Novel polyfluorinated compounds identified using high resolution mass spectrometry downstream of manufacturing facilities near Decatur, Alabama, USA

Supporting Information

Number of pages = 14

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Materials

Acetonitrile (ACN), dichloromethane (DCM), and methanol (B&J Brand High Purity Solvent) were purchased from Honeywell Burdick & Jackson (Muskegon, MI, USA). Ammonium acetate was purchased from Sigma Aldrich (St. Louis, MO, USA). Ultrapure deionized (DI) water was generated in house from a Barnsted Easypure UV/UF (Dubuque, IA, USA) coupled with activated charcoal and ion exchange resin canisters.

Target compounds were purchased in premixed ampules prepared by Wellington Laboratories, (Guelph, Ontario, Canada, PFCA MXA standard) containing the following compounds: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate, (PFHxS), and perfluorooctane sulfonate (PFOS). For internal standards (IS), the following compounds were purchased from Wellington Laboratories: 1,2-$^{13}C_2$-labeled perfluorohexanoic acid ($^{13}C_2$-PFHxA), 1,2-$^{13}C_2$-labeled perfluoroundecanoic acid ($^{13}C_2$-PFUnDA), and $^{18}O_2$-sodium perfluorohexanesulfonate ($^{18}O_2$-PFHxS). 1,2,3,4,5,6,7,8-$^{13}C_8$-labeled PFOA ($^{13}C_8$-PFOA) solution was purchased from Cambridge Isotope Laboratories, (Andover, MA), and $^{18}O_2$-ammonium perfluorooctane sulfonate ($^{18}O_2$-PFOS) was purchased from Research Triangle Institute (Research Triangle Park, NC). N-methyl perfluorobutane sulfonamidoacetic acid (N-MeFBSAA) was obtained from Jennifer Field's research group at Oregon State University.

QA/QC

Method blanks (1L DI water for water samples and an empty sampling container for sediment samples) were analyzed along with each batch of samples and solvent blanks were injected on the instrument as the first and last samples in the batch. Water samples were analyzed within 48 hours of arrival and sediments were frozen at -80 °C until analysis to ensure minimal loss of compounds of interest. A six point calibration curve for each matrix was created by spiking a set of method blanks and processing them along with the samples. The limit of quantification (LOQ) was defined as the lowest point on the standard curve (10 ng L-1 for water and 0.2 ng g-1 for sediment).

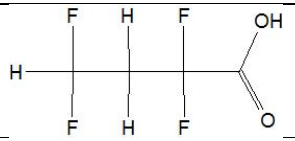
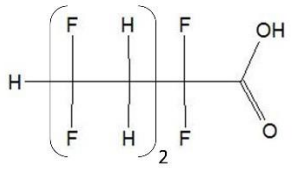
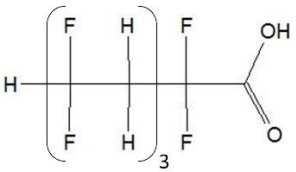
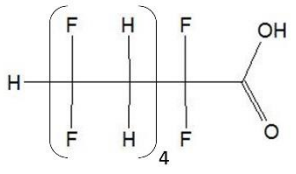
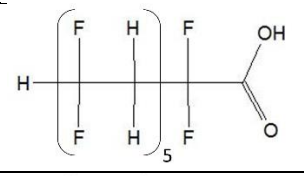
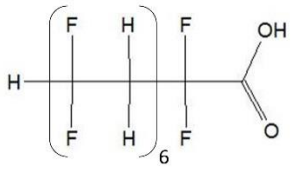
Table S1- Levels of legacy PFASs in water (ng L^{-1}). LOQ = limit of quantification = 10 ng L^{-1} for all compounds.

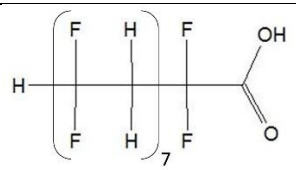
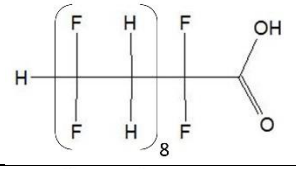
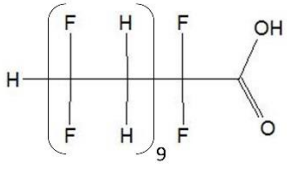
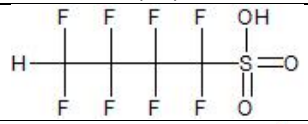
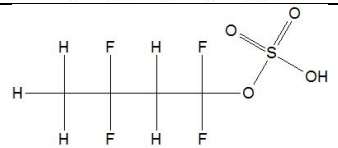
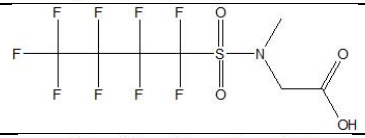
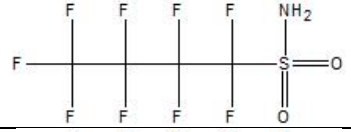
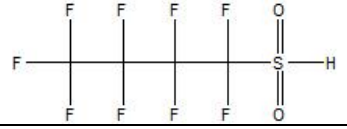
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9
PFBA	14	60	13	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10
PFPeA	<LOQ	23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFBS	36	160	10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHxA	16	93	18	11	11	<LOQ	<LOQ	<LOQ	11
PFHeA	11	44	15	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	11
PFHxS	<LOQ	39	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	21	120	53	<LOQ	11	<LOQ	<LOQ	<LOQ	11
PFNA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOS	33	220	71	<LOQ	15	<LOQ	<LOQ	<LOQ	<LOQ
PFDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Total	132	759	180	11	37	<LOQ	<LOQ	<LOQ	43

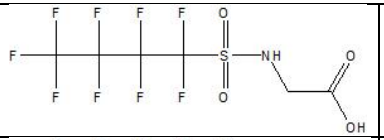
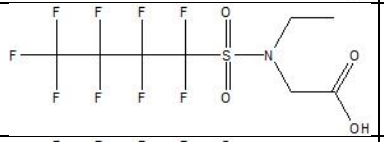
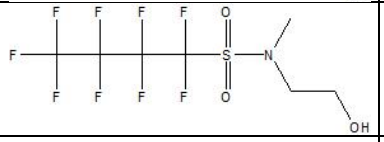
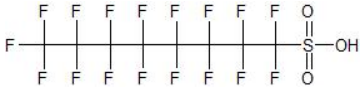
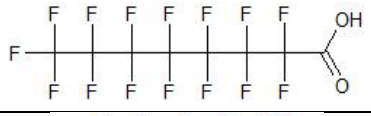
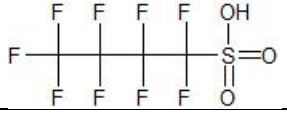
Table S2- Levels of legacy PFASs in sediment (ng g^{-1} dry weight). LOQ = limit of quantification = 2 ng g^{-1} for all compounds. Values shown that are less than the LOQ should be considered estimates.

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9
PFBA	<LOQ	1.4	0.52	0.30	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFPeA	<LOQ	0.39	<LOQ	0.30	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFBS	0.59	0.80	0.20	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHxA	<LOQ	0.64	0.28	1.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHeA	<LOQ	0.95	0.75	1.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHxS	<LOQ	0.99	0.33	0.21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	1.3	9.1	7.3	12	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFNA	<LOQ	<LOQ	<LOQ	0.28	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOS	13	23	32	32	1.7	<LOQ	0.22	<LOQ	1.5
PFDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Total	15	38	41	47	1.7	<LOQ	0.22	<LOQ	1.5

Table S3 - Formulas, observed m/z, ppm error, proposed structure, smiles, Schymanski scale identification level, and selected physical-chemical properties predicted using Episuite™ 4.11

Formula	Observed m/z	ppm error	Possible structure	SMILES	Schymanski Scale Identification Level[1]	Log K_{ow}	Log K_{oc}	Probability for Rapid Biodegra-dation[1]	Log BCF[2]	Biotransfor-mation half life (days)
$C_4H_4F_4O_2$	159.0075	3.65		FC(F)CC(F)(F)C(=O)O	2B	1.35	1.248	0.5601	0.5	0.3064
$C_6H_6F_6O_2$	223.0204	4.62		FC(F)(CC(F)(F)C(=O)O)CC(F)F	2B	2.81	2.138	0.3457	0.5	1.115
$C_8H_8F_8O_2$	287.0329	3.80		FC(F)(CC(F)(F)C(=O)O)CC(F)(F)CC(F)F	2B	4.27	3.028	0.1313	0.5	4.06
$C_{10}H_{10}F_{10}O_2$	351.0453	2.93		FC(F)(CC(F)(F)C(=O)O)CC(F)(F)CC(F)(F)CC(F)F	2B	5.72	3.917	-0.0831	1	14.78
$C_{12}H_{12}F_{12}O_2$	415.0578	2.60		FC(F)(CC(F)(F)C(=O)O)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)F	2B	7.18	4.807	-0.2976	1.75	53.8
$C_{14}H_{14}F_{14}O_2$	479.0700	1.73		FC(F)(CC(F)(F)C(=O)O)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)F	2B	8.64	5.697	-0.512	1	195.9

$C_{16}H_{16}F_{16}O_2$	543.0817	0.15		FC(F)(CC(F)(F)C(=O)O)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)F	2B	10.1	6.587	-0.7264	0.5	713
$C_{18}H_{18}F_{18}O_2$	607.0945	0.71		FC(F)(CC(F)(F)C(=O)O)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)F	2B	11.55	7.477	-0.9408	0.5	2596
$C_{20}H_{20}F_{20}O_2$	671.1066	0.12		FC(F)(CC(F)(F)C(=O)O)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)(F)CC(F)F	2B	13.01	8.367	-1.1552	0.5	9449
$C_7H_2F_{12}O_2$	344.9800	4.44	none proposed	none proposed	4	N/A	N/A	N/A	N/A	N/A
$C_6H_4F_8O_2$	259.0015	3.78	none proposed	none proposed	4	N/A	N/A	N/A	N/A	N/A
$C_4H_2F_8SO_3$	280.9532	4.77		FC(F)(C(F)(F)S(=O)(=O)O)C(F)(F)C(F)F	2B	1.21	2.089	0.1698	0.5	0.1705
$C_4H_6F_4SO_4$	224.9856	4.98		FC(F)(OS(=O)(=O)O)CC(F)(F)C	3	-0.01	2.124	0.272	0.5	0.04537
$C_7H_6F_9NSO_4$ (N-MeFBSAA)	369.9805	2.57		FC(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(C)CC(=O)O	1	3.06	2.119	-0.4287	0.5	3.159
$C_4H_2F_9NSO_2$ (FBSA)	297.9592	2.65		FC(F)(C(F)(F)S(N)(=O)=O)C(F)(F)C(F)(F)F	2B	3.13	2.951	-0.4671	1.729	1.137
$C_4HF_9SO_2$	282.9479	1.38		FC(F)(C(F)(F)S(=O)=O)C(F)(F)C(F)(F)F	2B	2.55	2.791	-0.4599	1.347	0.8247

$C_6H_4F_9NSO_4$ (FBSAA)	355.9644	1.40		FC(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)NCC(O)=O	2B	2.85	2.112	-0.422	0.5	0.2255
$C_8H_8F_9NSO_4$ (N-EtFBSAA)	383.9958	1.59		FC(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CC(O)=O)CC	2B	3.55	2.399	-0.4354	0.5	0.6387
$C_7H_8F_9NSO_3$ (N-MeFBSE)	402.0063[3]	1.24		FC(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(C)CCO	2B	2.83	2.24	-0.336	1.533	1.116
$C_8HF_{17}SO_3$ (PFOS)	498.9307	2.14		FC(F)(C(F)(F)S(=O)(=O)O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	1	4.49	4.855	-1.1901	0.5	9.421
$C_8HF_{15}O_2$ (PFOA)	412.9668	2.32		OC(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	1	4.81	4.419	-1.0009	0.5	26.32
$C_4HF_9SO_3$ (PFBS)	298.9436	3.91		OS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	1	1.82	2.249	-0.3592	0.5	-0.3487

1. Based on Biowin1 (linear model)
2. Fish bioconcentration factor calculated using Episuite's regression based method
3. Observed as a formate adduct

Calculations of adjusted mass defect plots

Mass defect plots can be used to screen for homologous series [2, 3] which are common in fluorinated compound production (e.g., perfluorinated carboxylic acids and sulfonates). Several approaches exist to construct these plots but here we have chosen to make an adjusted mass defect plot as described by Lui et al. [4] based on Kendrick mass defect plots.[5]

To construct the adjusted mass defect plots for a homologous series differing by CF_2CH_2, the measured *m/z* of all compounds are adjusted by the ratio of the nominal to exact mass of CF_2CH_2 (64/64.0124) resulting in what is called the Kendrick Mass:

1) Kendrick Mass = *m/z* * 64/64.0124

The Kendrick mass is then rounded up and the difference is taken between the rounded mass and the Kendrick Mass:

2) Kendrick mass defect = Kendrick mass rounded up to the nearest whole number– Kendrick mass

Next, 1 is added to any Kendrick mass defects that fall below 0.10 as a the rounding may have resulted in splitting a series with Kendrick mass defects close to 1:

3) Adjusted Mass Defect = Kendrick mass defect + 1 if Kendrick mass defect < 0.1

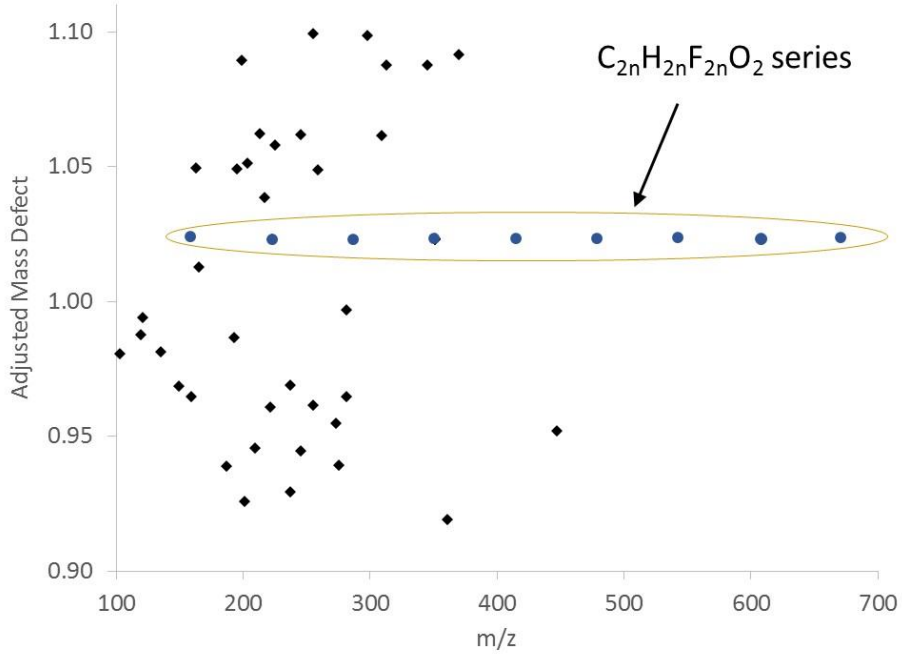


Figure S1 - Adjusted mass defect plot of top 100 features with the $C_{2n}H_{2n}F_{2n}O_2$ carboxylic acid series circled where n = 2-10.

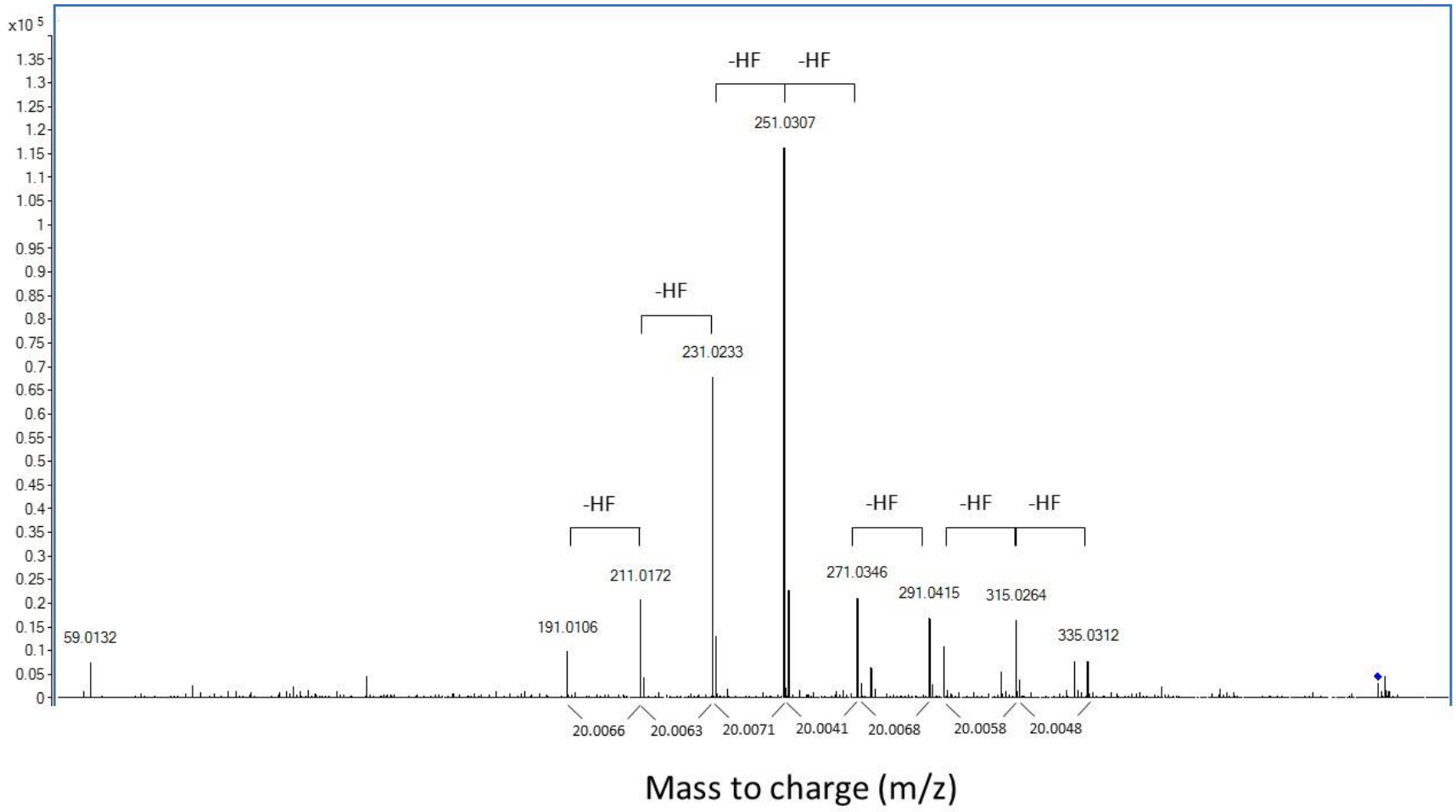


Figure S2 -MS/MS spectrum of $C_{12}H_{12}F_{12}O_2$ (415.0576 m/z) as an example spectrum in the $C_{2n}H_{2n}F_{2n}O_2$ series.

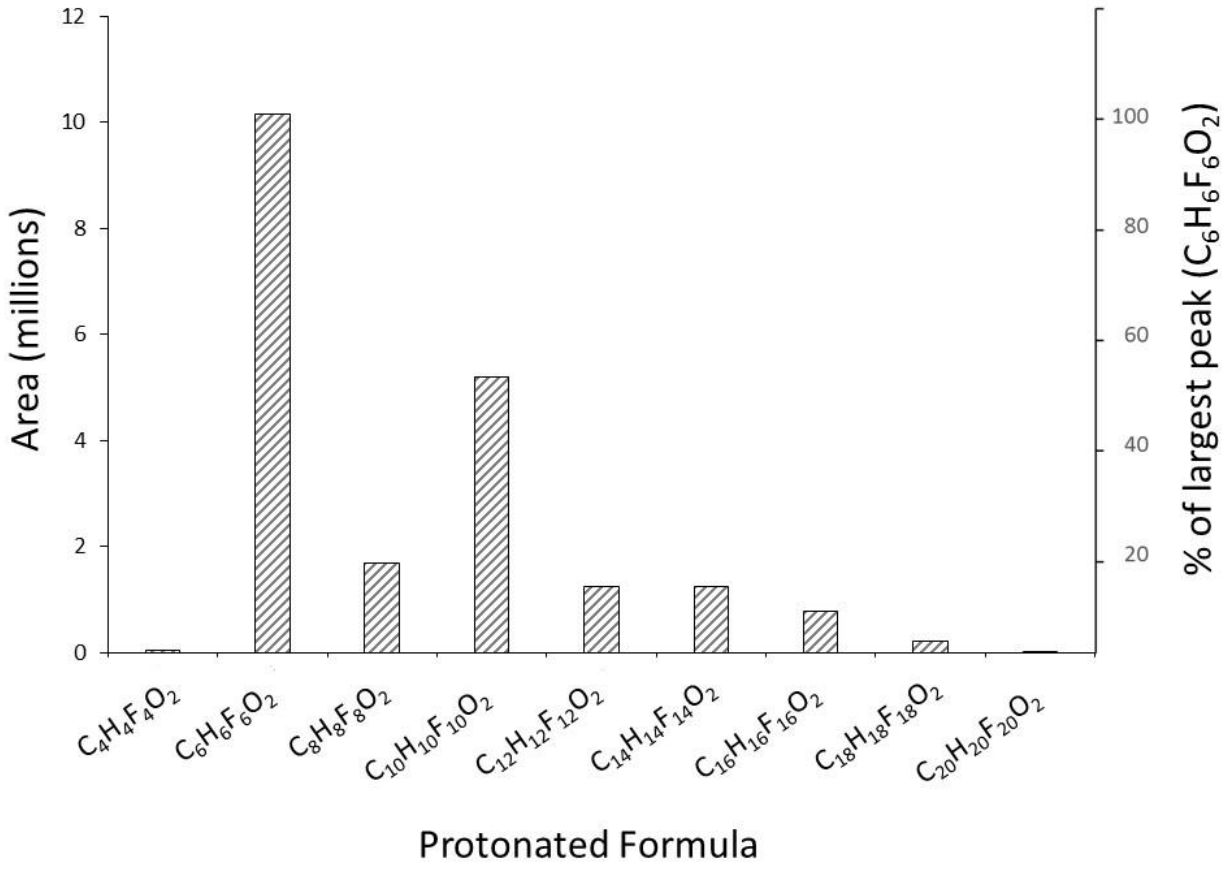


Figure S3 - Total area (sum of all isomers) of different species and their relative percentages in related series at Site 2.

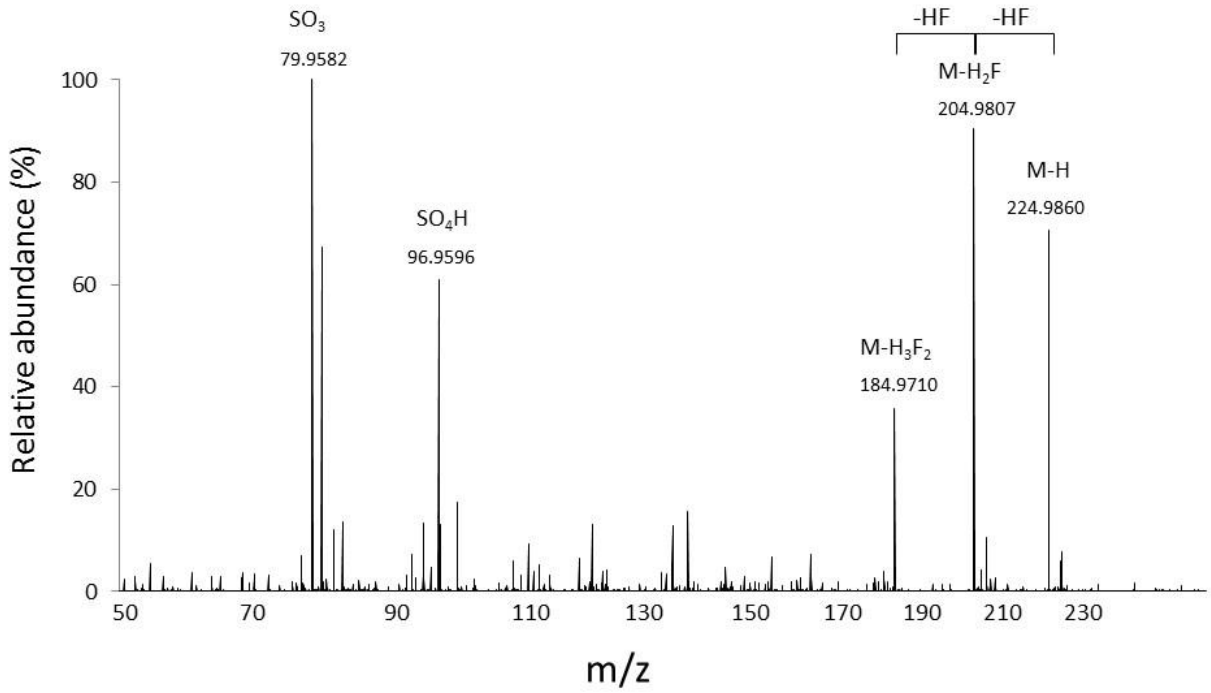


Figure S4 - MS/MS spectrum of the sulfate compound at 224.9860 m/z with formula $C_4H_6F_4SO_4$

Proposed structures for 224.9860 m/z:

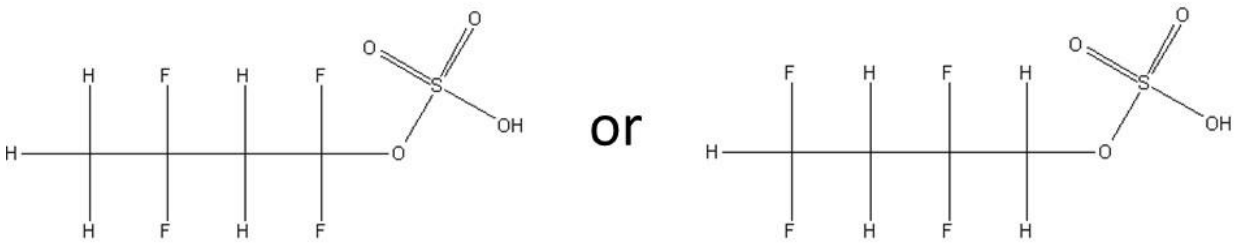


Figure S5 - Two possible structures for the sulfate compound at 224.9860 *m/z* and formula $C_4H_6F_4SO_4$

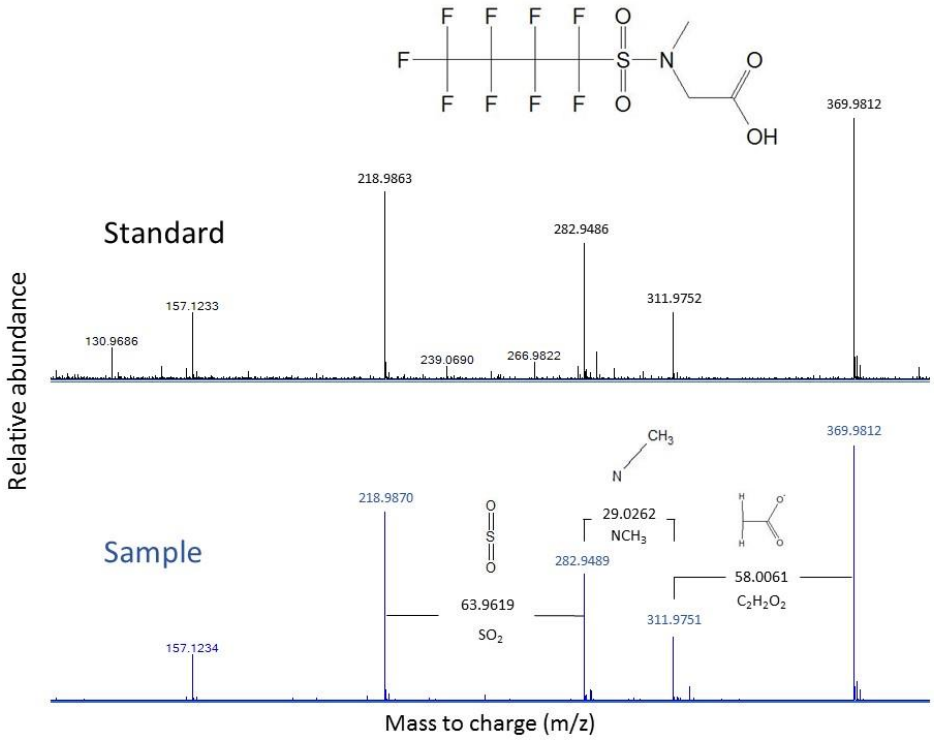
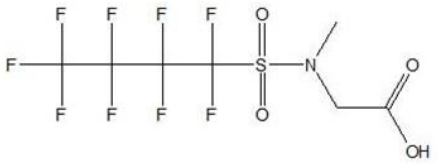
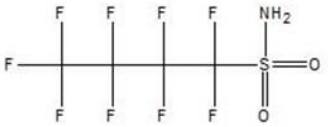


Figure S6 - MS spectra of N-MeFBSAA in the standard (above) and sample (below) with the corresponding structures for the most predominant fragments.



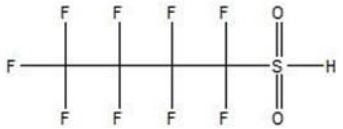
N-methyl perfluorobutane sulfonamidoacetic acid

(MeFBSAA)

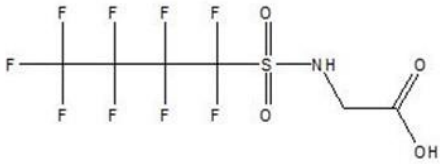


perfluorobutane sulfonamide

(FBSA)

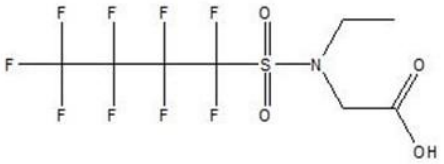


perfluorobutane sulfinic acid



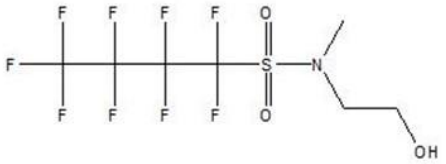
perfluorobutane sulfonamidoacetic acid

(FBSAA)



N-ethyl perfluorobutane sulfonamidoacetic acid

(EtFBSAA)



N-methyl perfluorobutane sulfonamdoethanol

(MeFBSE)

Figure S7 – Structures, names, and abbreviations for perfluorobutane sulfonamides (PBSAs)

SI References

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5. Kendrick, E., A Mass Scale Based on CH2= 14.0000 for High Resolution Mass Spectrometry of Organic Compounds. *Analytical Chemistry* **1963,** *35*, (13), 2146-2154.