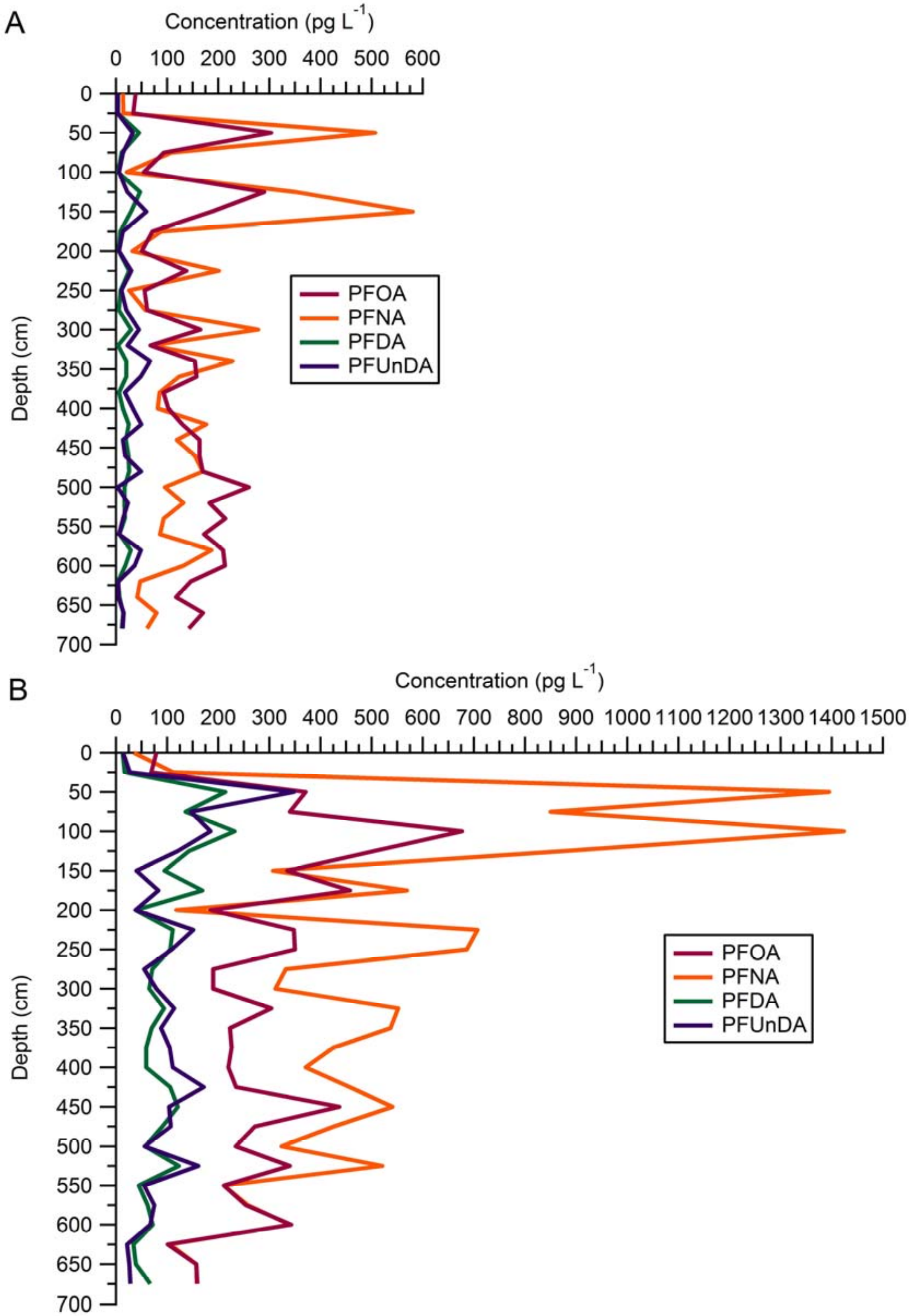


Figure S6. Comparison of PFCA concentrations from sampling campaigns at the Devon Ice Cap in 2006 (A) and 2008 (B).

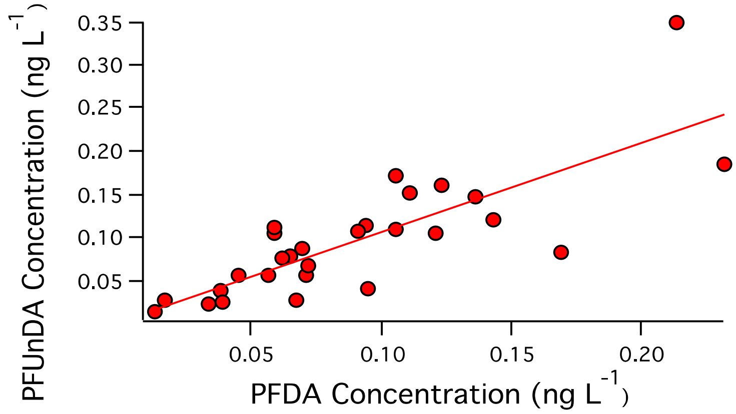


Figure S7. Evaluation of volatile precursor oxidation as a source of PFAA deposition on the Devon Ice Cap using PFDA and PFUnDA concentrations.

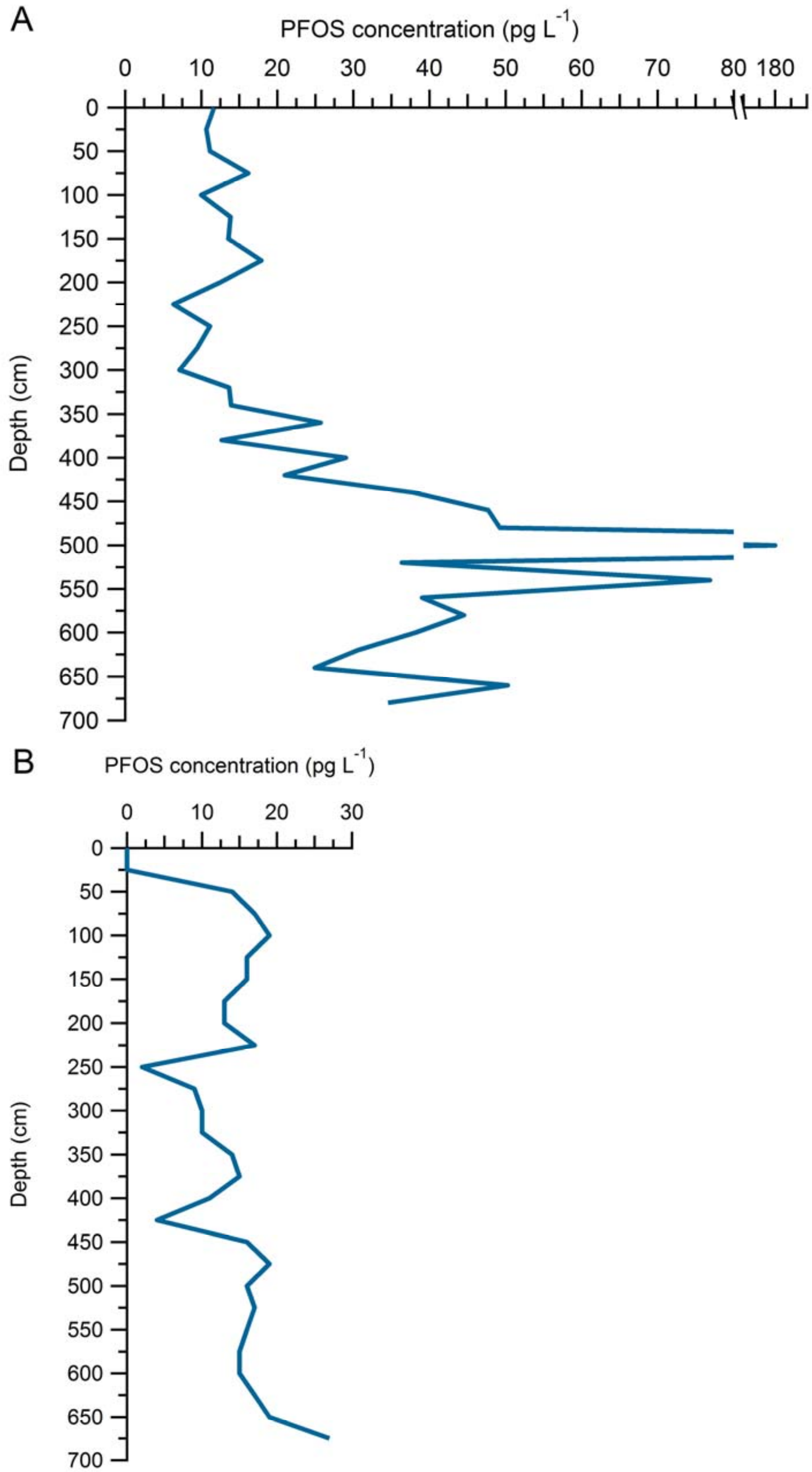


Figure S8. Comparison of PFOS concentrations from sampling campaigns at the Devon Ice Cap in 2006 (A) and 2008 (B).

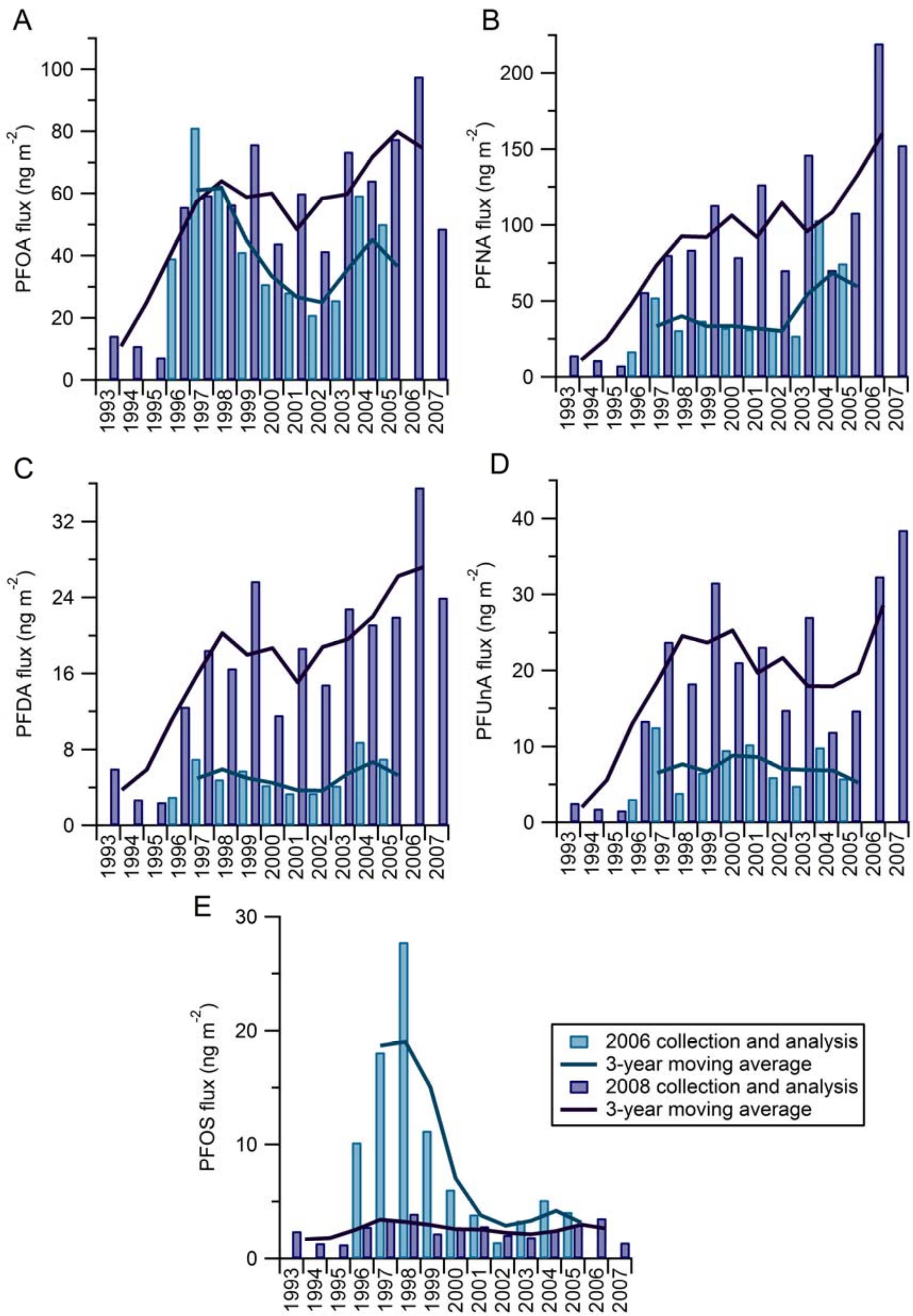
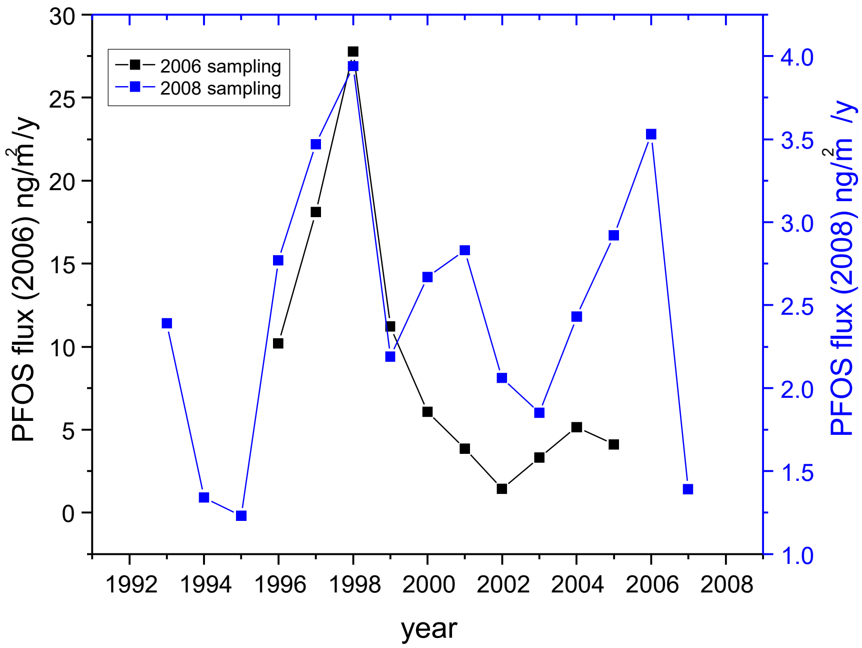


Figure S9. Temporal flux trend for PFOA (a), PFNA (b), PFDA (c), PFUnDA (d), and PFOS (e) calculated from samples collected in 2006 (blue) and 2008 (purple), along with three-year moving averages.

a)



b)

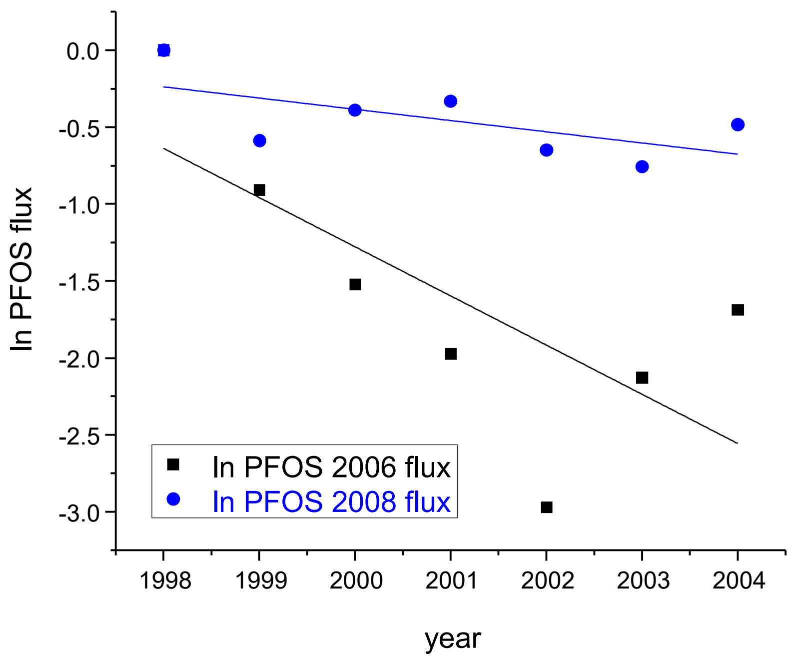


Figure S10. Comparison of a) PFOS flux using 2006 and 2008 sampling and b) first order elimination kinetics for PFOS flux from 1998-2004 using 2006 and 2008 data.

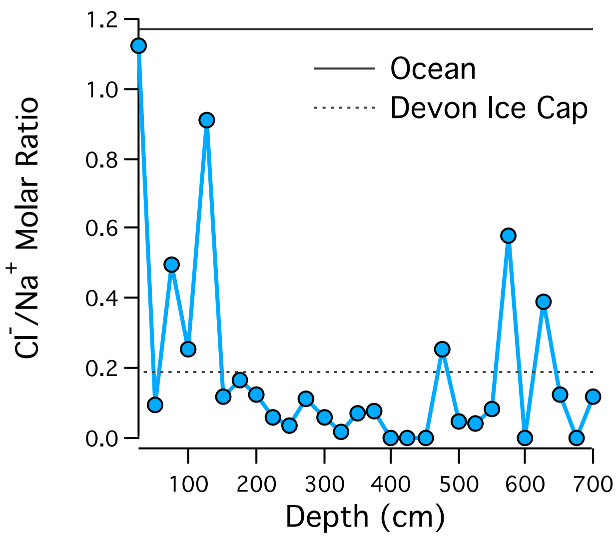


Figure S11. Comparison of chloride-sodium molar ratios on the Devon Ice Cap to expected ocean ratios. The gray dashed line corresponds to the average Cl^-/Na^+ ratio observed on the Devon Ice Cap, and the solid black line corresponds to the expected ocean ratio.[4]

References

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