Supporting Information

Vertical Profiles, Sources and Transport of PFASs in the Arctic Ocean

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Sample collection

Water samples at different depths were collected by a 24 CTD rosette sampler. Water samples collected from the CTD rosette sampler were stored in a 1 L PP bottle. For snow and meltpond water samples, they were first collected by a pre-cleaned stainless steel bucket, and then transferred into the 1L PP bottle. No field blank was available for meltpond and snow samples.

Chemicals

Analytical standards and reagents

Except for 4:2- and 10:2 diPAPs, all analytical and mass-labelled standards were obtained from the Wellington Laboratories (Guelph, ON); 4:2- and 10:2- diPAPs were synthesized as described elsewhere.[1] A list of PFAS monitored in the current investigation is given in Table S1. The purity of all standards was over 98%. The standards for the congeners of PFSA, FOSA, FOSAA, and PFOA were the linear isomer, whereas the samples were composed of both branched and linear isomers; the concentrations reported for the present study included both linear and branched isomers based on the linear isomer of the standard.

Ammonium acetate (>99%), and ammonia (NH_3, 30%) were obtained from Sigma-Aldrich. Methanol (MeOH, LCMS grade) was acquired from EMD Chemicals Inc. (Mississauga, ON). Solid phase extraction cartridges were purchased from cartridges from Waters for OASIS WAX-SPE cartridge (6 cc, 150 mg sorbent, 30 µm particle size) and Phenomenex (Torrence, CA) for Strata-X-AW cartridge (6 cc, 200 mg sorbent, 33 µm particle size).

Extraction method

Samples (Seawater, snow, meltpond water) were extracted using a solid phase extraction (SPE) cartridge (Strata-X-AW cartridge, Phenomenex, Torrence, CA) following the ISO 25101 method.[2] In brief, 1L of the seawater samples were transferred into 2 x 400 mL and 200 mL PP bottles. Methanol (3 x 2mL) was used to rinse the original bottle and collected, the 6 mL MeOH were divided and transferred to the three PP bottles. Snow and meltpond water samples did not have 1 L of volume, and the volume were measured using a graduated cylinder; MeOH (3 x 1 mL) was used to rinse the graduated cylinder and added to the snow or meltpond water samples. Samples (seawater: 400 mL, snow and meltpond water: 200mL) were first spiked with 20 pg of individual mass labelled standards before extraction. The SPE cartridge was first preconditioned by a passage of 4 mL of 0.1% NH_4OH in MeOH, 4 mL of MeOH, and 4 mL of polished Milli-Q water in sequence. After that, the 200/400 mL of samples were loaded onto the preconditioned cartridge. The flow rate was adjusted to 1-2 drops/s. After loading the samples, 4 mL of the buffer solution (25 mM ammonium acetate) was added to the cartridge. The cartridge was then centrifuge at 3500 rpm for 5 min and then dried under vacuum for 1 hr. The neutral fraction was collected by adding a 4 mL of MeOH, whereas the anionic fraction was collected by adding a 4 mL of 0.1% NH_4OH in MeOH. The 4 mL of the eluate was concentrated under a gentle stream of nitrogen in a heat block (40^oC), and then reconstituted to 200 uL with MeOH. The 200 uL extract was centrifuged at 6000 rpm for 5 min before transferring to HPLC vial for instrumental analysis.

Polished Milli-Q water

Water from the Milli-Q system in the laboratory contained detectable levels of PFOS and PFNA (range: 50-200 pg/L). Therefore, for every batch of extraction, the water (1 L) was first pre-cleaned (i.e., polished Milli-Q water) by passing through a WAX SPE cartridge and collected for procedure blanks. Cartridge and procedure blanks were performed to confirm

any contamination that might be introduced from the cartridge and during extraction process, respectively. Initially, Waters OASIS WAX-SPE cartridges were used for method development and validation. However, low levels of PFOA (0.08 – 2.1 pg) were observed from the cartridges (SI Figure S2). Another cartridge (Strata-X-AW cartridge, Phenomenex, Torrence, CA) of similar retention property was found to be free of PFOA, and thus all the method development and sample extraction were done using this cartridge.

Interlaboratory comparison between ALFONSE and MTM

Four randomly selected samples (200 mL from 1 L sample) and one blank sample (200 mL of pre-cleaned water) prepared from ALFONSE were sent to Man-Technology-Environment (MTM) Research Centre, Örebro University for analysis. In brief, samples (200 mL) were spiked with 100 pg of mass-labelled standards and extracted following the ISO25101.[1] Samples were concentrated to 0.2 mL and then transferred to LC vial with the addition of a recovery standard (7H-PFHpA) and 0.3 mL of 2 mM ammonium acetate in water before instrumental analysis. Samples were analyzed using a Acquity I-class UPLC couple to a Xevo TQ S tandem mass spectrometer. An Acquity BEH C18 column (2.1 × 100 mm, 1.7 μm, 100 Å), maintained at 60 °C was used to achieve chromatographic separation. A 10 μL extract aliquot was injected onto the column, with 2 mM ammonium acetate in Milli-Q water and MeOH (7/3: v/v) and 2 mM ammonium acetate in MeOH used as mobile phases. Detailed MS/MS conditions, including collision energies, cone voltages, and LC parameters can be found elsewhere.[3]

The four selected samples were PS80/227-surface, HL1203/70-4m, HL1203/66-10 m, and HL1203/78-29m, and their recoveries (%) for PFOA and PFOS were 87-97 and 93-95, respectively. Because of higher detection limit (MTM: 20 pg/L, ALFONSE: 5-20 pg/L) and smaller concentration factor (MTM: 1000x, ALFONSE: 2000x), fewer PFASs were detected in MTM. No detectable PFAS concentrations (<20 pg/L) were found in the blank sample, and detectable PFASs were C6-C9 PFCAs and PFOS (Table S6a).

Table S1. Analytical standards used in current investigation.

Class	Acronymn	Name	Mass-labelled standard used for quantification	External calibration
Perfluoroalkane sulfonate (PFSA)	PFBS	Perfluorobutane sulfonate	$^{18}O_2$ PFHxS	
	PFPeS	Perfluoropentane sulfonate	$^{18}O_2$ PFHxS	
	PFHxS	Perflurohexane sulfonate	$^{18}O_2$ PFHxS	
	PFHpS	Perfluoroheptane sulfonate	$^{13}C_4$ PFOS	
	PFOS	Perfluorooctane sulfonate	$^{13}C_4$ PFOS	
	PFNS	Perfluorononane sulfonate	$^{13}C_4$ PFOS	
	PFDS	Perfluorodecane sulfonate	$^{13}C_4$ PFOS	
Perfluroinated carboxylate (PFCA)	PFHxA	Perfluorohexanoate	$^{13}C_2$ PFHxA	
	PFHpA	Perfluoroheptanoate	$^{13}C_4$ PFHpA	
	PFOA	Perfluorooctanoate	$^{13}C_4$ PFOA	
	PFNA	Perfluorononanoate	$^{13}C_5$ PFNA	
	PFDA	Perfluorodecanoate	$^{13}C_2$ PFDA	
	PFUnDA	Perfluoroundecanoate	$^{13}C_2$ PFUnDA	
	PFDoDA	Perfluorododecanoate	$^{13}C_2$ PFDoDA	
	PFTrDA	Perfluorotridecanoate	$^{13}C_2$ PFDoDA	
	PFTeDA	Perfluorotetradecanoate	$^{13}C_2$ PFTeDA	
Fluorotelomer carboxylate (FTCA)	3:3 FTCA	3:3 Fluorotelomer carboxylate	$^{13}C_2$ 6:2 FTUCA	
	5:3 FTCA	5:3 Fluorotelomer carboxylate	$^{13}C_2$ 6:2 FTUCA	
	7:3 FTCA	7:3 Fluorotelomer carboxylate	$^{13}C_2$ 6:2 FTUCA	
Fluorotelomer unsatuated carboxylate (FTUCA)	6:2 FTUCA	6:2 Fluorotelomer unsaturated carboxylate	$^{13}C_2$ 6:2 FTUCA	
	8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylate	$^{13}C_2$ 8:2 FTUCA	
	10:2 FTUCA	10:2 Fluorotelomer unsaturated carboxylate	$^{13}C_2$ 10:2 FTUCA	
Fluorotelomer sulfonate (FTSA)	4:2 FTSA	4:2 Fluorotelomer sulfonate	$^{13}C_2$ 4:2 FTSA	
	6:2 FTSA	6:2 Fluorotelomer sulfonate	$^{13}C_2$ 6:2 FTSA	
	8:2 FTSA	8:2 Fluorotelomer sulfonate	$^{13}C_2$ 8:2 FTSA	
polyfluoroalkyl phosphate diester (diPAP)	4:2 diPAP	4:2 Fluorotelomer phosphate diester	$^{13}C_4$ 6:2 diPAP	
	6:2 diPAP	6:2 Fluorotelomer phosphate diester	$^{13}C_4$ 6:2 diPAP	
	6:2/8:2 diPAP	6:2/8:2 Fluorotelomer phosphate diester	$^{13}C_4$ 6:2 diPAP	
	8:2 diPAP	8:2 Fluorotelomer phosphate diester	$^{13}C_4$ 8:2 diPAP	
	10:2 diPAP	10:2 Fluorotelomer phosphate diester	$^{13}C_4$ 8:2 diPAP	
Perfluorinated phosphinate (PFPiA)	C6/C6 PFPiA	Bis (perfluorohexyl) phosphinate		x

	C6/C8 PFPiA	Perfluoro (hexyloctyl) phosphinate		x
	C8/C8 PFPiA	Bis (perfluorooctyl) phosphinate		x
Perfluorooctane sulfonamide (FOSA)	FOSA	Perfluorooctane sulfonamide	$^{13}C_8$ FOSA	
	MeFOSA	Methyl perfluorooctane sulfonamide	d_3MeFOSA	
	EtFOSA	Ethyl perfluorooctane sulfonamide	d_5EtFOSA	
Perfluorooctane sulfonamidoacetate (FOSAA)	FOSAA	Perfluorooctane sulfonamidoacetate		x
	MeFOSAA	Methyl perfluorooctane sulfonamidoacetate	d_3MeFOSAA	
	EtFOSAA	Ethyl perfluorooctane sulfonamidoacetate	d_5EtFOSAA	

Table S2. Sample information i) location and ii) details with water depth (m), Temperature (°C), salinity (‰) from the Central Arctic (a)-(d) and the Arctic shelf (e)-(k)

i)

Sampling location	Date	Start time	Latitude	Longitude	Sample type	Research vessel
PS80/364 Near the Pole	2012-09-22	17:31	88.8090	57.2545	Seawater	Polarstern
PS80/275 Amundsen Basin - East Gakkel Ridge	2012-08-25	00:43	83.3837	125.0888	Seawater	Polarstern
PS80/227 North Barents Sea	2012-08-09	19:25	84.0243	31.2277	Seawater	Polarstern
PS80/254 Nansen Basin - West Gakkel Ridge	2012-08-20	06:02	82.7087	109.1437	Seawater	Polarstern
HL1203/70	2012-10-19	08:13	69.7063	-139.3698	Seawater	Healy
HL1203/71	2012-10-19	09:06	69.6533	-139.5620	Seawater	Healy
HL1203/62	2012-10-19	00:42	70.1845	-138.7717	Seawater	Healy
HL1203/66	2012-10-19	05:17	69.8922	-139.0093	Seawater	Healy
HL1203/72	2012-10-19	17:35	70.1922	-144.6363	Seawater	Healy
HL1203/76	2012-10-19	20:52	70.5315	-144.2693	Seawater	Healy
HL1203/78	2012-10-19	22:51	70.697	-144.0855	Seawater	Healy
PS80/224 Station 1	2012-08-09	not available	84.0505	31.1138	snow, meltpond water	Polarstern
PS80/255 Station 3	2012-08-20	not available	82.6707	109.5895	meltpond water	Polarstern
PS80/323 Station 5	2012-09-05	not available	81.9255	131.1287	snow	Polarstern
PS80/360 Station 8	2012-09-22	not available	88.8277	58.8635	snow	Polarstern

ii) a. PS80/364 Near the Pole

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	4354.7	-0.6286	34.9440	
2	4249.8	-0.6405	34.9443	
3	4000.4	-0.6668	34.9442	
4	3500	-0.7179	34.9395	
5	2999.7	-0.7457	34.9333	x
6	2499.6	-0.7448	34.9261	
7	2000.2	-0.6666	34.9210	
8	1500.1	-0.5094	34.9133	
9	999.8	-0.1405	34.9000	x
10	799.7	0.0833	34.8912	
11	499.8	0.6959	34.8816	
12	499.8	0.7051	34.8811	x
13	300.1	1.2413	34.8663	
14	249.9	1.1546	34.8309	x
15	199.5	0.9394	34.7714	
16	149.6	-0.1360	34.4941	x
17	100.1	-1.3445	34.1227	
18	74.8	-1.7755	33.8193	x
19	49.9	-1.8048	33.6920	x
20	29.7	-1.7820	33.1713	
21	19.8	-1.7852	33.0015	
22	19.8	-1.7902	32.9391	
23	9.9	-1.7880	32.9535	x
24	1.1	-1.7873	32.9495	x

ii) b. PS80/275 Amundsen Basin - East Gakkel Ridge

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	4219.9	-0.6447	34.9440	
2	4119.8	-0.6555	34.9442	
3	3499.8	-0.7196	34.9420	
4	3000.1	-0.7578	34.9353	x
5	2500.3	-0.7642	34.9275	
6	2000	-0.7183	34.9209	
7	1500.4	-0.5841	34.9143	
8	1000	-0.2175	34.9042	x
9	800	-0.0108	34.8962	
10	700.1	0.1376	34.8911	
11	600.5	0.3477	34.8873	
12	500	0.6510	34.8869	x
13	400.3	0.9951	34.8860	
14	350.3	1.2686	34.8959	
15	249.8	1.1181	34.8314	x
16	199.6	1.1857	34.8342	
17	149.7	0.3732	34.6243	x
18	100.6	-1.0930	34.3030	
19	75	-1.5085	34.0751	x
20	50.4	-1.6972	33.3272	x
21	30	-1.7153	32.6602	
22	19.6	-1.5415	31.4763	
23	10.1	-1.0860	30.2386	x
24	1.3	-1.0547	30.1041	x

ii) c. PS80/227 North Barents Sea

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	3993.7	-0.6587	34.9437	
2	3993.7	-0.6587	34.9437	
3	3993.7	-0.6588	34.9436	
4	3500.1	-0.7120	34.9427	
5	3500.1	-0.7122	34.9427	
6	2999.9	-0.7567	34.9384	x
7	1999.7	-0.7500	34.9239	
8	1999.7	-0.7500	34.9238	
9	1500.3	-0.6268	34.9187	
10	1500.3	-0.6251	34.9187	
11	1000.2	-0.2527	34.9068	x
12	500	1.1964	34.9229	
13	500	1.2040	34.9241	
14	500	1.2075	34.9243	
15	250.5	2.1436	34.9369	
16	250.5	2.1536	34.9353	x
17	200.3	2.0113	34.8967	x
18	150	1.8652	34.8578	x
19	100.2	0.2212	34.5707	
20	75.2	-0.7544	34.3851	x
21	50.1	-1.7382	34.2058	x
22	24.7	-1.5504	34.0287	
23	8.2	-1.5947	33.0609	x
24	1.6	-1.5697	33.1511	x

ii) d. PS80/254 Nansen Basin - West Gakkel Ridge

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	3549	-0.6988	34.9428	
2	3448.7	-0.7085	34.9428	
3	2999.8	-0.7616	34.9373	x
4	2500.3	-0.7732	34.9294	
5	2000.3	-0.7381	34.9227	
6	1500.4	-0.6152	34.9163	
7	1001	-0.2675	34.9021	
8	800.7	0.0126	34.8930	
9	701.3	0.2827	34.8965	
10	600.1	0.6615	34.9061	
11	500	1.1034	34.9178	
12	500	1.1111	34.9181	x
13	399.6	1.5816	34.9277	
14	300.1	1.7453	34.9115	
15	249.9	1.8958	34.9101	x
16	199.7	1.7763	34.8670	x
17	147.7	1.0555	34.6883	x
18	99.7	-1.1461	34.3106	
19	74.8	-1.6903	34.1503	x
20	49.6	-1.7985	34.0350	x
21	25	-1.6711	33.9440	
22	19.8	-1.6011	33.7887	
23	9.7	-1.5884	33.0241	x
24	1.1	-1.5668	32.7281	x

ii) e. HL1203/70, Bottom depth 35 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	28.813	1.3995	27.7318	
3	20.417	1.4052	27.7127	x
4	10.081	1.3973	27.7104	x
5	3.6	1.3952	27.7108	x

ii) f. HL1203/71, Bottom depth 28 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	22.976	0.9744	27.7005	
3	19.891	1.0203	27.6959	x
4	9.934	1.0724	27.6931	x
5	2.661	1.0813	27.6932	x

ii) g. HL1203/62, Bottom depth 385 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	367.58	0.5097	34.7878	
3	348.87	0.3092	34.6882	
4	300.52	-0.1024	34.4925	x
5	251.9	-0.9271	33.9795	
6	199.24	-1.2591	33.5018	
7	175.2	-1.3848	33.0714	
8	149.74	-1.3925	32.7876	x
9	124.36	-1.3268	32.4943	
10	99.94	-1.1913	32.2183	
11	75.55	-0.907	31.8240	x
12	50.14	-0.9124	31.8251	x
14	39.9	-0.6185	31.5794	
15	29.7	-0.4883	31.0223	
16	19.31	-0.2219	30.3842	x
17	10.1	1.1034	29.0266	x
18	2.68	1.2917	28.7653	x

ii) h. HL1203/66, Bottom depth 175 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	162.52	-1.3569	33.2138	
3	151	-1.3771	33.1345	x
4	125.23	-1.405	32.9343	
5	99.7	-1.3903	32.6812	
6	74.8	-1.2485	32.2927	x
7	50.23	-0.728	31.4914	x
8	39.41	-0.401	30.9368	
9	29.16	1.3025	29.0177	
10	20.34	2.0517	27.8702	x
12	9.97	1.5895	27.6544	x
13	2.27	1.5891	27.6529	x

ii) i. HL1203/72, Bottom depth 28 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	22.21	1.3037	27.4026	x
3	10.201	1.1333	27.274	x
4	2.757	1.1469	27.2681	x

ii) j. HL1203/76, Bottom depth 53 m

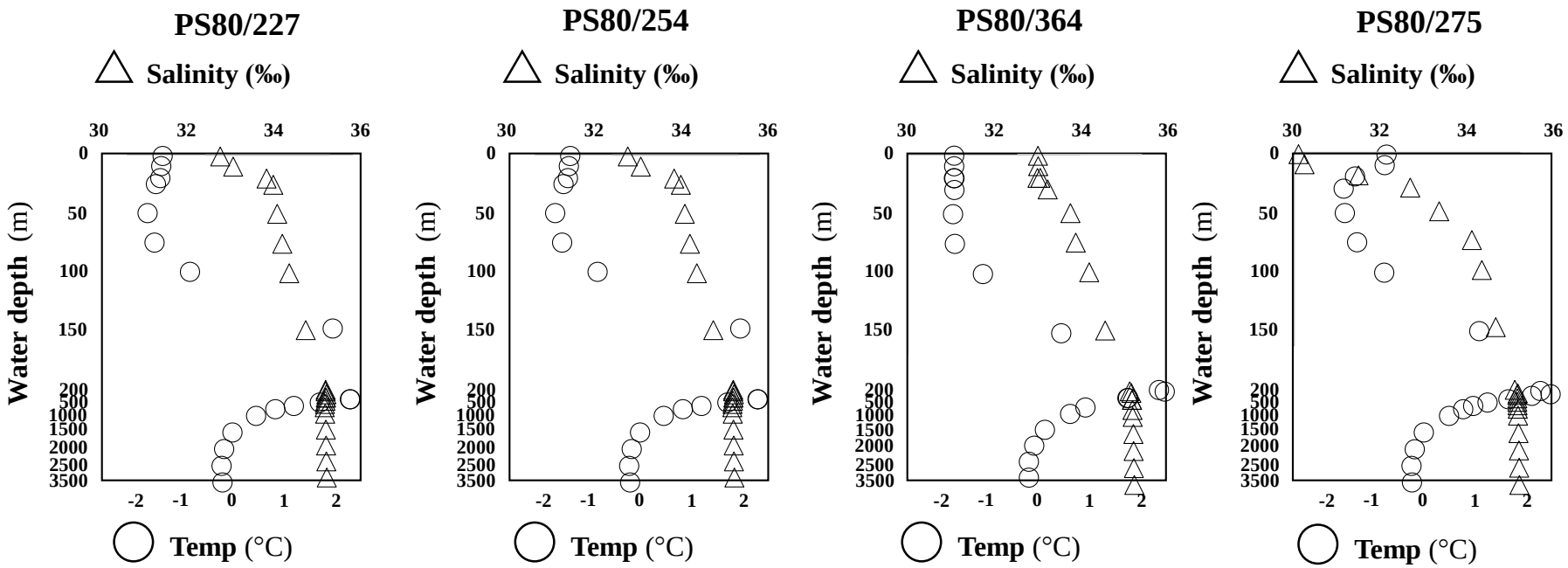
Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
2	46.669	-0.3408	31.8644	x
4	40.25	-0.5319	31.6018	
6	20.146	-0.1992	30.3325	x
7	10.327	1.0149	28.9166	x
8	1.821	1.3818	27.1171	x

ii) k. HL1203/78, Bottom depth 357 m

Bottle No.	Depth water [m]	Temp [°C]	Sal [‰]	Samples for PFAS analysis
1	340.46	0.4197	34.7181	x
3	300.35	0.3416	34.6846	
4	250.7	-0.0482	34.4904	
5	199.45	-0.9898	33.6443	x
6	174.58	-1.3089	33.2522	
7	149.72	-1.1807	32.9097	
8	124.15	-0.9953	32.7109	
9	100.2	0.0517	32.4492	x
11	74.29	0.0732	32.2655	
12	50.16	0.1035	31.8957	
13	39.32	0.6616	31.0666	
14	29.18	-0.0469	30.3637	
15	19.47	1.1002	29.7457	x
16	9.5	1.9112	26.6612	x
17	1.6	1.9164	26.6487	x

Figure S1. Temperature (ºC) and salinity (‰) of the samples collected in a) the Central Arctic and b) the Arctic shelf (see Table S2 for sample location)

(a)



(b)

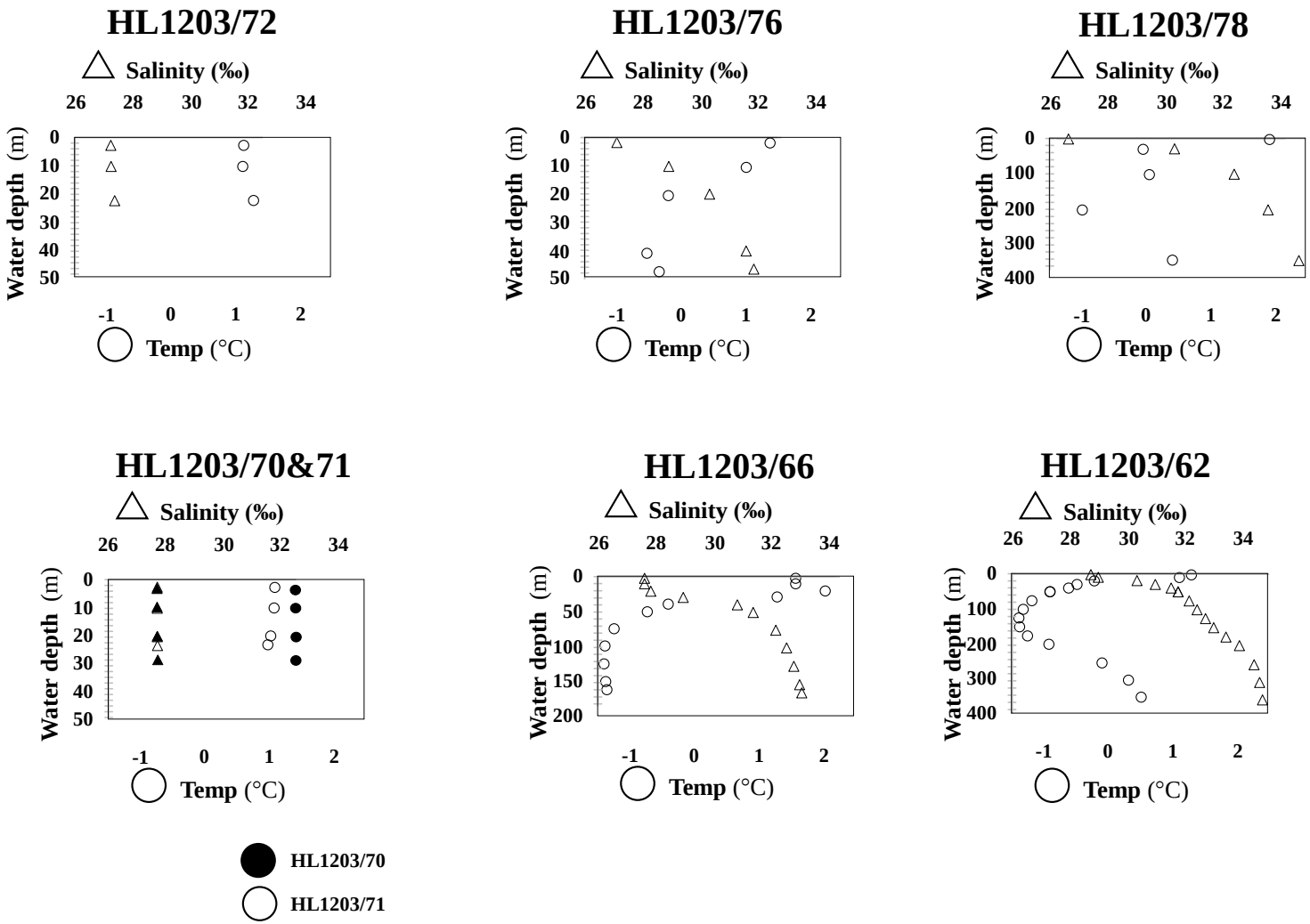

HL1203/72
HL1203/76
HL1203/78
HL1203/70&71
HL1203/66
HL1203/62
Salinity (‰)
Water depth (m)
Temp (°C)
HL1203/70
HL1203/71

Figure S2. An example showing PFOA concentration in cartridge blanks during method development stage.

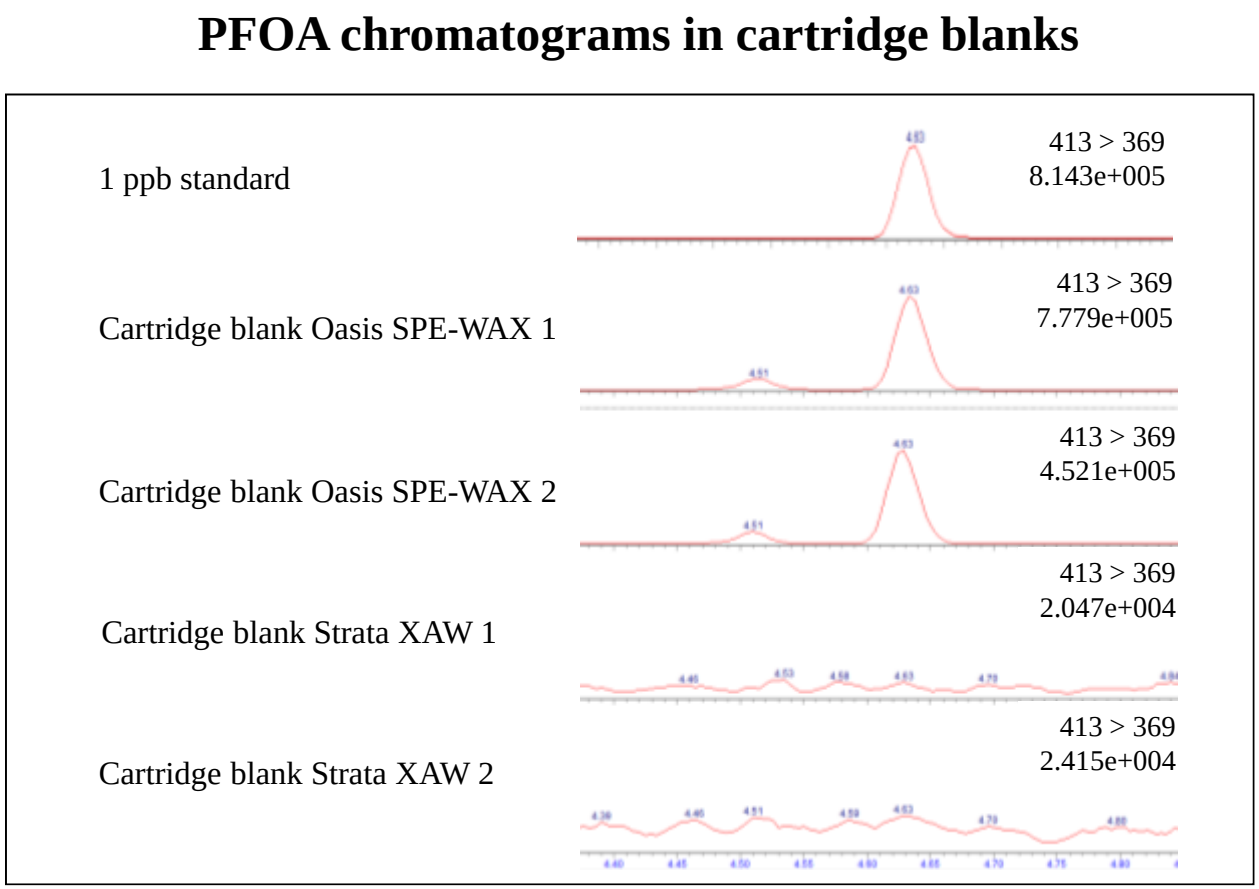


Table S3. Matrix recoveries and Limits of quantitation

a) Matrix recoveries (%) using the deep layer water samples (*n*=4)

Matrix recoveries (*n*=4)		
Analyte	**mean**	SD
PFPeA	104	10
PFHxA	104	8
PFHpA	95	9
PFOA	96	13
PFNA	88	13
PFDA	89	7
PFUnDA	87	10
PFDoDA	83	10
PFTriDA	81	9
PFTeDA	82	8
PFBS	103	5
PFHxS	105	8
PFOS	93	5
PFDS	92	5
FOSAA	75	10
MeFOSAA	85	10
EtFOSAA	91	8
FOSA	60	8
6:2 FTUCA	105	6
8:2 FTUCA	87	8
10:2 FTUCA	85	10

b) Limits of quantification (LOQs)

	LOQ
Analyte	pg/L
PFPeA	10
PFHxA	5
PFHpA	5
PFOA	5
PFNA	5
PFDA	5
PFUnDA	5
PFDoDA	10
PFTriDA	10
PFTeDA	10
PFBS	5
PFHxS	5
PFOS	5
PFDS	10
FOSAA	10
MeFOSAA	5
EtFOSAA	5
FOSA	20
6:2 FTUCA	10
8:2 FTUCA	10
10:2 FTUCA	10

LOQs of 6:2-, 8:2- and 10:2-FTCA were 1ng/L.

Table S4. A summary of mass labelled standard recoveries (%) based on external calibration curve in the samples (*n*=69)

Analyte	mean	SD
PFPeA	102	9
PFHxA	104	8
PFHpA	103	14
PFOA	99	9
PFNA	97	12
PFDA	97	12
PFUnDA	100	11
PFDoDA	101	9
PFHxS	109	8
PFOS	92	12
MeFOSAA	95	7
EtFOSAA	101	15
FOSA	65	4

Table S5. Mass labelled standard recoveries (%) based on external calibration curve in the samples collected at the Central Arctic (a)-(d) and the Arctic shelf (e)-(k), and different ice stations (l) (see Table S2 for sample location)

a) PS80/364

	PS80/364	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	1	107	109	98	105	95	82	97	105		93	85		79	80		59
	10	91	91	107	92	93	96	98	106		81	84		88	84		65
	50	100	98	105	101	109	112	121	116		100	103		116	106		68
	75	93	92	91	106	100	108	117	119		104	105		103	101		65
	150	93	89	84	103	100	98	105	113		87	93		109	107		56
	250	102	95	95	103	109	101	109	122		100	103		105	109		63
	500	101	96	98	103	110	113	116	125		107	107		108	108		65
	1000	91	89	114	96	87	93	101	106		88	90		94	93		67

b) PS80/275

	PS80/275	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	1	79	87	81	91	100	91	102	104		103	104		112	107		58
	10	78	91	91	104	103	87	102	102		106	109		97	91		55
	50	92	102	96	114	105	98	110	109		107	113		96	94		70
	75	84	91	83	99	100	89	100	103		103	111		95	90		68
	150	96	111	101	116	119	111	115	105		104	111		108	108		52
	250	95	98	88	98	114	110	110	110		103	117		97	99		65
	500	109	112	83	121	101	114	117	103		98	119		96	103		70
	1000	109	116	106	108	110	101	109	105		99	111		99	108		61

c) PS80/227

	PS80/227	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	1	99	91	68	105	115	102	112	98		93	105		132	104		61
	8	101	95	90	115	108	99	98	106		99	101		120	104		60
	50	101	93	85	108	108	102	110	105		92	96		114	107		70
	75	105	95	79	102	107	116	121	114		107	110		125	113		72
	150	98	88	97	103	96	106	93	93		93	95		117	102		68
	200	83	73	68	87	81	76	90	76		85	80		89	87		76
	250	103	97	105	108	107	98	111	99		103	104		119	107		73
	1000	98	94	89	110	109	105	110	102		97	101		121	112		67

d) PS80/254

	PS80/254	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	1	92	80	87	88	94	88	102	86		78	83		72	88		64
	10	93	88	96	111	117	104	118	115		78	81		78	84		60
	50	93	68	74	73	77	76	89	78		98	81		76	76		67
	75	90	70	74	71	82	75	91	84		78	73		73	81		69
	150	102	101	107	105	115	114	129	115		95	106		122	120		65
	200	103	108	92	105	115	109	132	112		56	54		62	58		61
	250	90	88	97	90	99	100	115	104		92	95		105	100		76
	500	96	98	108	109	109	107	120	110		97	95		117	113		68

e) HL1203/70

	HL1203/70	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	4	89	90	86	104	85	95	111	109		117	87		85	106		71
	10	83	90	78	113	101	96	108	115		119	88		89	106		67
	20	91	90	102	106	101	102	111	106		112	110		89	112		69

f) HL1203/71

	HL1203/71	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	3	94	106	103	106	101	102	110	111		113	113		95	98		61
	10	95	97	101	110	96	112	114	97		107	113		99	96		63
	20	92	101	93	100	103	116	116	112		107	111		102	101		61

g) HL1203/66

	HL1203/66	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	2	105	100	106	101	94	93	95	102		89	92		86	101		61
	10	99	100	103	102	87	84	91	100		95	93		87	104		62
	20	107	107	93	92	100	103	108	100		104	107		97	93		65
	50	107	116	127	97	109	113	114	103		100	108		96	96		69
	75	102	99	105	96	112	106	93	109		117	91		87	114		67
	150	92	101	98	88	110	96	94	101		110	93		84	120		71

h) HL1203/62

	HL1203/62	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	3	111	115	119	100	110	94	109	109		111	104		98	100		60
	10	111	107	104	89	102	88	97	110		102	89		99	101		62
	20	115	105	115	94	104	96	105	106		103	90		95	99		62
	50	111	103	94	106	108	116	104	108		112	94		93	112		64
	75	114	108	97	103	108	116	104	103		104	102		90	108		60
	150	101	106	107	89	107	98	74	89		115	88		90	118		64
	300	95	103	108	94	109	94	97	99		115	91		91	122		62
	352	98	101	105	89	98	92	93	94		101	94		94	117		61

i) HL1203/72

	HL1203/72	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	3	102	100	92	100	79	81	82	82		109	80		95	95		65
	10	102	97	102	101	77	82	83	80		103	83		98	101		63
	22	96	91	94	93	86	89	93	97		109	90		101	103		68

j) HL1203/76

	HL1203/76	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	2	109	112	116	105	87	90	91	91		106	75		98	96		61
	10	102	105	105	104	76	78	88	92		113	74		103	99		63
	20	110	112	115	111	87	96	97	104		110	80		102	99		65
	47	107	113	92	112	84	90	90	100		124	82		103	98		67

k) HL1203/78

	HL1203/78	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
Depth (m)	2	107	108	104	88	93	83	91	91		107	85		90	89		62
	29	100	105	97	87	93	98	95	97		110	81		101	96		65
	101	105	109	107	99	100	98	107	102		116	88		101	94		66
	202	90	106	100	87	93	87	104	88		109	82		99	94		68
	344	97	107	115	90	94	84	97	96		110	83		99	99		62

l) Ice station

	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA		$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS		d_3 MeFOSAA	d_5 EtFOSAA		C_8 FOSA
PS80/224 Station 1 snow	119	101	124	112	86	98	92	91		112	115		98	89		71
PS80/224 Station 1 melt pond water	111	102	69	99	88	95	88	98		97	108		97	88		75
PS80/255 Station 3 melt pond water	115	102	81	107	96	94	108	119		110	106		97	95		67
PS80/323 Station 5 snow	110	105	98	113	99	94	106	118		105	104		95	93		68
PS80/360 Station 8 snow	112	105	122	94	92	99	96	103		105	99		93	105		70

Table S6a. Concentrations (pg/L) of detectable PFASs in the samples analyzed by MTM.

PS80/227 surface	PFHpA	PFOA	PFOS
ALFONSE	22	50	41
MTM	20	67	51
HL1203/70 - 4m	**PFHpA**	**PFOA**	**PFOS**
ALFONSE		29	25
MTM		43	30
HL1203/66 - 10m	**PFHpA**	**PFOA**	**PFOS**
ALFONSE		42	5
MTM		47	
HL1203/78 - 29m	**PFHpA**	**PFOA**	**PFOS**
ALFONSE	20	91	19
MTM		111	

Blank cell indicates sample below respective LOQs.

Table S6b. Relative standard deviation (%) of detectable PFASs between ALFONSE and MTM in the samples.

	PFHpA	PFOA	PFOS
PS80/227 surface	6	20	15
HL1203/70 - 4m		27	14
HL1203/66 - 10m		8	
HL1203/78 - 29m		14	

Table S6c. Recoveries (%) of PFOA and PFOS in the samples.

	PFOA	PFOS
PS80/227 surface	97	95
HL1203/70 - 4m	93	93
HL1203/66 - 10m	89	93
HL1203/78 - 29m	87	94

Recovery was calculated by comparing the peak area of the mass-labelled standards to those of the recovery standard (7H-PFHpA)

Table S7. PFAS concentrations (pg/L) in different samples collected from the Central Arctic (a)-(d), the Arctic shelf (e)-(k), and different ice stations (l) (see Table S2 for sample location) (value shown in the table were an average between duplicate extractions; blank cell indicate sample below corresponding LOQ: 5 pg/L for C6-C11 PFCAs, C4, C6, C8 PFSAs, MeFOSAA, EtFOSAA; 10pg/L for PFDoDA and PFDS; 20pg/L for FOSA)

a) PS80/364

		PS80/364	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	PML	1		11												
		10		17	16	9				9		18				
	HL	50	26	32	64	20				21	22	17				
		75	22	35	49	21				20	17	14				
	AW	150														
		250														
		500														
	DW	1000														

b) PS80/275

		PS80/275	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	PML	1	24		30	39		17		12		18				
		10	37	17	44	19		5		18	9	10				
	HL	50	20	17	43	12				16	10	13				
		75	8		9											
	AW	150								40						
		250														
	DW	500														
		1000														

c) PS80/227

		PS80/227	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	PML	1	12	22	50	23				11	15	41				
		8			15	9										
	HL	50										10				
		75			23							11				
	AW	150										12				
		200				13						37				
		250										11				
		1000														

d) PS80/254

		PS80/254	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	PML	1				14		11		15			26			
		10			15	9				16		19	27			
	HL	50		15	37	14				18	14	47				
		75														
		150														
	AW	200														
		250														
		500														

e) HL1203/70

	HL1203/70	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	4			29	18	9		8			25				
	10		30	40	23	8					41				
	20			23	10						6				

f) HL1203/71

	HL1203/71	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	3		10	22	14	6					20				
	10		23	50	18	6					13				
	20		18	84	16						17		7.2		

g) HL1203/66

	HL1203/66	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	MeFOSAA	EtFOSAA	FOSA
Depth (m)	2		6	44	9					5	8		6.5		
	10			42	8						5		7.3		
	20			41	14						8		7.7		
	50		13	43	12						5		8.0		
	75		10	40	16						6		10.1		
	150			39							8				

h) HL1203/62

	HL1203/62	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EtFOSAA		FOSA
Depth (m)	3		6	40	5					5	6	28			6.0			
	10			26								27						
	20			54	6						9	19						
	50			40						6	5	7						
	75			27	8													
	150			34	7													
	300	10		53	11													
	352	15		43	17													

i) HL1203/72

	HL1203/72	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EtFOSAA		FOSA
Depth (m)	3			29	15						5	10			5.0			
	10			11	9							7						
	22		17	65	17						5	14			7.1			

j) HL1203/76

	HL1203/76	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EtFOSAA		FOSA
Depth (m)	2		8	41	12					6		7						
	10		15	56	27	9						8			6.5			
	20			42	26	5				5		21				9.7		
	47			56	14					9		7			7.3			

k) HL1203/78

	HL1203/78	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EtFOSAA		FOSA
Depth (m)	2			21	4							11			5			
	29		20	91	8					9	8	19			21			
	101			55	15							15			8			
	202			52	14					11		11						
	344			80	21							10						

l) Ice stations

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA		PFBS	PFHxS	PFOS	PFDS		MeFOSAA	EtFOSAA		FOSA
PS80/224 Station 1 snow	44	14	72	33	33	21					34	11			36		
PS80/224 Station 1 melt pond water	16	39	57	85							34						23
PS80/255 Station 3 melt pond water	150	29	62	106	14	13					42						
PS80/323 Station 5 snow	109	49	294	253	142	92	88			18	343			36	19		156
PS80/360 Station 8 snow	26	25	91	61	49	45					43				9		20

Table S8. Range (pg/L) and detection frequency (%) of the thirteen detectable PFASs.

	PFHxS	PFOS	FOSA	EtFOSAA	MeFOSAA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
Range (pg/L)	<5-22	<5-343	<5-156	<5-36	<5-36	<5-150	<5-49	<5-294	<5-253	<5-142	<5-92	<5-88
Detection frequency (%)	12	48	4	6	25	150	49	54	49	14	6	2

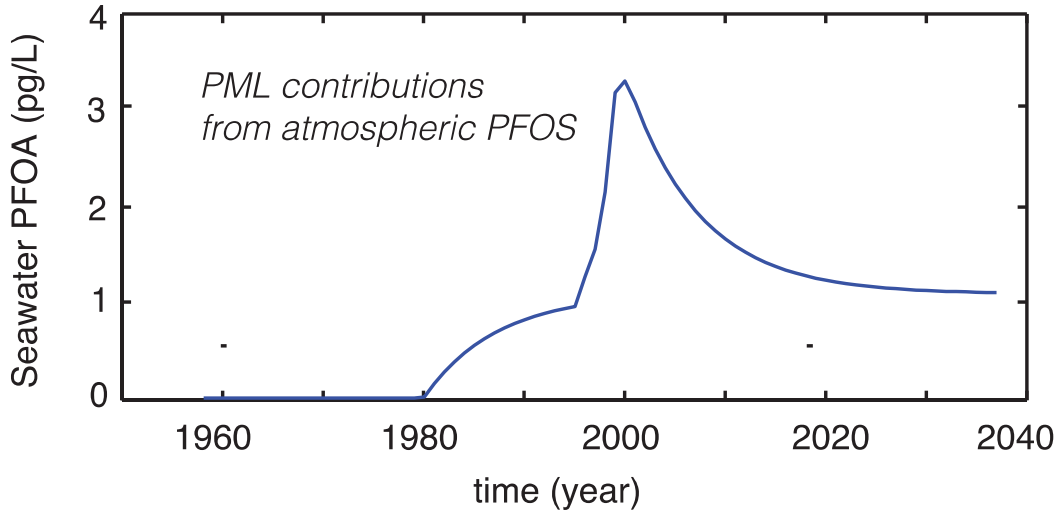
Table S9: Linear regression of PFAS concentrations in snow/meltwater versus latitude or longitude

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFOS	EtFOSAA	FOSA
n	5	5	5	5	4	4	5	3	3
R^2 with latitude	0.42	0.20	0.15	0.33	0.09	0.03	0.23	0.31	0.56
R^2 with longitude	**0.74**	0.34	0.50	**0.70**	0.32	0.30	0.54	0.17	0.92
Significance with longitude	**0.06**	0.30	0.18	**0.08**			0.16		

Table S10. Ratios of different pair PFCAs in snow and meltpond water samples.

	PFHxA/PFHpA	PFOA/PFNA	PFDA/PFUnDA
PS80/224 Station 1 snow	3.1	2.2	1.6
PS80/224 Station 1 melt pond water	0.4	0.7	
PS80/255 Station 3 melt pond water	5.1	0.6	1.0
PS80/323 Station 5 snow	2.2	1.2	1.5
PS80/360 Station 8 snow	1.1	1.5	1.1

Figure S3. Modeled PFOS concentration in the PML due to atmospheric deposition.



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