Supporting Information

Suspect Screening of Hydrocarbon Surfactants in AFFFs and AFFF-Contaminated Groundwater by High Resolution Mass Spectrometry

García, Raymmah Aleyda[1]; Chiaia-Hernández, Aurea C [2]; Lara-Martin, Pablo A.[3]; Loos, Martin[4]; Hollender, Juliane[5,6]; Oetjen Karl,[7] Higgins Chris[7] and Field, Jennifer[8*]

[1]Department of Chemistry, Oregon State University, Corvallis, Oregon, 97331, United States

[2] Institute of Geography and Oeschger Center for Climate Change Research, University of Bern, Bern, Switzerland

[3] Department of Physical Chemistry, University of Cadiz, Faculty of Marine and Environmental Sciences, Campus Rio San Pedro, CEI-MAR, Puerto Real, 11510, Cadiz, Spain

[4] Loos computing, Zürich, Switzerland

[5]Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

[6]Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zurich, 8092 Zurich, Switzerland

[7]Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, Colorado, 80401, United States

[8]Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, OR, United States:Jennifer.Field@oregonstate.edu

*Corresponding author

Number of Pages: 12

Number of Tables: 3

Number of Figures: 4

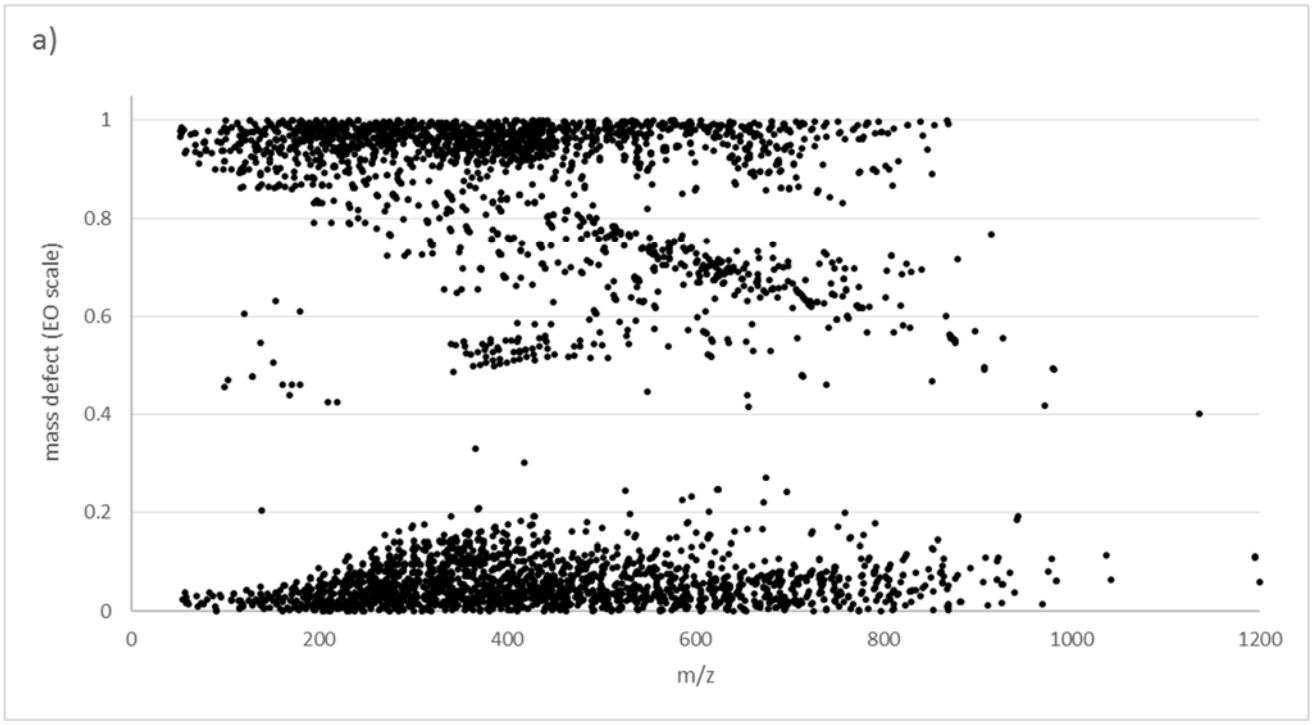
source: https://doi.org/10.7892/boris.131971 | downloaded: 5.12.2023

MATERIALS AND METHODS

Chromatography. Separations were performed on the same liquid chromatography-quadrupole time of flight instrumentation as reported by Barzen-Hanson et al.,[1] and Backe et al. 2013,[2] which consisted of a propylamine guard column placed in line with a silica guard column that retains anions, zwitterions and cations by ion exchange from the 900 □L sample injected. However, during the initial phase of this study, separations were also performed on a Zorbax diol guard column instead of the propylamine guard column. Nonionic surfactants including alcohol ethoxylates and octylphenol polyethoxylates were detected only on the propylamine guard column but not on the diol guard column. Propylamine columns are used primarily for separating carbohydrates and sugars through hydrophilic interactions.[3-5] Oxygen-containing nonionic surfactants were not retained by the diol guard column since it retains analytes by anion exchange.[2] We hypothesize that the non-bonded electrons on the repeating oxygen units are electrostatically attracted to the positive charge on the propylamine Thus, it is essential to use the propylamine guard column to retain the oxygen-containing nonionic surfactants when injecting 900 □L of an organic extract onto the orthogonal chromatographic system. However, if the more common reverse-phase columns are used,[6] retention of nonionic surfactants is also achieved.

Data Processing. Parameters chosen for enviMass were dependent on alkyl [CH_2CH_2; Δm/z 28], ethoxylate [CH_2CH_2O; Δm/z 44], and glucoside [$C_6H_{12}O_5$; Δm/z 162] repeating units. Note that EnviMAss uses nominal masses (e.g., m/z 28, 44, and 162) to search for series. All files were background subtracted. A minimum of three points was needed in order for a series to be considered. Each peak needed to contain at least 10 centroids per peak and peak width could not exceed 120s. Retention time difference between homologues was 120 s for alkyl repeating units and 10-30s for ethoxylate and glucoside repeating units.

Figure S1. Preliminary attempts to search for homologous series in Kendrick Mass Defect Plots normalized to both a) EO and b) alkyl units in groundwater Site G.



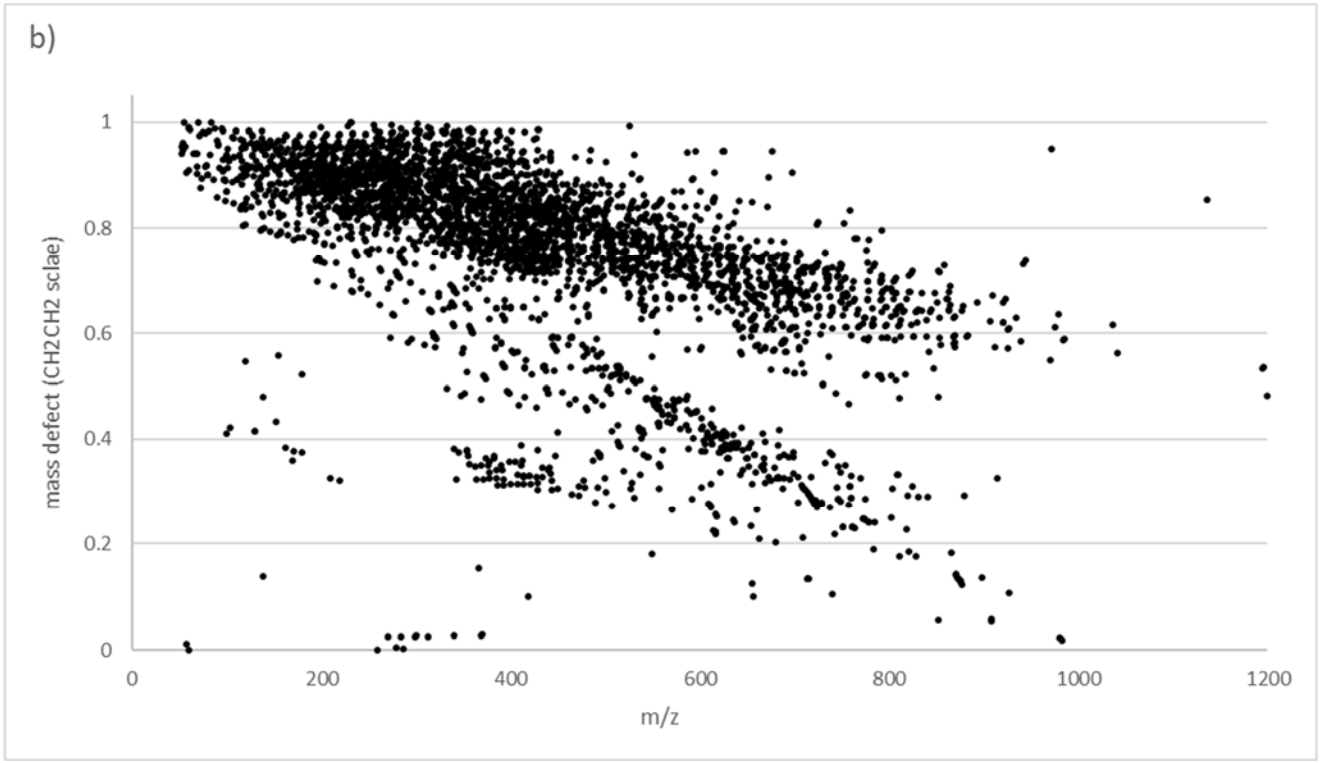


Figure S2. Homologous series of alkyl amine oxides in Reference Material 1 is represented by a nearly vertical line in Figure S1.

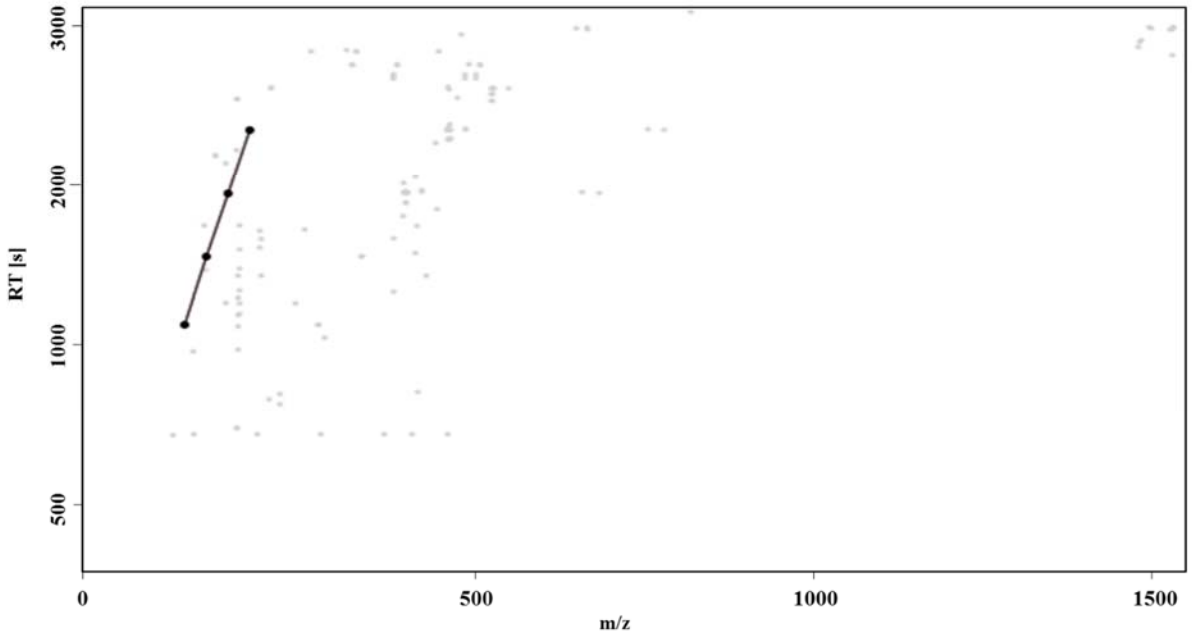


Figure S3. Homologous series of a) repeating alkyl units represented by a nearly vertical line in and b) repeating glucoside units represented by a horizontal line in Reference Material 2, an alkyl polyglucoside. Other homologous series are present in the Reference Material, but where not identified since the main series indicate on the MSDS (dark symbols and line) was successfully identified.

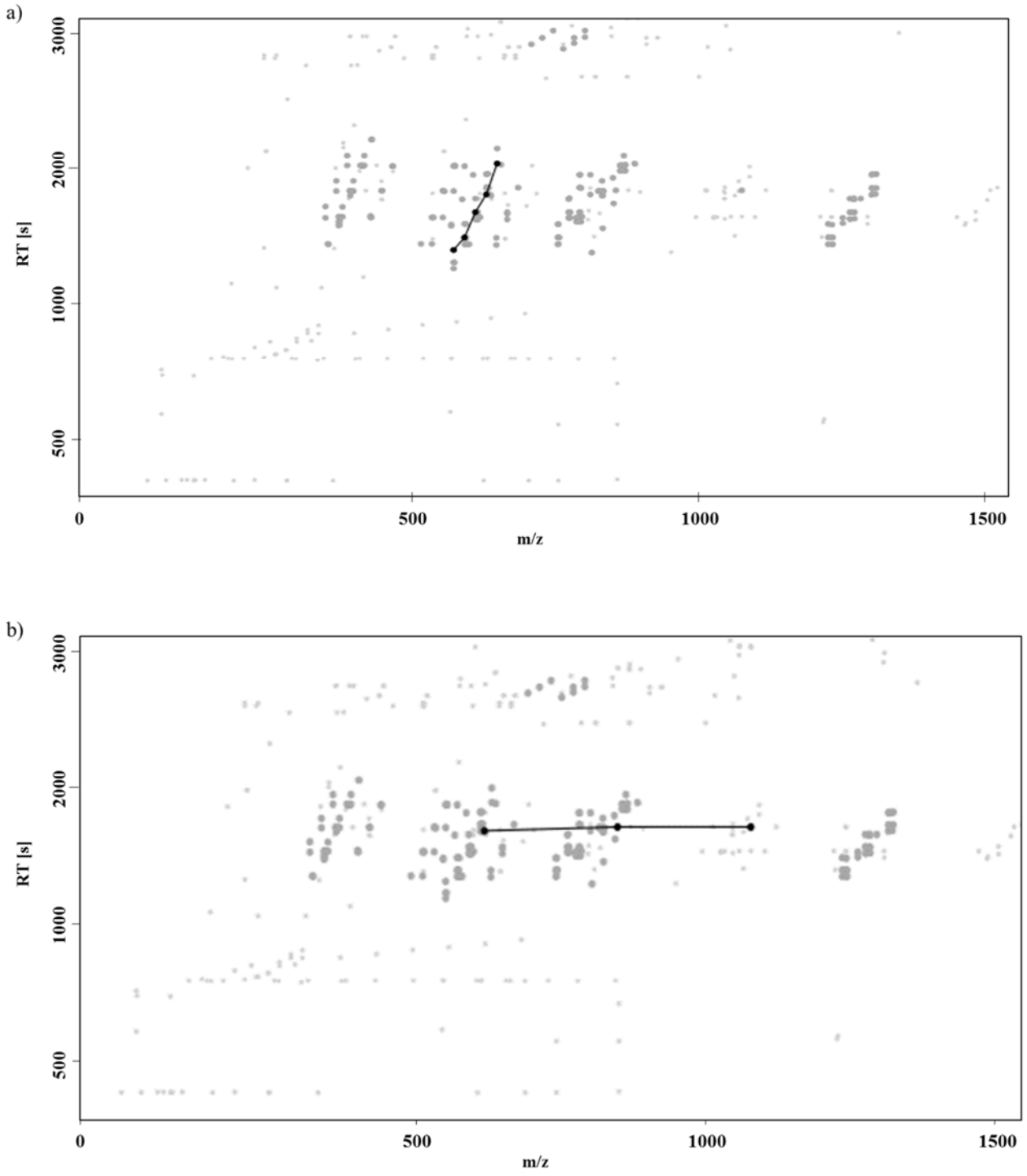


Figure S4. Homologous series in Reference Material 7 (CalFoam ES302) characterized by repeating EO units and a curve. The main homologous series indicated on the MSDS is the series highlighted.

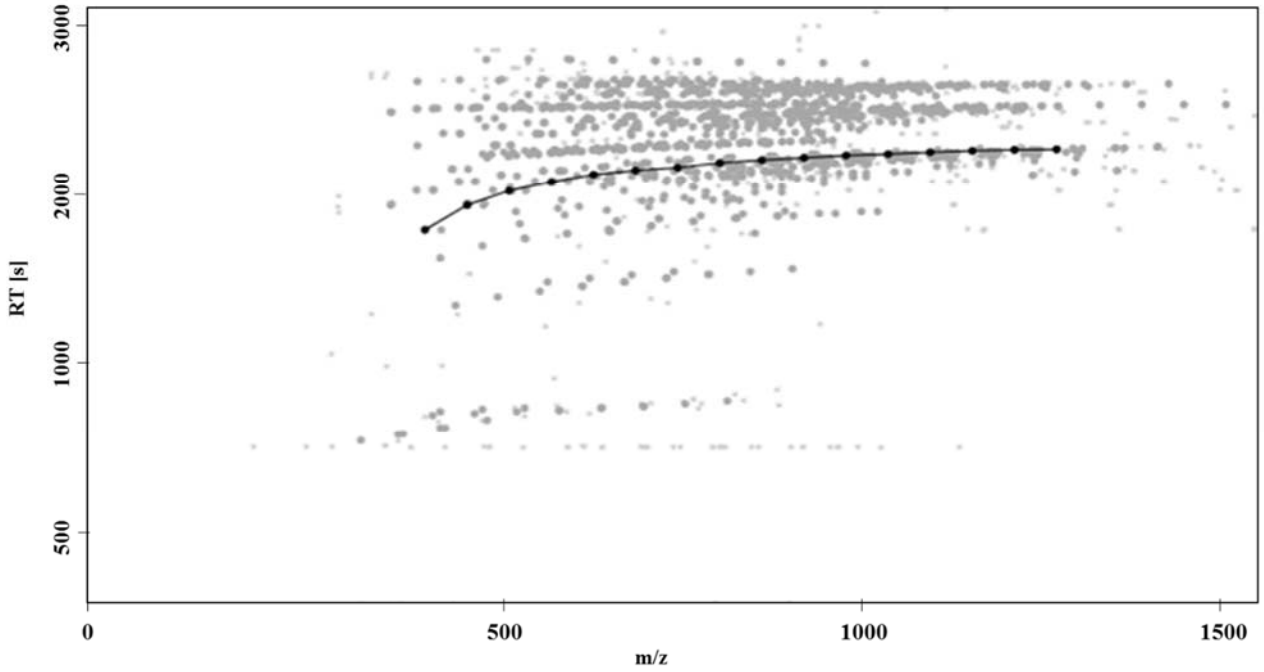
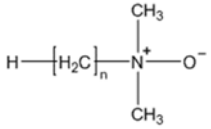
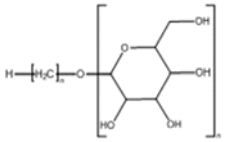
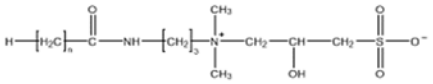
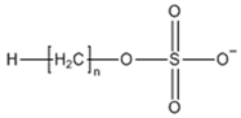
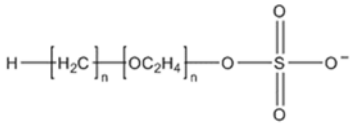


Table S1. Hydrocarbon surfactant classes found in seven reference materials and their respective alkyl (Cn), ethoxylate (EOn), and glucose (GLUCn) repeating units. Multiple repeating units are separated by "/".

Class [repeating unit]	General Structure	Reference Material 1 (Stepan Ammonix Lo)	Reference Material 2 (BASF APG 325 N)	Reference Material 3 (Cola Teric CSB)	Reference Material 4 (Colonial TEALS)	Reference Material 5 (Lubrizol Sulfochem NADS-40)	Reference Material 6 (Colonial SOS)	Reference Material 7 (CalFoam ES-302)
Alkyl amine oxide [C_n]		10,12,14,16	ND	ND	ND	ND	ND	ND
Glucoside [C_n / $GLUC_n$]		ND	9,10,11/1 10/1,2,3 11/2,3,4	ND	ND	ND	ND	ND
Cocamidopropyl hydroxysultaine [C_n]		ND	ND	7,9,11,13,15	ND	ND	ND	ND
Alkyl sulfate [C_n]		ND	ND	ND	12,14,16	8,9,10,11,12	8,9,10,11	ND
Alkyl ether sulfate [C_n/EO_n]		ND	ND	ND	ND	ND	ND	12/1,2,3,4,5,6,7,8, 9,10,11

ND = not detected

Table S2. Hydrocarbon surfactant classes found in AFFF and groundwater and their respective errors (ppm) and confidence levels.

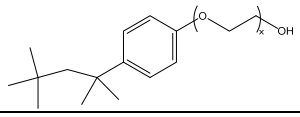
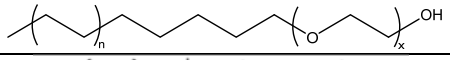
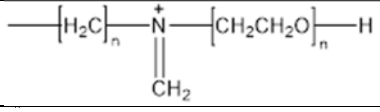
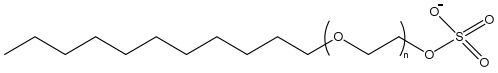
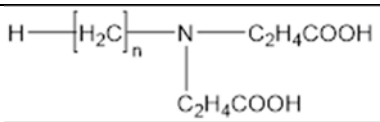
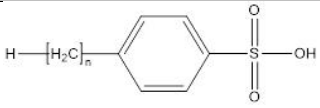
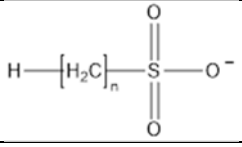
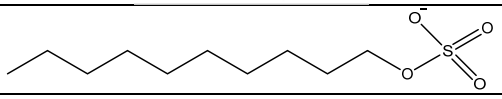
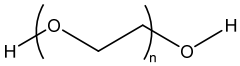
Class	n	Precursor neutral mass	Adduct	observed m/z	Error (ppm)	Confidence Level AFFF	Confidence Level Groundwater
Octylphenol polyethoxylate EOn (+ Mode)	3	338.24516	[M+NH4]+	356.2797	0.6	3	2a
	4	382.27138	[M+NH4]+	400.3054	-0.8	2a	2a
	5	426.29759	[M+NH4]+	444.332	0.1	2b	2a
	6	470.32381	[M+NH4]+	488.3556	-5.3	2a	2a
	7	514.35002	[M+NH4]+	532.3837	-1.4	2a	2a
	8	558.37623	[M+NH4]+	576.4096	-1.7	2a	2a
	9	602.40245	[M+NH4]+	620.4357	-1.8	2a	2a
	10	646.42866	[M+NH4]+	664.4617	-2.0	2a	2a
	11	690.45488	[M+NH4]+	708.4876	-2.4	2a	2a
	12	734.48109	[M+NH4]+	752.5135	-2.6	3	NA
	13	778.50731	[M+NH4]+	796.5399	-2.2	3	NA
	14	822.53352	[M+NH4]+	840.5669	-1.2	3	NA
	15	866.55974	[M+NH4]+	884.5926	-1.7	3	NA
	16	910.58595	[M+NH4]+	928.6182	-2.3	3	NA
	17	954.61217	[M+NH4]+	972.6454	-1.2	3	NA
	18	998.63838	[M+NH4]+	1016.672	-1.2	3	NA
	19	1042.6646	[M+NH4]+	1060.699	-0.4	3	NA
	20	1086.69081	[M+NH4]+	1104.725	-0.6	3	NA
linear alcohol ethoxylate Cn / EOn (+ mode)	C10 EO2	246.22016	[M+NH4]+	264.2351	-1.0	2a	3
	C10 EO3	290.24637	[M+NH4]+	308.2794	-0.4	2a	3
	C10 EO4	334.27259	[M+NH4]+	352.3052	-1.5	2a	3
	C10 EO5	378.2988	[M+NH4]+	396.3313	-1.6	2a	3
	C10 EO6	422.32502	[M+NH4]+	440.3567	-3.4	2a	3
	C10 EO7	466.35123	[M+NH4]+	484.3829	-3.1	2a	3
	C10 EO8	510.37745	[M+NH4]+	528.4086	-3.9	2a	3
	C10 EO9	554.40366	[M+NH4]+	572.4352	-2.8	2a	NA
	C10 EO10	598.42988	[M+NH4]+	616.4607	-3.7	2a	NA
Ethoxylated cocoamine Cn/ EOn (+ mode)	14	301.26169	[M+Na]+	324.2381	-0.8	2a	2a
	15	315.26477	[M+Na]+	338.2529	-3.1	2a	2a
	16	329.28042	[M+Na]+	352.269	-2	2a	2a
	17	343.29607	[M+Na]+	366.2854	-1.6	2a	NA

Class	N	Precursor neutral mass	Adduct	observed m/z	Error (ppm)	Confidence Level AFFF	Confidence Level Groundwater
Alkyl ether sulfate Cn / EOn (- mode)	C12 EO8	618.36504	[M-H]-	617.3582	0.9	2a	NA
	C12 EO9	662.39124	[M-H]-	661.3856	2.6	2a	NA
	C12 EO10	706.41744	[M-H]-	705.4084	-2.3	2a	NA
	C14 EO1	338.21284	[M-H]-	337.2053	-0.3	2a	NA
	C14 EO2	382.23904	[M-H]-	381.2319	0.8	2a	NA
	C14 EO3	426.26524	[M-H]-	425.2576	-0.6	2a	NA
	C15 EO1	352.22844	[M-H]-	351.2185	-7.3	2a	2a
	C15 EO2	396.25456	[M-H]-	395.2446	-6.8	NA	2a
	C15 EO3	440.31379	[M-H]-	439.2732	-0.6	NA	2a
	C15 EO4	484.30714	[M-H]-	483.2998	0.2	NA	2a
	C15 EO5	528.33321	[M-H]-	527.3257	-0.4	NA	2a
	C15 EO6	572.35954	[M-H]-	571.3522	0.0	NA	2a
	C16 EO1	366.23672	[M-H]-	365.2371	1.0	2a	NA
	C16 EO8	674.40813	[M-H]-	673.4206	0.5	NA	2a
	C16 EO9	718.45384	[M-H]-	717.4477	1.8	NA	2a
	C16 EO10	762.47993	[M-H]-	761.4727	0.0	NA	2a
	C17EO1	380.26019	[M-H]-	379.2524	0.0	2a	NA
Alkyl amido dipropionate Cn (+ mode)	4	217.13086	[M+H]+	218.1385	-1.0	2a	2a
	6	245.16022	[M+H]+	246.1699	-0.3	2a	2a
	8	273.19346	[M+H]+	275.2083	-2.9	2a	2a
	10	301.22476	[M+H]+	303.2405	0.4	2a	2a
	12	329.25606	[M+H]+	330.2642	1.0	2a	2a
	13	343.27171	[M+H]+	344.2793	-0.6	2a	NA
	14	357.28736	[M+H]+	358.2951	-0.2	2a	NA

Class	N	Precursor neutral mass	Adduct	observed m/z	Error (ppm)	Confidence Level AFFF	Confidence Level Groundwater
Linear alkyl benzene sulfonate Cn (- mode)	10	298.16081	[M-H]-	297.1528	-0.5	2a	2a
	11	312.17646	[M-H]-	311.1687	0.2	2a	2a
	12	326.19211	[M-H]-	325.1846	0.9	2a	2a
	13	340.20776	[M-H]-	339.1999	0.0	2a	2a
	14	354.22341	[M-H]-	353.2177	6.0	NA	2a
Alkyl sulfates Cn (- mode)	8	210.09313	[M-H]-	209.0854	0.6	1	NA
	9	224.10878	[M-H]-	223.1009	-0.2	1	NA
	10	238.12443	[M-H]-	237.1166	-0.1	1	NA
	12	266.15573	[M-H]-	265.1479	-0.1	1	NA
Polyethylene Glycol EOn (+ mode)	8	370.21973	[M+NH4]+	388.2542	0.1	2a	NA
	9	414.24595	[M+NH4]+	432.2801	-0.5	2a	NA
	10	458.27216	[M+NH4]+	476.3063	-0.6	2a	NA
	11	502.29838	[M+NH4]+	520.3333	1.0	2a	NA
	12	546.32459	[M+NH4]+	564.3595	1.0	2a	NA
	13	590.35081	[M+NH4]+	608.3857	0.8	2a	NA
Alkyl amido betaine Cn (+ mode)	4	245.1860	[M+H]+	246.1938	-0.1	3	2a
	5	259.20162	[M+H]+	260.2077	-6.6	3	2a
	6	273.21727	[M+H]+	274.2273	7.9	3	2a
	7	287.23292	[M+H]+	288.2404	-1.2	2b	2a
Diethanolamine Cn (+ mode)	7	231.18344	[M+H]+	232.1902	-2.1	NA	2a
	9	259.213531	[M+H]+	260.222	1.9	NA	2a
	11	287.24604	[M+H]+	288.2531	-0.7	NA	2a
	13	315.27734	[M+H]+	316.2844	-0.8	NA	2a

NA= Not available indicating the homologous series was not present in either AFFF or groundwater.

Table S3. Summary of surfactants detected in AFFFs and AFFF-impacted groundwater.

Surfactant	Structure	Archived AFFFs	Groundwaters
Octylphenol polyethoxylates		✓	✓
Linear alcohol ethoxylates		✓	✓
Ethoxylated cocoamines		✓	✓
Alkyl ether sulfates		✓	✓
Alkyl amido dipropionates		✓	✓
Linear alkyl benzene sulfonates		✓	✓
Alkyl sulfonates		✓	
Alkyl sulfates		✓	
Polyethylene glycols		✓	
Alkyl amido betaine			✓
Diethanolamines			✓

References

1. Barzen-Hanson, K. A.; Roberts, S. C.; Choyke, S.; Oetjen, K.; McAlees, A.; Riddell, N.; McCrindle, R.; Ferguson, P. L.; Higgins, C. P.; Field, J. A., Discovery of 40 classes of per- and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFF) and AFFF-impacted groundwater. *Environ Sci Technol* **2017,** *51*, (4), 2047-2057.
2. Backe, W. J.; Day, T. C.; Field, J. A., Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from us military bases by nonaqueous large-volume injection HPLC-MS/MS. *Environmental Science and Technology* **2013,** *47*, (10), 5226-5234.
3. Jandera, P., Stationary and mobile phases in hydrophilic interaction chromatography: a review. *Analytica Chimica Acta* **2011,** *692*, (1-2), 1-25.
4. Hao, Z. G.; Xiao, B. M.; Weng, N. D., Impact of column temperature and mobile phase components on selectivity of hydrophilic interaction chromatography (HILIC). *J. Sep. Sci.* **2008,** *31*, (9), 1449-1464.
5. Agilent Technologies, Column Selection Guide for HPLC. In 2012.
6. Ferrer, I.; Thurman, E. M., Analysis of hydraulic fracturing additives by LC/Q-TOF-MS. *Anal Bioanal Chem* **2015,** *407*, (21), 6417-28.