Supporting Information

Distribution of Legacy and Emerging Per- and Polyfluoroalkyl substances in Riverine and Coastal Sediments of SouthEast North Carolina, USA

Megumi Shimizu*[a], Rosa S. Garcia[a], G. Brooks Avery[a], Robert J. Kieber[a], Stephen A. Skrabal[a] and Ralph N. Mead*[a,b]

[a] Department of Chemistry and Biochemistry, University of North Carolina Wilmington, Wilmington, NC 28403 USA
[b] Earth and Ocean Sciences, University of North Carolina Wilmington, Wilmington, NC 28403 USA

Table of Contents

PFAS Recovery from Sediment

Recoveries were calculated based on a matrix-matched spike extraction from several sediment locations (Table S3). Roughly 10 g of sediment were added to three 50 mL tubes labeled matrix blank (BLK), matrix spike B (SB), and matrix spike A (SA). Before extraction, SB was spiked with a known concentration (0.0231-0.136 ng) of working standards (WS), PFMOAA, PFMOPrA, PFMOBA, HFPO-DA, PFOA and PFOS. After elution, a known concentration of internal surrogates (IS), M-PFBA, M-PFHxA, M-PFOA, M-PFOS and M-HFPO-DA, was added to SB, SA, and BLK. The same amount of WS was also added to SA eluate after elution. Recoveries were determined by subtracting the area ratio of BLK from SB and SA and then calculating the area ratio between SB and SA (see equation 1).

Equation 1. $$Recovery = \frac{SB - BLK}{SA - BLK}$$

Where

SB = response for SPE extract of matrix spiked before SPE
SA = response for SPE extract of matrix spiked after SPE
BLK = response for SPE extract of matrix without spike

Table S1. Sample locations and date/time of collections of sediment used in this study.

Sample Location	Lat °N	Long °W	Sample Name	Collection Date/ Time
Lock and Dam 1	34°24’16”	78°17’37”	LD1_170919, LD1_180130, LD1_180326	Sept 19, 2017 / 13:45 Jan 30, 2018 / 15:43 March 26, 2018 / 14: 22
Lock and Dam 2	34°37’35”	78°34’39”	LD2_170919	Sept 19, 2017 / 14:33
William O’ Huske Dam	34°50’06”	78°49’23”	WOD_171909 WOD_171102 WOD_180130 WOD_180326	Sept 19, 2017 / 15:30 Nov 2, 2017 / 14:43 Jan 30, 2018 / 15:43 March 26, 2018 / 16:00
Chemours Creek	34°50’20”	78°49’30”	Chemours_180326	March 26, 2018/ 16:15
Fayetteville	34°59’48”	78°51’01”	FBR_170919 FBR_171102 FBR_180130 FBR_180326	Sept 19, 2017 / 15:50 Nov 2, 2017 / 15:16 Jan 30, 2018 / 16:45 March 26, 2018 / 16:45
Elizabethtown	34°37’52”	78°36’17”	EB_180130 EB_180326	Jan 30, 2018 / 15:10 March 26, 2018 / 15:05
Horseshoe Bend	34°14’37”	77°58’11”	HB_171023 HB_181029	Oct 23, 2017 / 12:00 Oct 29, 2018 / 12:05
CF Mile Marker 61	34°11’37”	77°57’26”	M61_171023 M61_181029	Oct 23, 2017 / 11:00 Oct 29, 2018 / 11:20
CF Mile Marker 54	34°08’21”	77°56’45”	M54_171023 M54_181029	Oct 23, 2017 / 10:25 Oct 29, 2018 / 10:30
CF Mile Marker 35	34°02’00”	77°56’13”	M35_181029	Oct 29, 2018 / 10:15
CF Mile Marker 23	33°56’44”	77°58’10”	M23_181029 M23_190917	Oct 29, 2018 / 09:30 Sept 17, 2019 / 09:45
CF Mile Marker 18	33°54’46”	78°01’01”	M18_181029	Oct 29, 2018 / 09:00
Mouth of CF River	33°49’38”	78°02’20”	MCF_181029 MCF_191008	Oct 29, 2018 / 11:00 Oct 8, 2019 / 10:10
Fort Sumter	32°45’47”	79°52’47”	FS_191010	Oct 10, 2019 / 14:20
Beaufort	34°39’02”	76°39’09”	BFT_190401	April 1, 2019 / 15:35

Table S2. The pH of the surface water at time of collection and the sediment % organic carbon content at each sample location.

Sample Location	Sample Name	pH	%OC
Lock and Dam 1	LD1_170919,	na	0.4
	LD1_180130,	na	2.0
	LD1_180326	na	2.0
Lock and Dam 2	LD2_170919	na	3.0
William O' Huske Dam	WOD_171909	na	0.2
	WOD_171102	na	0.1
	WOD_180130	na	0.1
	WOD_180326	na	0.1
Chemours Creek	Chemours_180	na	0.8
	326		
Fayetteville	FBR_170919	na	0.8
	FBR_171102	na	0.6
	FBR_180130	na	2.6
	FBR_180326	na	1.0
Elizabethtown	EB_180130	na	3.0
	EB_180326	na	3.0
Horseshoe Bend	HB_171023	7.4	0.3
	HB_181029	6.9	3.0
CF Mile Marker 61	M61_171023	7.5	1.0
	M61_181029	7.2	0.1
CF Mile Marker 54	M54_171023	7.5	3.0
	M54_181029	7.4	0.04
CF Mile Marker 35	M35_181029	7.6	0.8
CF Mile Marker 23	M23_181029	7.8	0.7
	M23_190917	7.9	---
CF Mile Marker 18	M18_181029	7.9	3.0
Mouth of CF River	MCF_181029	7.9	0.8
	MCF_191008	8.1	----
Fort Sumter	FS_191010	na	0.9
Beaufort	BFT_190401	na	0.7

na= not analyzed

Table S3. The mobile phase gradient program for quantitative analysis.

Time (min)	A (%)	B (%)	Flow rate (mL/min)
0	95	5	0.4
0.1	45	55	0.4
4.5	1	99	0.4
8.0	1	99	0.4
8.5	95	5	0.4
10.0	95	5	0.4

Table S4. MS transitions, MRM parameters (CE: collision energy, DP: declustering potential, CXP: cell exit potential, EP: entrance potential), and internal standards for PFAS analysis.

Analyte	Isolation mass	Quantifier mass	CE (V)	DP (V)	CXP (V)	EP (V)	Internal Standard
PFMOAA	179	85	-15	-30	-5	-10	M-PFBA
PFMOPrA/ PMPA	229	85	-20	-50	-5	-10	M-PFBA
PFMOBA	279	85	-25	-40	-5	-14	M-PFHxA
HFPO-DA	329	285	-15	-30	-5	-10	M-HFPO-DA
PFOA	413	369	-14	-50	-6	-10	M-PFOA
PFOS	499	99	-70	-120	-14	-14	M-PFOS
M-PFBA	217	172	-15	-40	-7	-14	
M-PFHxA	315	270	-15	-48	-12	-10	
M-HFPO-DA	332	169	-18	-30	-1	-10	
M-PFOA	421	376	-14	-50	-6	-10	
M-PFOS	507	99	-70	-120	-14	-14	

Table S5. Spiked recoveries of each target analyte and the corresponding LOQ and LODs for each compound. The average, standard deviation and percent relative standard deviation is shown below each analyte. n/a = not available and – is due to contamination

Sample	PFOA	PFMOAA	PFMOBA	PFMOPrA/ PMPA	HFPO-DA	PFOS
EB_180130	36.5%	109%	140%	87%	127%	113%
Chemours_180326	108.%	50%	95%	72%	115%	89%
WOD_170919	98%	80%	130%	96%	132%	96%
LD1_180326	80%	n/a	141%	157%	67%	105%
MCF_190401	76%	74%	31%	101%	47%	69%
M35_181029	90%	98%	100%	104%	--%	54%
Average	81	82	106	102	97	87
Std dev	25	22	41	28	38	22
%RSD	30	27	39	28	39	25
LOQ (pg on column)	3	4.	4	4	4	4
LOQ (pg/g dry sediment)	3	5	2	9	2	12

Table S6. The environmental concentrations obtained for precision performance. The average and standard deviations are listed below each set of samples (n=2-3). These averages were used as the reported values.

Sample	PFMOAA	PFMOPrA/PMPA	PFMOBA	HFPO-DA	PFOA	PFOS
FBR_170919 (1)	<LOQ	<LOQ	<LOQ	0.2	0.1	0.7
FBR_170919 (2)	<LOQ	<LOQ	<LOQ	0.5	0.1	0.4
FBR_170919 (3)	<LOQ	<LOQ	<LOQ	0.5	0.1	0.4
Average	---	---	---	0.4	0.1	0.5
Std dev	---	---	---	0.2	0	0.2
Chemours_180326 (1)	5	0.1	<LOQ	2	0.4	0.4
Chemours_180326 (2)	4	<LOQ	<LOQ	2	0.4	<LOQ
HB_181029 (1)	0.1	<LOQ	<LOQ	0.9	0.1	0.9
HB_181029 (2)	<LOQ	<LOQ	<LOQ	0.2	0.2	0.4
HB_181029 (3)	<LOQ	<LOQ	0.1	0.4	0.2	1
Average	---	---	--	0.5	0.2	0.8
Std dev	---	---	--	0.3	0.1	0.3

Table S7: Full list of PFAS screened for at each sample location along the Cape Fear River. Structures can be found in Figure S2 and two numbers indicate isomers in order of elution from left to right.

Category	Structure Number	CAS	Confidence	Formula (M-1)	Monoisotopic Mass M-1 (u)	Reference
[a]***Perfluorinated Ether Acids***						
	1	39492-88-1	4	$C_4F_7O_4$	244.9685	Strynar et al., 2015
	2	39492-89-2	4	$C_5F_9O_5$	310.9602	Strynar et al., 2015
	3	151772-58-6	4	$C_5F_9O_4$	294.9653	chen et al., 2020
	4	39492-90-5	4	$C_6F_{11}O_6$	376.9519	Sun et al. 2016
	5	39492-91-6	4	$C_7F_{13}O_7$	442.9436	Roebuck et al., 2020
	6	801212-59-9	4	$C_7F_{13}O_3$	378.964	McCord et al., 2018
	7	69087-46-3	4	$C_8F_{13}O_4$	406.9589	McCord and Strynar 2019
	8	113507-82-7	4	$C_4F_9O_4S$	314.9374	Strynar et al., 2015
	9	29311-67-9	4	$C_7F_{13}O_5S$	442.9259	Strynar et al., 2015
[b]***H-Polyfluorinated***	10	801209-99-4	4	$C_4HF_8O_4S$	296.9468	Saleeby et al.,
	11	2416366-21-5	4	$C_6HF_{12}O_4S$	396.9404	McCord and Strynar 2019
	12	749836-20-2	3	$C_7HF_{14}O_5S$	462.9321	Saleeby et al.,
	13	773804-62-9	4	$C_8HF_{14}O_4$	426.9651	McCord and Strynar 2019
[c]***PerFluoro Ether Multi-Acidic***	14a/b	2416366-18-0/852157-01-8	4	C7HF12O6S	440.9302	Zhouet al 2007
	15	2416366-19-1	4	$C_7H_2F_{11}O_7S$	438.9346	McCord and Strynar 2019
	16	1235024-21-1	4	$C_8H_1F_{14}O_7S_1$	506.922	Zhou et al 2007
	17	1235024-21-1	4	C5HF8O6S	340.9366	Takasaki et al 2013

a= general formula of $CF_3(CF_2)_n(CF_2O)_m(R_1)$ where R is $-SO_3H$ or -COOH
b= where one F is replaced with an H
c= general formula of R_1-$(CF_2)n(CF_2O)m$-R_2 where R_1 and R_2 are variable acidic groups of $-SO_3H$ or -COOH

Figure S1. Chemical structures of each targeted PFAS for quantitative analysis. *Note PFMOPrA and PMPA could not be chromatographically resolved.

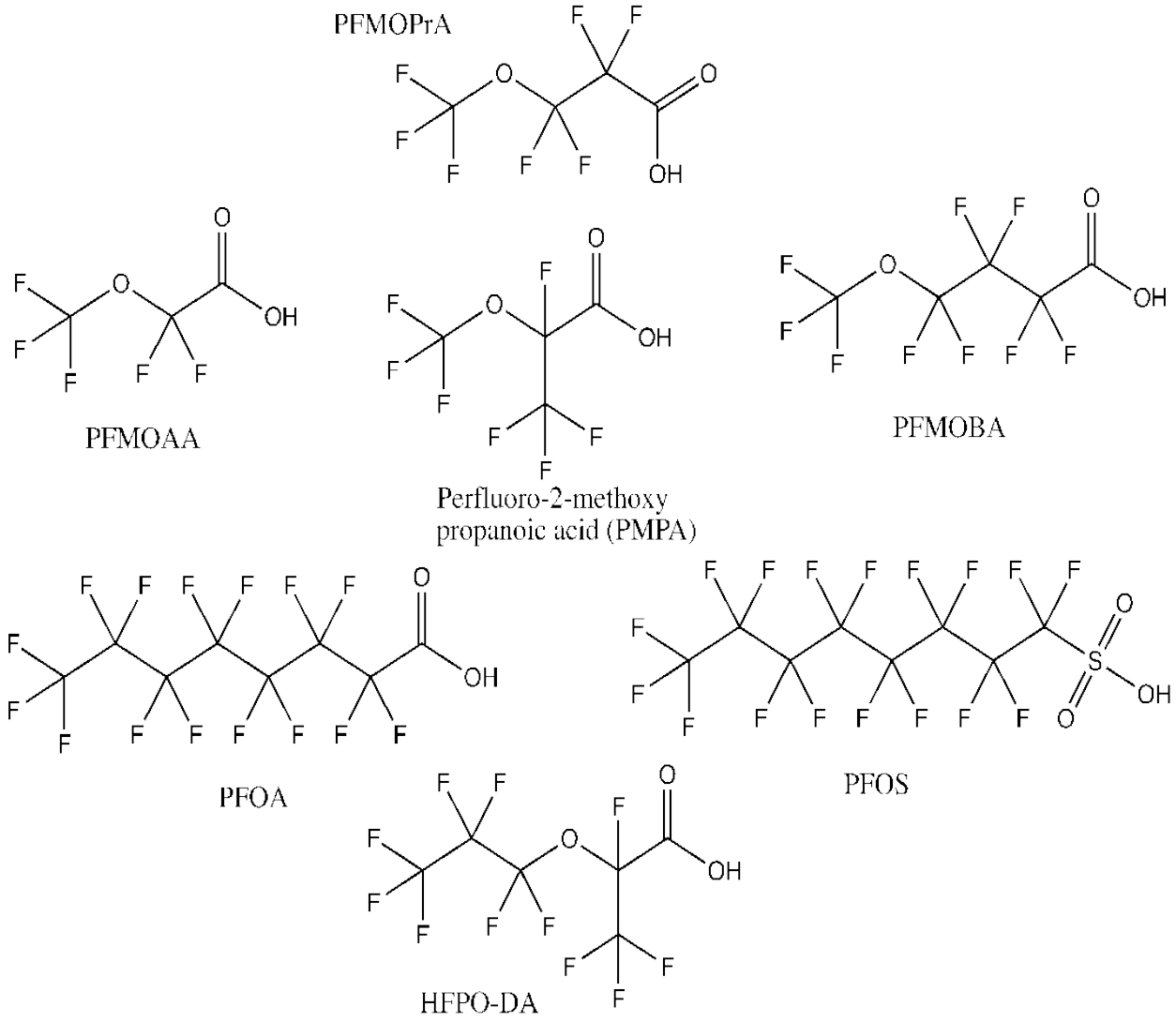

Figure S2: Structures of PFAS screened for in sediment extracts by LC-QTOF. The structures and CAS numbers are based upon previously published information and remain tentative as no authentic standard was available at the time of study.