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SUPPLEMENTAL INFORMATION

Laboratory Validation of an Integrative Passive Sampler for Per- and Polyfluoroalkyl Substances in Water

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Table S1: PFAS Compound List

Abbreviation	Name	Type	CAS #
PFOSA	perfluorooctanesulfonamide	analyte	754-91-6
PFBA	perfluorobutanoic acid	analyte	375-22-4
PFPeA	perfluorpentanoic acid	analyte	2706-90-3
PFHxA	perfluorohexanoic acid	analyte	307-24-4
PFHpA	perfluoroheptanoic acid	analyte	375-85-9
PFOA	perfluorooctanoic acid	analyte	335-67-1
PFNA	perfluorononanoic acid	analyte	375-95-1
PFDA	perfluorodecananoic acid	analyte	335-76-2
PFUdA	perfluoroundecanoic acid	analyte	2058-94-8
PFDoA	perfluorododecanoic acid	analyte	307-55-1
PFTrDa	perfluorotridecanoic acid	analyte	72629-94-8
PFTeDA	perfluorotetradecanoic acid	analyte	376-06-7
PFBS	perfluorobutanesulfonic acid	analyte	375-73-5
PFHxS	perfluorohexanesulfonic acid	analyte	355-46-4
PFOS	perfluorooctanesulfonic acid	analyte	1763-23-1
[M]4:2 FTS	1H, 1H, 2H, 2H-[1,2-$^{13}C_2$]perfluorohexane sulfonic acid	surrogate	2708218-88-4
[M]6:2 FTS	1H, 1H, 2H, 2H-[1,2-$^{13}C_2$]perfluorooctane sulfonic acid	surrogate	2708218-89-5
[M]8:2 FTS	1H, 1H, 2H, 2H-[1,2-$^{13}C_2$]perfluorodecane sulfonic acid	surrogate	2708218-90-8
[M]PFOSA	Perfluoro-2-[$^{13}C_4$]octanesulfonamide	surrogate	960315-53-1
[M]HFPO-DA	Tetrafluoro-2-(heptafluoropropoxy)^{13}C-propanoic acid	surrogate	-
[M]PFBA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	surrogate	1017281-29-6
[M5]PFPeA	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]pentanoic acid	surrogate	-
[M]PFHxA	Perfluoro-n-[1,2,-$^{13}C_3$]hexanoic acid	surrogate	960315-47-3
[M4]PFHpA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	surrogate	2328024-55-9
[M]PFOA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	surrogate	960315-51-9
[M]PFNA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]nonanoic acid	surrogate	960315-49-5
[M]PFDA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]decanoic acid	surrogate	960315-50-8
[M]PFUdA	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	surrogate	960315-51-9
[M]PFDoA	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	surrogate	960315-52-0
[M]PFTeDA	Perfluoro-n-[1,2-$^{13}C_2$]tetradodecanoic acid	surrogate	864071-08-9
[M3]PFBS	Perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonate	surrogate	2708218-84-0
[M]PFHxS	Perfluoro-1-[$^{18}O_2$]hexanesulfonate	surrogate	-
d_5-N-EtFOSAA	N-ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid	surrogate	1265205-97-7
d_3-N-MeFOSA	N-methyl-d_3-perfluoro-1-octanesulfonamide	surrogate	936109-37-4
d_7-N-MeFOSE	2-(N-methyl-d_3-perfluoro-1-octanesulfonamido)ethan-d_4-ol	surrogate	1265205-95-5
d_9-N-EtFOSE	2-(N-ethyl-d_5-perfluoro-1-octanesulfonamido)ethan-d_4-ol	surrogate	1265205-96-6
[M8]PFOS	Sodium perfluoro-1-[$^{13}C_8$]octanesulfonate [$^{13}C_8$]octanoic	internal std	2522762-16-7
[M2]PFOA	Perfluoro-n-[1,2-$^{13}C_2$]octanoic acid	internal std	864071-08-9
d_3-N-MeFOSAA	N-methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid	internal std, surrogate	

Table S2. PFAS concentrations for column breakthrough measurements measured by HPLC-MS/MS

.

PFAS	**Concentration (μg/L)**
PFBA	820
PFPeA	720
PFHxA	870
PFHpA	230
PFOA	470
PFNA	400
PFDA	67
PFBS	520
PFHxS	530
PFOS	240
PFOSA	77

Table S3. Simulated groundwater composition

Solute	**Concentration (mg/L)**
Cations	
Ca^{2+}	10
Mg^{2+}	1.5
Na^{+}	14
Anions	
HCO_3^-	25
Cl^-	22
SO_4^{2-}	10
Natural Organic Matter	
Humic acid	1.0
pH	7.2
conductivity	128 mS

Note: for 90-day passive sampler experiment humic acid was not added.

Table S4. MRM transitions used in HPLC-MS/MS measurements

Compound	Retention Time (min)	MRM Transition (*m/z*)		MS Parameters	
		precursor	product(s)	fragmentor	CE
4:2 FTS	15.19	327	307	69	18
		327	80	69	32
[M]4:2 FTS		329	309	69	18
6:2 FTS	19.33	427	407	66	24
			80	66	44
[M]6:2 FTS		429	409	66	24
8:2 FTS	21.86	527	507	66	32
		527	80	66	52
[M]8:2 FTS		529	509	66	32
PFOSA	22.41	498	78	69	40
[M]PFOSA		506	78	69	40
HFPO-DA	15.93	285	169	70	8
[M]HFPO-DA		287	169	70	8
PFBA	10.32	213	168.9	50	8
[M]PFBA		217	172	50	8
PFPeA	13.21	263	218.9	60	8
[M5]PFPeA		268	223	60	8
PFHxA	15.35	313	268.9	70	8
			119	70	18
[M]PFHxA		318	273	70	8
PFHpA	17.44	362.9	319	72	6
			169	72	12
[M4]PFHpA		367	322	72	6
PFOA	19.36	413	369	69	4
			169	69	12
[M]PFOA		415	370	69	4
[M8]PFOA		421	376	69	4
PFNA	20.89	463	419	66	4
			169	66	17
[M]PFNA		472	427	66	4
PFDA	21.81	513	469	69	8
			218.7	100	16
[M]PFDA		519	474	69	8
PFUdA	22.46	563	519	66	4
[M]PFUdA		570	525	66	4
PFDoA	22.99	613	569	79	8
[M]PFDoA		615	570	79	8
PFTrDa	23.51	663	619	79	14
PFTeDA	24.07	713	669	79	14
[M]PFTeDA		715	670	79	14
PFBS	13.55	298.9	98.9	69	44
			79.9	69	32
[M3]PFBS		302	80	69	32
PFHxS	17.49	398.9	99	90	75
			80	90	41
[M]PFHxS		402	80	90	41
PFOS	20.86	498.9	99	100	50
			80	100	50
[M]PFOS		403	80	100	50
[M8]PFOS		407	80	100	50
N-MeFOSAA	21.90	570	418.9	115	20

d_3-N-MeFOSAA	22.20	573	418.9	115	20
N-MeFOSA	23.50	512	168.9	115	20
d_3-N-MeFOSA	23.50	515	168.9	115	20
d_3-N-MeFOSE	23.20	623	59.2	115	20
d_3-N-EtFOSE	24.01	639	59.2	115	16

Table S5. Surrogate recoveries from passive samplers.

Surrogate	**Percent Recovery**	
	Range	Average
[M]4:2 FTS	33-129	71 ± 24
[M]6:2 FTS	30-169	88 ± 37
[M]8:2 FTS	36-147	77 ± 29
[M]FOSA	6-119	51 ± 24
[M]HFPO-DA	36-114	88 ± 25
[M]PFBA	27-131	67 ± 23
[M5]PFPeA	37-188	87 ± 37
[M]PFHxA	29-145	71 ± 27
[M4]PFHpA	33-158	81 ± 27
[M]PFOA	43-153	79 ± 30*
[M]PFNA	40-120	74 ± 19
[M]PFDA	35-155	84 ± 31
[M]PFUdA	23-110	60 ± 20
[M]PFDoA	9-162	49 ± 26
[M]PFTeDA	5-104	35 ± 19
[M]PFBS	45-146	87 ± 27
[M]PFHxS	38-109	64 ± 17
[M]PFOS	36-143	71 ± 25*

(n=31) * Recoveries of PFOA and PFOS reduced by ion suppression with several samples with high concentrations. Nominal recoveries are 80-100%

Table S6: HPLC Parameters

Solvent		
Solvent A	water, 5 mM ammonium acetate	
Solvent B	95% methanol, 5 mM ammonium acetate	
Flow rate	0.250 mL/min	
Temp	45°C	
Solvent Program	A	B
0.00 min	70%	30%
3.00 min	70%	30%
5.00 min	40%	60%
14.00 min	20%	80%
17.00 min	0%	100%
26.00 min	0%	100%
Post time	7 min	
Inj. volume	5 μL (with needle wash)	

QQQ Parameters

Mode	Negative ion
Needle voltage	-4,000 V
Gas Flow	11 L/min
Gas Temp	300°C
Accelerator voltage	2 V

Table S7: LOQs and LODs for passive samplers and grab samples measured using SPE

	Concentration (ng/L)			
	Passive Sampler(1)		Grab Sample(2)	
Analyte	MDL(3)	LOD	MDL	LOD
4:2 FTS	3.0	1.4	3.2	1.6
6:2 FTS	3.7	1.7	3.9	2.0
8:2 FTS	4.4	2.1	4.6	2.4
HFPO-DA	49.2	22.9	51.5	26.4
PFOSA	3.2	1.5	3.3	1.7
PFBA	7.6	3.6	2.5	1.3
PFPeA	4.4	2.1	2.2	1.1
PFHxA	6.2	2.9	4.8	2.5
PFHpA	0.7	0.3	0.7	0.4
PFOA	1.5	0.7	1.6	0.8
PFNA	0.5	0.2	0.5	0.3
PFDA	1.2	0.5	1.4	0.7
PFUdA	0.9	0.4	1.0	0.5
PFDoA	0.8	0.4	0.8	0.4
PFTrDA	1.2	0.5	1.2	0.6
PFTeDA	1.7	0.8	1.8	0.9
PFBS	1.8	0.8	1.9	1.0
PFHxS	2.5	1.2	2.7	1.4
PFOS	1.1	0.5	1.1	0.6

(1) Values correspond to a 10-day sampling time at 25°C in a flowing water stream.
(2) 250 mL grab sample reconstituted in 1.0 mL prior to LC-MS.
(3) Method detection limit.
(4) Limit of detection.

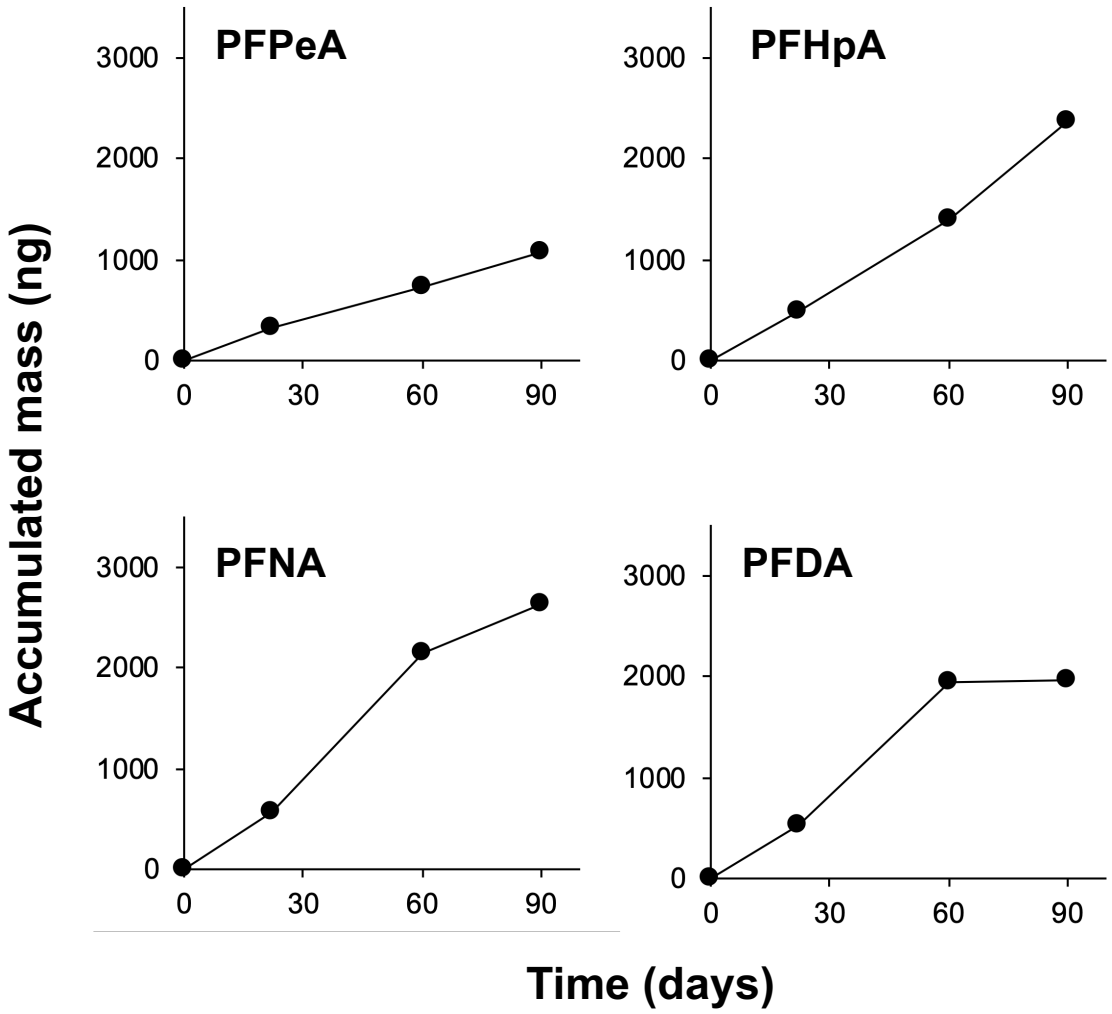

Fig S1. Accumulated mass by passive samplers over time for PFPeA, PFHpA, PFNA, and PFDA in bench-scale measurements. The flow rate was 0.38 cm/min with 2.5 μg/L of each PFAS compound in simulated groundwater without humic acid.

Table S8. Sampling rates (R_S) measured for 90-day passive sampling compared to sampling rates measured previously for 12 day sampling times.

PFAS	**R_S (L/day) 90 days**	**R_S (L/day) 12 days**[1]
PFBA	0.0029	0.0027
PFPeA	0.0047	0.0060
PFHxA	0.0127	0.0081
PFHpA	0.0105	0.0092
PFOA	0.0110	0.0111
PFNA	0.0124	0.0114
PFDA	0.0132	n/m
PFBS	0.0103	0.0119
PFHxS	0.0152	0.0200
PFOS	0.0141	0.0116

[1](Hartman et al. 2021) n/m: not measured

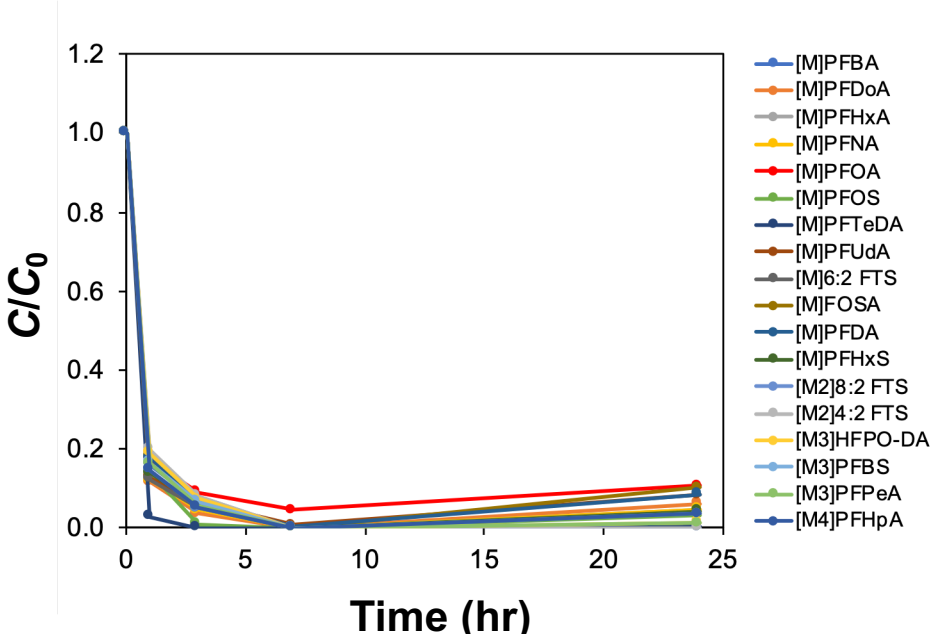

Fig S2. Normalized surrogate concentration C/C_0 (where C_0 is the initial concentration) vs. time depicting uptake during passive sampler analysis.

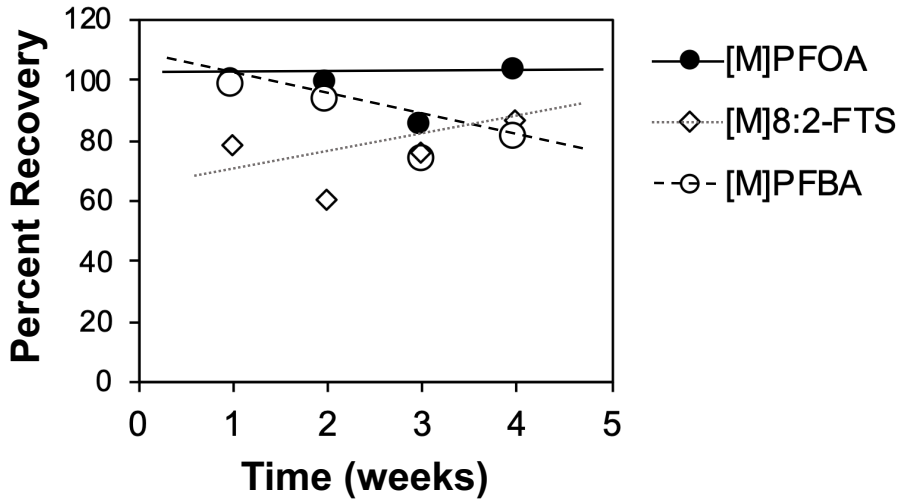

Fig S3. Change in the percent recovery of [M]PFOA, [M]8:2-FTS, and [M]PFBA over 4 weeks of passive sampler storage at 4°C.

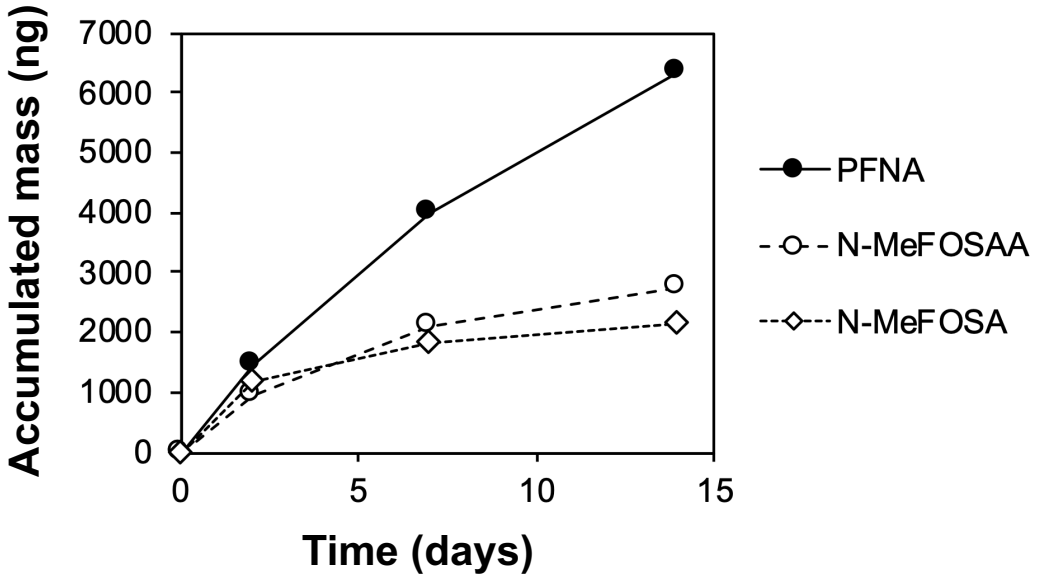

Fig S4. Accumulated mass vs time plots for PFNA, N-MeFOSAA, and N-Me-FOSA.

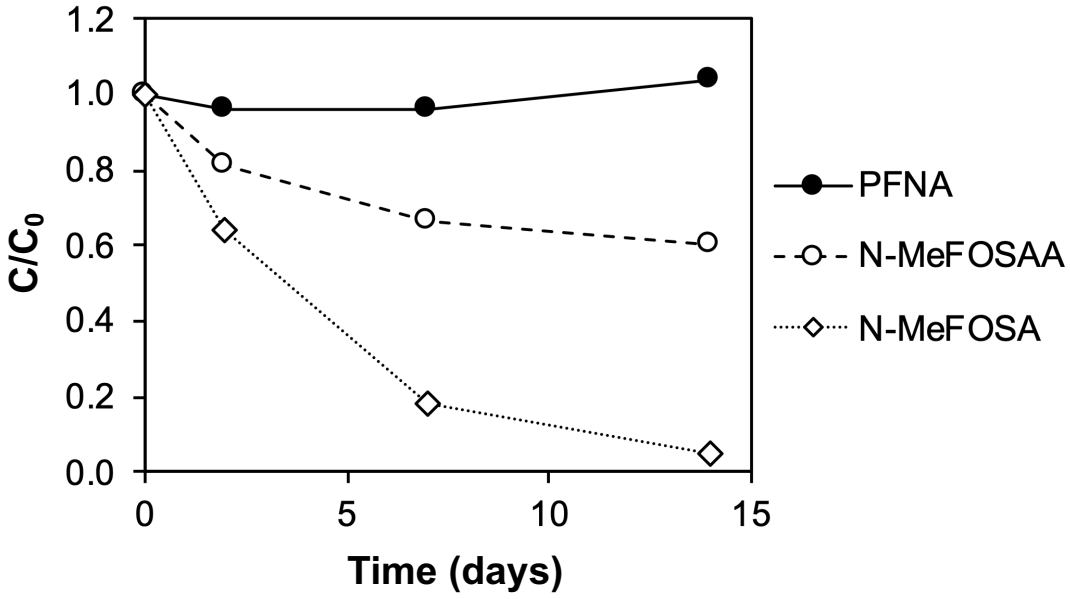

Fig S5. Concentration of PFNA, N-MeFOSAA, and N-Me-FOSA during 14-day passive sampler exposure vs. time testing.

Table S9. R_S values for desorption and (ration adsorption/desorption rates) estimated from variable concentration experiments.

Analyte	**Estimated $R_{s,\ desorb}$ (desorption)**	**Ratio $R_{s,\ adsorb}$/ $R_{s,\ desorb}$**
Perfluorobutanoic acid (PFBA)	0.00062	13.0
Perfluoropentanoic acid (PFPeA)	0.00038	26.6
Perflurohexanoic acid (PFHxA)	0.00032	40.8
Perfluoroheptanoic acid (PFHpA)	0.00017	75.8
Perfluorooctanoic acid (PFOA)	0.00005	240.5
Perfluorononanoic acid (PFNA)	0.00014	89.9
Perfluorodecanoic acid (PFDA)	0.00021	62.6
perfluorobutanesulfonic acid (PFBS)	0.00023	68.5
Perfluorohexanesulfonic acid (PFHxS)	0.00016	98.2
Perfluorooctanesulfonic acid (PFOS)	0.00021	77.9

Table S10. R_S values measured to date for the passive sampler.

Water Flow Rate 0-2 cm/min (e.g., Monitoring Well)		
Analyte	Sampling Rate (R_s in L/day) Water Temp	
	<10°C	10-25°C
PFBA	0.0033	0.0033
PFPeA	0.0054	0.0063
PFHxA	0.0062	0.0093
PFHpA	0.0056	0.0112
PFOA	0.0056	0.0124
PFNA	0.0066	0.0131
PFDA	0.0066	0.0131
PFUdA	0.0056	0.0124
PFDoA	0.0056	0.0124
PFTeDA	0.0005	0.0012
PFTrDA	0.0054	0.0120
PFBS	0.0054	0.0121
PFHxS	0.0068	0.0150
PFOS	0.0056	0.0125
4:2 FTS	0.0054	0.0120
6:2 FTS	0.0054	0.0120
8:2 FTS	0.0054	0.0120
PFOSA	0.0054	0.0120
HFPO-DA	0.0054	0.0120
NMeFOSA	0.0055	0.0125
NMeFOSAA	0.0050	0.0063

Water Flow Rate > 2 cm/min (e.g., Flowing Stream)			
Analyte	Sampling Rate (R_s in L/day) Water Temp		Conditional Limit of Detection
	<10°C	10-25°C	(ng/L)
PFBA	0.0120	0.0120	3.6
PFPeA	0.0146	0.0170	2.1
PFHxA	0.0342	0.0510	2.9
PFHpA	0.0305	0.0610	0.3
PFOA	0.0293	0.0650	0.7
PFNA	0.0340	0.0680	0.2
PFDA	0.0340	0.0680	0.5
PFUdA	0.0293	0.0650	0.4
PFDoA	0.0270	0.0600	0.4
PFTeDA	0.0270	0.0600	0.8
PFTrDA	0.0270	0.0600	0.5
PFBS	0.0248	0.0550	0.8
PFHxS	0.0315	0.0700	1.2
PFOS	0.0293	0.0650	0.5
4:2 FTS	0.0270	0.0600	1.4
6:2 FTS	0.0270	0.0600	1.7
8:2 FTS	0.0270	0.0600	2.1
PFOSA	0.0270	0.0600	1.5
HFPO-DA	0.0270	0.0600	22.9
NMeFOSA	0.0300	0.0670	1.9
NMeFOSAA	0.0171	0.0380	1.9