Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

ELECTRONIC SUPPLEMENTRAY INFORMATION FOR:

TITLE: Exploring Matrix Effects and Quantifying Organic Additives in Hydraulic Fracturing Associated Fluids Using Liquid Chromatography Electrospray Ionization Mass Spectrometry

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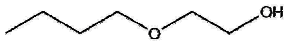
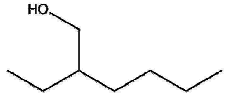
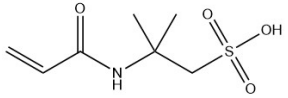
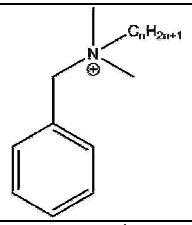
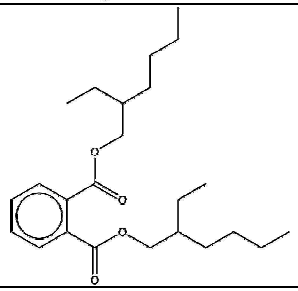
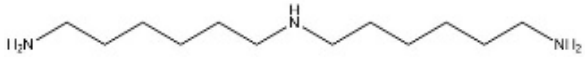
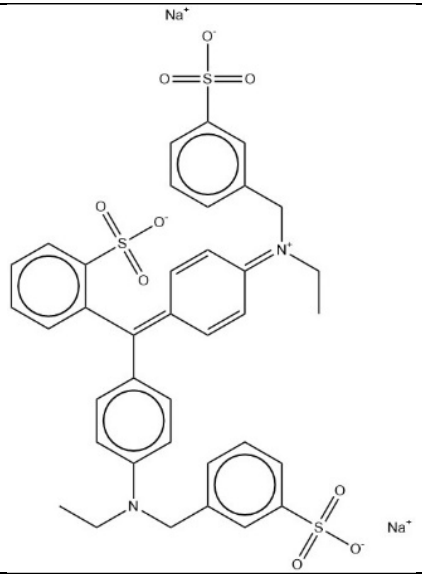
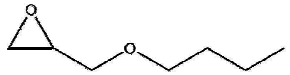
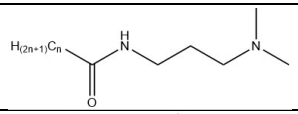
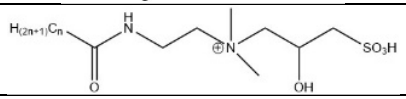
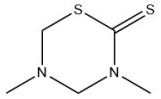
Methods – Standards and Reagents

Table ESI1. Target compounds and justification for inclusion in the study.

Compound Name ***Compound Use***	**CAS Number**	**Chemical Structure**	**Reason for Inclusion**
2-butoxyethanol *surfactant, corrosion inhibitor, and nonemulsifier*	111-76-2		Elevated exposure potential[1]
2-ethyl-1-hexanol *surfactant and nonemulsifier*	104-76-6		Elevated exposure potential[1]
2-acrylamido-2-methylpropanesulfonic acid *possible degradation product*	15214-89-8		Monomer of polymer used in MIP 3H
Alkyl dimethyl benzyl ammonium chloride (ADBAC) *biocide and surfactant*	63449-41-2		Biocidal properties and frequency of use[2]; Amenability to LC-MS[3]
Bis(2-ethylhexyl) phthalate *diverting agent*	117-81-7		Associated with reproductive or developmental toxicity[4]

Bis(hexamethylene) triamine *possible degradation product of scale inhibitor*	143-23-7		Possible product of BMPA, a contaminant with elevated exposure potential[1]
Brilliant Blue FCF *dye tracer and gelling agent*	3844-45-9		Elevated exposure potential[1]
Butyl glycidyl ether *resin*	2426-08-6		Elevated exposure potential[1]
Cocamidopropyl dimethylamine (CAPDMA) *surfactant*	68140-01-2		Amenability to LC-MS[3]
Cocamidopropyl hydroxysultaine (CAPHS) *surfactant*	68139-30-0		Amenability to LC-MS[3]
Dazomet (Thiadiazine) *biocide*	533-74-4		Associated with reproductive or developmental toxicity[5]

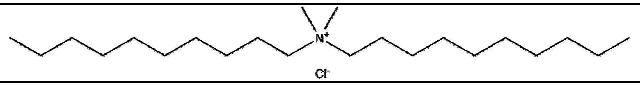
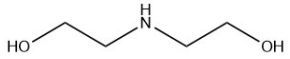
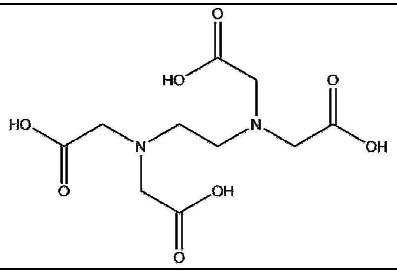
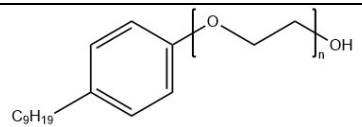
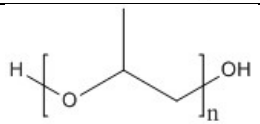
Didecyldimethylammonium chloride *biocide*	7173-51-5		Frequency of use and toxicity[6]
Diethanolamine *surfactant, crosslinker, and breaker*	111-42-2		Mobility and toxicity[6]
Ethylenediaminetetraacetic acid (EDTA) *complexing agent*	60-00-4		Persistence in environment[7]
Glutaraldehyde *biocide*	111-30-8		Most frequently used biocide,[2] disclosed in MIP 3H, Amenability to LC-MS[3]
Nonylphenol Ethoxylates *solvent and surfactant*	9002-93-1 and 127087-87-0		Frequency of use[7]; precursor to nonylphenol
Polyethylene Glycol *solvent and surfactant*	25322-68-3		Amenability to LC-MS[8]
Polypropylene Glycol *solvent and surfactant*	25322-69-4		Amenability to LC-MS[9]

Table ESI2. Information on supplier and purity of individual target compounds.

Compound Name	Supplier	Percent Purity	Other Ingredients in Standard
2-butoxyethanol	Fluka	99.5%	Not listed
2-ethyl-1-hexanol	Fluka	99.5%	Not listed
2-acrylamido-2-methylpropanesulfonic acid	Aldrich	50%	Water
Benzyldimethyldodecyl ammonium chloride (ADBAC-C12)*	Sigma-Aldrich	99%	Not listed
Bis(2-ethylhexyl) phthalate	Fluka	99.7%	Not listed
Bis(hexamethylene) triamine	Aldrich	94%	Not listed
Brilliant Blue FCF	Fluka	97%	Not listed
Butyl glycidyl ether	Aldrich	95%	Not listed
Dazomet (Thiadiazine)	Fluka	99.9%	Not listed
Didecyldimethylammonium chloride	Fluka	88.5%	Not listed
Diethanolamine	Fluka	99.7%	Not listed
Ethylenediaminetetraacetic acid tetra-sodium salt hydrate	Sigma	99%	Not listed
Glutaraldehyde	Sigma	50%	Water

*The pure ADBAC-C12 standard was acquired for use in the ADBAC-C12 calibration curve and was not included in the standard mixture that was used in compound tuning and the matrix recovery experiment.

Table ESI3. Information on supplier and purity of target compounds obtained in mixtures.

Homologous Series Name (Industrial Blend)	Supplier	Percent Purity	# Homologues in Standard (>5% Relative Intensity)	Other Ingredients in Mix
Benzalkonium chloride	Fluka	95%	3	Not listed
Cocoamidopropyl dimethylamine (Schercodine C)	Lubrizol	90-100%	5	Glycerin (1-4.9%), Coconut oil (1-4.9%)
Cocoamidopropyl hydroxysultaine (Chembetaine CAS)	Lubrizol	30-39.9%	6	Water (40-49.9%), Glycerin (1-4.9%), NaCl (5-9.9%)
Polyethylene Glycol (Kollisolv PEG E 400)	Sigma	~98%	11	≤0.1% sulfated ash ≤0.25% ethylene glycol and diethylene glycol (sum) ≤0.5 g acetic acid (per 100 g) ≤1 ppm ethylene oxide ≤1 ppm lead (verified on random samples only) ≤1.0% water ≤10 ppm dioxan ≤15 ppm formaldehyde ≤5 ppm heavy metals (verified on random samples only) ≤620 ppm ethylene glycol
Polypropylene Glycol (P 400)	Aldrich	Not listed	10	Not listed
Nonylphenol Ethoxylates (Nonidet P 40)	Sigma	10%	13	Water
Nonylphenol Ethoxylates (Tergitol NP-40)	Sigma	70%	>15	Water

Methods – Sample Collection

Table ESI4. Description of samples collected from Morgantown, WV.

Sample Description	Sample Date	Date Received	pH (prior to adjustment)	TDS[1]
Hydraulic Fracturing Fluid (HFF) 3H	11/9/15	11/23/15	6.86	398 ppm
Hydraulic Fracturing Fluid (HFF) 5H	11/6/15	11/23/15	6.98	351 ppm
Makeup Water (MW) 3H	11/9/15	11/23/15	7.32	303 ppm
Makeup Water (MW) 5H	11/6/15	11/23/15	7.38	297 ppm
Flowback Water (FW) 3H	12/10/15	12/22/15	7.85	16.1 ppth
Flowback Water (FW) 5H	12/10/15	12/22/15	5.73	65.4 ppth
Produced Water (PW) 3H Week 1	12/17/15	12/22/15	6.97	29.1 ppth
Produced Water (PW) 5H Week 1	12/17/15	12/22/15	6.6	16.5 ppth
Produced Water (PW) 3H Week 2	12/22/15	2/1/16	6.08	30.4 ppth
Produced Water (PW) 5H Week 2	12/22/15	2/1/16	6.72	30.4 ppth
Produced Water (PW) 3H Week 3	1/6/16	2/1/16	7.3	34.0 ppth
Produced Water (PW) 5H Week 3	1/6/16	2/1/16	6.55	27.5 ppth
Produced Water (PW) 3H Week 4	1/20/16	2/1/16	5.93	32.9 ppth
Produced Water (PW) 5H Week 4	1/20/16	2/1/16	6.11	31.2 ppth

[1]ppm = parts per million; ppth = parts per thousand.

Methods – Matrix Recovery Experiment

Table ESI5. Concentration of standards spiked into each sample.

Compound or Homologous Series Names (Standard Used)	Concentration in Samples after Spiking (µg/L)	LOD (in µg/L)
2-acrylamido-2-methylpropanesulfonic acid	125	0.5
2-butoxyethanol	125	0.05
2-ethyl-1-hexanol	250	50
Benzalkonium chloride (ADBAC)	2.5	0.05
Bis(2-ethylhexyl) phthalate	5	0.05
Bis(hexamethylene) triamine	125	50
Brilliant Blue FCF	25	5
Butyl glycidyl ether	250	50
Cocoamidopropyl dimethylamine (CAPDMA, Schercodine C)	1.25	0.05
Cocoamidopropyl hydroxysultaine (CAPHS, Chembetaine CAS)	2.5	0.5
Dazomet (Thiadiazine)	12.5	0.5
Didecyldimethylammonium (Didecycldimethylammonium chloride)	1.25	0.05
Diethanolamine	250	0.5
Ethylenediaminetetraacetic acid (Ethylenediaminetetraacetic acid tetra-sodium salt hydrate)	5	50
Glutaraldehyde	1250	50
Polyethylene Glycol (PEG, Kollisolv PEG E 400)	2.5	0.05
Polypropylene Glycol (PPG, P 400)	2.5	0.05
Nonylphenol Ethoxylates (NPE, Nonidet P 40)	12.5	0.05
Nonylphenol Ethoxylates (NPE, Tergitol NP-40)	25	0.05

Methods – Analytical HPLC-ESI-MS Method

We injected 5 mL samples onto the trap column using a low-pressure loading pump (Dionex Ultimate 3000, Thermo Fisher Scientific) delivering 1 $mL \cdot min^{-1}$ of an isocratic mobile phase and eluted samples from the trap column onto the analytical column using a high-pressure elution pump (Dionex Ultimate 3000, Thermo Fisher Scientific) delivering 0.2 $mL \cdot min^{-1}$ of the same mobile phase.

Table ESI6. Gradient program for large-volume injection (loading pump).

Retention Time (min)	Flow (mL/min)	% LC-MS Grade Water with 0.1% Formic Acid (v/v)	% LC-MS Grade Methanol with 0.1% Formic Acid (v/v)
0.0	1.0	98	2
0.0	1.0	98	2
5.1	1.0	98	2
5.2	0.0	98	2
30.2	0.0	98	2
30.2	1.0	2	98
37.3	1.0	2	98
37.4	1.0	98	2
38.6	1.0	98	2

Table ESI7. Gradient program for chromatographic separation (elution pump).

Retention Time (min)	Flow (mL/min)	% LC-MS Grade Water with 0.1% Formic Acid (v/v)	% LC-MS Grade Methanol with 0.1% Formic Acid (v/v)
0.0	0.2	90	10
0.0	0.2	90	10
5.1	0.2	90	10
9.1	0.2	50	50
22.1	0.2	5	95
30.1	0.2	5	95
30.2	0.2	90	10
38.6	0.2	90	10

Full scan mass spectra (MS) were acquired with an m/z range of 100 to 1000 and data-dependent tandem mass spectra (MS/MS) were acquired at the exact masses of the dominant adducts for all individual compounds and homologues included in our standard mixture.

Table ESI8. Parameters for full scan MS acquisition and data-dependent MS/MS experiments.

Parameter		
Voltage (positive mode/negative mode)		4 kV/-3 kV
Sheath Gas		40
Auxiliary Gas		20
Capillary Temperature		320°C
Source Temperature (Aux Gas Heater Temperature)		50°C
Full Scan MS	Resolution	140,000
	Polarity	Positive and Negative mode, run simultaneously using rapid polarity switching
	AGC Target	5e5
	Maximum IT	250 ms
	Scan Range	100 to 1000 m/z
dd-MS2	Resolution	17,500
	AGC Target	2e5
	Maximum IT	100 ms
	Loop Count	5
	Isolation Window	1.0 m/z
	Dynamic Exclusion	3.0 sec

Results – Analytical Response to HFF Additives

Table ESI9. MS and MS/MS properties of individual compounds and representative homologues. Adducts or ions in **bold** represent the dominant adduct or ion in nanopure water.

Compound Name	Molecular Formula	Adducts or Ions	Exact Mass	Accurate Mass	Error (ppm)	NCE	Fragments	RT	LOD (in µg/L)[2]
2-acrylamido-2-methylpropanesulfonic acid	$C_7H_{13}NO_4S$	**$[M-H]^-$**	206.0482	206.0487	-0.715	45	135.0109	7.5	0.5
2-butoxyethanol	$C_6H_{14}O_2$	$[M+H]^+$ **$[M+Na]^+$**	119.1067 141.0886	119.1068 141.0885	0.840 -0.708	30	57.0707 105.0034	10.7	0.05
2-ethyl-1-hexanol	$C_8H_{18}O$	$[M-H_2O+H]^+$ **$[M+CH_3OH+H]^+$**	113.1325 163.1693	113.1325 163.1692	0.000 -0.613	NA[1]	NA[1]	16.0	50
Benzyldimethyldodecyl ammonium (ADBAC-C_{12})	$C_{21}H_{28}N^+$	**$[M]^+$**	304.2999	304.3000	0.274	45	212.2372 91.0544 58.0659	18.0	0.05[3]
Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	**$[M+H]^+$** $[M+Na]^+$ $[2M+Na]^+$	391.2843 413.2662 803.5432	391.2842 413.2661 803.5936	-0.836 -1.091 -1.430	45	149.0230 72.0861 57.0707	24.0	0.05
Bis(hexamethylene) triamine	$C_{12}H_{29}N_3$	**$[M+H]^+$**	216.2429	216.2431	-1.501	45	100.112 83.0858 55.0549 182.1900 199.2167	6.05	50
Brilliant Blue FCF	$C_{37}H_{34}N_2Na_2O_9S_3$	$[M+H]^+$ $[M+Na]^+$ $[M+2Na]^{2+}$ **$[M-2Na+3H]^+$** $[M-Na+2H]^+$	793.1295 815.1114 419.0500 749.1656 771.1475	793.1290 815.1127 419.0507 749.1667 771.1486	1.221 1.594 0.378	45	247.9730 215.9829 527.1382 541.1540	11.1	5
Butyl glycidyl ether	$C_7H_{14}O_2$	$[M+H]^+$ **$[M+Na]^+$**	131.1067 153.0886	131.1070 153.0880	-0.106 -0.141	45	138.9540 120.9430	11.6	50
CAPDMA-$C_{11}H_{23}$	$C_{17}H_{36}O_2N_2$	**$[M+H]^+$**	285.2900	285.2900	0.209	60	240.2320	17.2	0.05[3]
CAPHS-$C_{11}H_{23}$	$C_{20}H_{43}N_2O_5S^+$	**$[M]^+$**	423.2890	423.2880	0.592	30	240.2320	18.2	0.5[3]

Dazomet (Thiadiazine)	$C_5H_{10}N_2S_2$	**$[M+H]^+$**	163.0353	163.0357	-0.652	30	119.9940 90.0375	8.7	0.5
Didecyldimethylammonium	$C_{22}H_{48}N$	**$[M]^+$**	326.3781	326.3773	-2.381	45	186.2210 57.0706	20.3	0.05
Diethanolamine	$C_4H_{11}NO_2$	**$[M+H]^+$**	106.0863	106.0862	1.554	NA[1]	NA[1]	6.2	0.5
Ethylenediaminetetraacetic acid (EDTA)	$C_{10}H_{16}N_2O_8$	**$[M+H]^+$** $[M+Na]^+$ $[M-H]^-$	293.0979 315.079 291.0834	293.0981 315.0800 291.0846	0.138 0.109 1.451	30	160.0606 132.0657 114.0551 56.0503	6.3	50
Glutaraldehyde	$C_5H_8O_2$	$[M+H]^+$ $[M+Na]^+$ **$[M+CH_3OH+Na]^+$**	101.0597 123.0416 155.0679	101.0598 123.0416 155.0678	0.104 -0.081 -0.115	45	NA[1]	8.1	50
PEG-EO9	$C_{18}H_{38}O_{10}$	$[M+H]^+$ **$[M+Na]^+$**	415.2532 437.2352	415.2541 437.2361	0.762 0.896	30	89.0599 133.0858	9.6	0.05[3]
PPG-PO8	$C_{24}H_{50}O_9$	**$[M+H]^+$** $[M+Na]^+$	483.3528 505.3347	483.3532 505.3348	0.870 0.269	30	58.0499 117.091	15.4	0.05[3]
NPE-EO7	$C_{29}H_{52}O_8$	**$[M+H]^+$** $[M+Na]^+$	529.3735 551.3554	529.3740 551.3570	0.878 0.944	30	89.0900 133.0859 71.0861 121.0647	21.3	0.05[3]
NPE-E037	$C_{89}H_{172}O_{38}$	**$[M+3H]^{3+}$**	617.3915	617.3919	0.670	15	89.0599 133.0858 177.1120	21.2	0.05[3]

[1]Parent compound is too small for detection of fragments.

[2]LODs were determined as the lowest point in the external calibration curve with at least five MS scans measured across the chromatographic peak and the most intense MS/MS fragment still detected.

[3]LOD for all homologous series is based on total concentration of all homologues in the mixture.

Results – Matrix Recovery Experiment

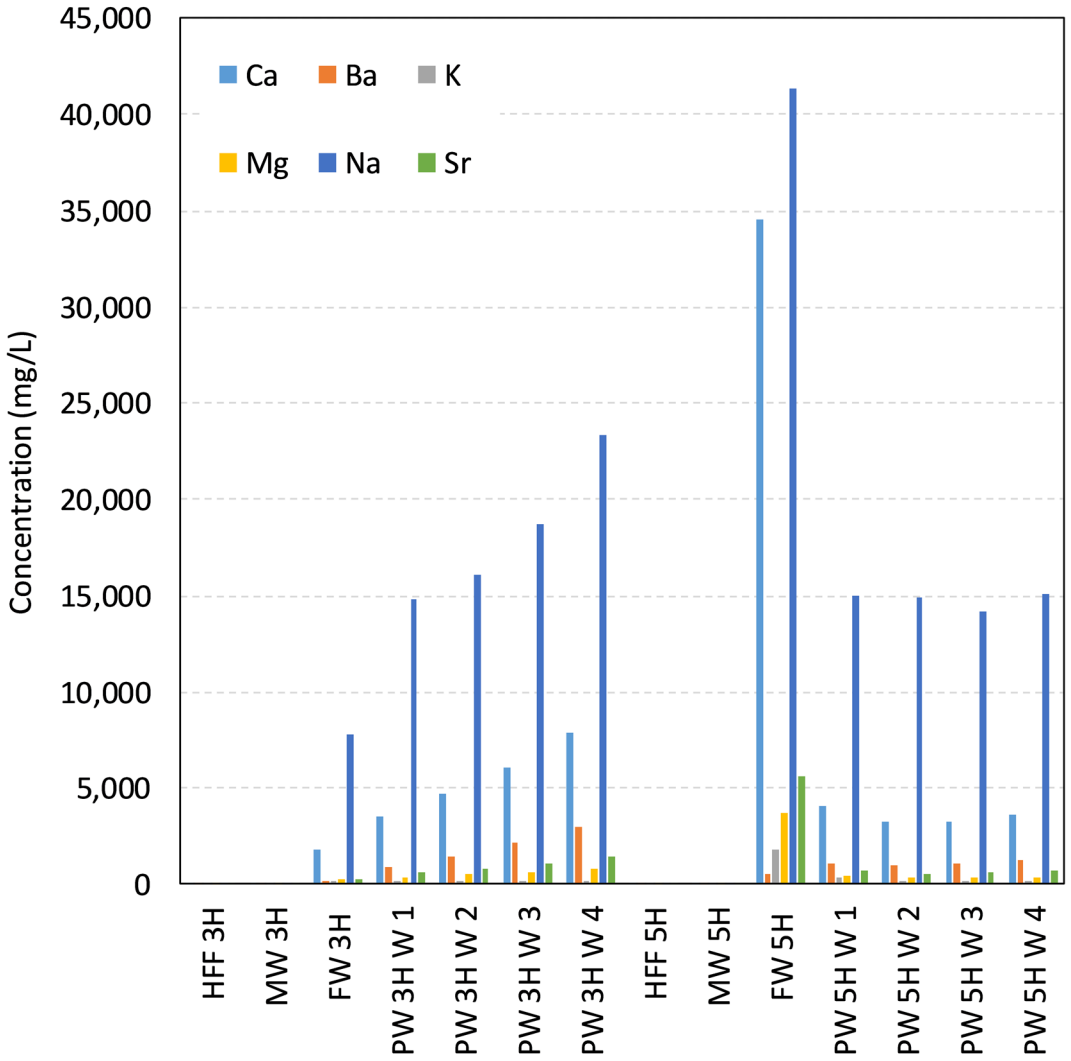


Figure ES1. Inorganic content of samples determined by means of inductively coupled plasma-optical emission mass spectrometry.

Table ESI10.MRFs calculated for each target analyte. MW is makeup water; HFF is hydraulic fracturing fluid; FW is flowback water; PW is produced water. Negative values occasionally occurred when the native concentration of a spiked compound was significantly higher than the amount included in the spike. These values could not be utilized in quantification.

Component Name	Adduct or Ion	MW 3H	MW 5H	FW 3H	FW 5H	HFF 3H	HFF 5H	PW 3H W1	PW 3H W2	PW 3H W3	PW 3H W4	PW 5H W1	PW 5H W2	PW 5H W3	PW 5H W4
2-acrylamido-2-methlypropanesulfonic acid	M-H	0.96	0.96	0.13	0.39	0.81	0.86	0.66	0.59	0.63	0.59	0.72	0.64	0.65	0.65
2-butoxyethanol	M+H	0.90	0.76	0.56	1.14	1.17	0.89	0.95	0.86	0.72	0.75	0.88	0.81	0.73	0.73
2-butoxyethanol	M+Na	0.67	0.72	0.85	0.32	0.28	0.51	1.44	1.69	1.35	1.34	1.09	1.33	1.28	1.38
2-ethyl-1-hexanol	M+MeOH	0.92	0.93	0.90	0.59	1.17	1.23	0.87	0.81	0.76	0.77	0.76	0.70	0.62	0.73
2-ethyl-1-hexanol	M-H2O+H	0.94	0.92	0.85	0.43	0.96	1.05	0.97	0.81	0.84	0.86	0.91	0.83	0.84	0.79
ADBAC-C12	M+	0.89	0.66	0.72	0.86	1.65	1.49	0.87	1.04	0.96	0.98	0.89	0.96	0.84	0.86
Bis-2-ethylhexyl phthalate	M+H	0.95	0.86	0.84	0.88	1.31	1.19	0.83	0.52	0.49	0.50	0.44	0.58	0.45	0.55
Bis-2-ethyl-hexyl phthalate	M+Na	1.00	0.92	1.04	0.56	0.34	0.38	2.51	2.84	1.80	2.08	1.77	2.12	2.12	2.33
Brilliant Blue FCF	M+2Na+3H	0.12	0.16	0.09	0.01	0.21	0.26	0.16	0.05	0.04	0.00	0.00	0.04	0.05	0.00
Butyl glycidyl ether	M+H	0.95	0.94	0.86	0.55	1.01	1.08	0.61	0.67	0.74	0.66	0.79	0.56	0.64	0.61
Butyl glycidyl ether	M+Na	0.84	0.85	0.98	0.61	0.24	0.43	1.32	1.99	1.66	1.67	1.57	0.96	1.30	1.30
CAPDMA-C7H15	M+H	0.95	0.99	0.74	0.43	1.03	1.02	0.62	0.84	0.79	0.84	0.78	0.63	0.67	0.73
CAPDMA-C9H19	M+H	0.98	0.96	0.98	0.38	1.09	1.10	1.00	1.11	1.05	1.03	1.01	1.00	0.99	1.01
CAPDMA-C11H23	M+H	1.06	0.99	1.16	1.23	0.99	1.30	1.17	1.26	1.35	1.38	1.27	1.28	1.22	1.31
CAPDMA-C11H23	M+Na	1.25	1.47	2.97	0.00	1.77	4.35	0.43	1.18	0.58	0.49	0.51	0.63	0.79	0.89
CAPDMA-C13H27	M+H	0.81	0.59	0.68	0.78	0.57	0.68	1.00	1.11	0.95	0.96	0.99	0.98	0.78	0.76
CAPHS-C7H15	M+	0.94	0.91	0.71	0.41	1.20	1.20	0.42	0.39	0.38	0.37	0.40	0.43	0.38	0.41
CAPHS-C9H19	M+	0.94	0.97	0.74	0.45	1.29	1.30	0.48	0.46	0.43	0.43	0.50	0.48	0.45	0.45
CAPHS-C11H23	M+	0.91	0.88	0.76	0.51	1.13	1.36	0.45	0.46	0.46	0.49	0.56	0.52	0.46	0.46
CAPHS-C13H27	M+	0.75	0.64	0.51	0.35	0.89	1.29	0.35	0.38	0.35	0.34	0.35	0.38	0.30	0.32
CAPHS-C15H31	M+	0.46	0.38	0.19	0.13	0.41	0.58	0.23	0.19	0.15	0.15	0.23	0.13	0.10	0.09
Dazomet	M+H	0.24	0.09	0.04	0.00	0.01	0.00	0.30	0.05	-0.02	0.01	0.01	0.02	0.00	0.01
Didecyldimethylammonium	M+	0.46	0.29	0.25	0.21	0.27	0.18	0.60	0.39	0.29	0.21	0.44	0.19	0.19	0.20
Diethanolamine	M+H	0.97	0.95	0.20	0.06	1.01	0.94	0.16	0.14	0.15	0.14	0.17	0.15	0.15	0.16
Diethanolamine	M+Na	1.66	1.55	0.13	0.00	0.16	0.87	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Glutaraldehyde	M+H	0.91	0.80	0.49	-0.27	0.59	0.87	0.38	0.00	0.43	0.51	0.00	0.41	0.44	0.46
Glutaraldehyde	M+Na	0.73	0.88	0.49	0.99	0.19	0.48	2.58	2.62	2.44	2.56	2.34	2.13	2.29	2.25
Glutaraldehyde	4M+H2O+Na	0.66	0.65	0.24	0.02	0.40	0.58	0.23	0.20	0.15	0.12	0.16	0.22	0.19	0.21
NPE-EO5	M+H	0.69	0.58	0.46	0.38	1.10	1.62	0.47	0.35	0.38	0.33	0.34	0.38	0.34	0.32
NPE-EO5	M+Na	0.70	0.65	0.69	0.71	0.43	0.62	1.30	1.27	1.22	1.18	1.09	1.27	1.21	1.11
NPE-EO6	M+H	0.69	0.56	0.42	0.35	1.21	1.81	0.44	0.31	0.34	0.29	0.31	0.34	0.32	0.28
NPE-EO6	M+Na	0.66	0.60	0.62	0.63	0.45	0.71	1.24	1.06	1.05	0.99	0.90	1.08	1.02	0.92
NPE-EO7	M+H	0.69	0.55	0.42	0.34	1.30	1.92	0.45	0.29	0.33	0.27	0.29	0.34	0.30	0.27
NPE-EO7	M+Na	0.63	0.56	0.53	0.47	0.38	0.67	1.30	0.94	0.95	0.86	0.82	0.97	0.95	0.85
NPE-EO8	M+H	0.70	0.54	0.42	0.31	1.24	1.90	0.45	0.28	0.30	0.25	0.27	0.31	0.29	0.26
NPE-EO8	M+Na	0.63	0.53	0.49	0.39	0.37	0.67	1.27	0.81	0.82	0.73	0.69	0.82	0.80	0.72

NPE-EO9	M+H	0.71	0.54	0.41	0.29	1.20	1.93	0.44	0.26	0.28	0.24	0.26	0.30	0.27	0.24
NPE-EO9	M+Na	0.64	0.53	0.48	0.33	0.40	0.72	1.19	0.73	0.69	0.62	0.57	0.66	0.68	0.60
NPE-EO10	M+H	0.72	0.54	0.40	0.27	1.12	1.83	0.44	0.27	0.27	0.24	0.25	0.28	0.27	0.25
NPE-EO10	M+Na	0.65	0.54	0.47	0.31	0.40	0.75	1.10	0.66	0.60	0.54	0.47	0.57	0.58	0.52
NPE-EO37	M+2H	0.88	0.67	0.54	0.25	1.00	1.39	0.57	0.36	0.38	0.34	0.36	0.29	0.38	0.34
NPE-EO37	M+2Na	0.59	1.87	0.00	0.00	0.35	0.00	ND	ND	ND	ND	ND	ND	ND	ND
PEG-EO8	M+H	0.86	0.89	0.58	1.18	0.80	0.96	0.50	0.42	0.66	0.52	0.70	0.58	0.60	0.58
PEG-EO8	M+Na	0.61	0.74	0.38	0.50	0.28	0.51	1.49	1.16	1.32	1.06	1.35	1.65	1.39	1.48
PEG-EO9	M+H	0.89	0.87	0.63	0.65	0.79	0.93	0.51	0.52	0.65	0.53	0.67	0.60	0.65	0.61
PEG-EO9	M+Na	0.67	0.74	0.44	-0.06	0.27	0.49	1.36	1.39	1.25	1.12	1.28	1.51	1.42	1.40
PEG-EO10	M+H	0.88	0.88	0.56	0.66	0.83	0.86	0.73	0.52	0.74	0.63	0.76	0.64	0.63	0.73
PEG-EO10	M+Na	0.67	0.75	0.37	-0.23	0.28	0.45	2.05	1.62	1.64	1.53	1.62	1.74	1.51	1.85
PEG-EO11	M+H	0.88	0.84	0.58	0.54	0.88	0.96	0.68	0.50	0.70	0.63	0.75	0.67	0.69	0.76
PEG-EO11	M+Na	0.62	0.68	0.34	-0.37	0.28	0.48	1.88	1.53	1.72	1.61	1.69	1.89	1.71	1.94
PEG-EO12	M+H	0.84	0.83	0.65	0.78	0.86	0.87	0.58	0.43	0.67	0.63	0.56	0.70	0.66	0.73
PEG-EO12	M+Na	0.61	0.68	0.40	-0.20	0.28	0.45	1.49	1.32	1.46	1.45	1.27	1.66	1.59	1.75
PPG-PO4	M+H	0.73	0.76	0.71	15.28	1.17	1.08	0.27	0.45	0.36	0.53	-0.19	0.07	0.46	0.31
PPG-PO4	M+Na	0.61	0.66	-0.75	-2.22	0.37	0.55	0.68	1.36	0.52	1.62	-0.45	0.93	1.11	1.00
PPG-PO5	M+H	0.88	0.90	0.30	1.88	1.44	1.25	0.57	0.49	0.62	0.65	0.53	0.45	0.57	0.59
PPG-PO5	M+Na	0.79	0.81	0.22	-0.52	0.45	0.58	1.24	1.44	1.17	1.40	0.76	1.05	1.15	1.25
PPG-PO6	M+H	0.90	0.91	0.46	0.55	1.47	1.41	0.70	0.58	0.78	0.78	0.73	0.74	0.74	0.76
PPG-PO6	M+Na	0.83	0.85	0.76	0.30	0.33	0.55	1.57	1.68	1.24	1.37	0.59	1.29	1.29	1.38
PPG-PO7	M+H	0.91	0.91	0.72	0.64	1.49	1.42	0.73	0.59	0.86	0.78	1.00	0.88	0.86	0.82
PPG-PO7	M+Na	0.82	0.86	1.12	0.54	0.30	0.49	1.66	1.63	1.42	1.31	1.35	1.48	1.45	1.42
PPG-PO8	M+H	0.93	0.99	0.72	0.82	1.59	1.49	0.73	0.59	0.87	0.85	1.03	0.90	0.82	0.81
PPG-PO8	M+Na	0.81	0.91	1.06	0.54	0.26	0.41	1.58	1.55	1.29	1.34	1.30	1.34	1.23	1.25
PPG-PO9	M+H	0.96	0.98	0.94	1.03	1.60	1.62	0.81	0.63	0.84	0.84	0.96	0.98	0.88	0.88
PPG-PO9	M+Na	0.86	0.89	1.27	0.56	0.23	0.39	1.70	1.65	1.29	1.35	1.19	1.41	1.32	1.38
PPG-PO10	M+H	0.93	0.94	0.93	1.32	1.65	1.91	0.87	0.71	1.02	0.87	1.14	1.10	0.97	1.05
PPG-PO10	M+Na	0.81	0.86	1.25	0.72	0.27	0.46	1.92	1.93	1.68	1.55	1.63	1.70	1.52	1.80

Results – Qualitative evaluation of chemical additives in water samples

Table ESI11. FracFocus disclosure for well MIP 3H – Basic Information.

Job Start Date:	11/6/2015
Job End Date:	11/15/2015
State:	West Virginia
County:	Monongalia
API Number:	47-061-01707-00-00
Operator Name:	Northeast Natural Energy LLC
Well Name and Number:	MIP 3H
Longitude:	-79.97612300
Latitude:	39.60178300
Datum:	NAD83
Federal/Tribal Well:	NO
True Vertical Depth:	7,483
Total Base Water Volume (gal):	10,647,966
Total Base Non Water Volume:	0

Table ESI12. FracFocus disclosure for well MIP 3H. Proppant Transport, Supplier – Schlumberger, Purpose - Corrosion Inhibitor, Scale Inhibitor, Biocide, AntiFoam Agent, Acid, Breaker, Gelling Agent, Friction Reducer, Iron Control Agent, Fluid Loss Additive.

Ingredients	CAS #	Max Conc in Additive (% by mass)	Max Conc in HF Fluid (% by mass)
Water (Including Mix Water Supplied by Client)*	NA		87.63568%
Quartz, Crystalline silica	14808-60-7	99.06784	12.21724%
Hydrochloric acid	7647-01-0	0.66726	0.08228%
Ammonium sulfate	7783-20-2	0.06845	0.00844%
Guar gum	9000-30-0	0.05865	0.00724%
Acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, sodium salt polymer	38193-60-1	0.05052	0.00623%
Glutaraldehyde	111-30-8		0.00349%
Ethanol, 2,2',2''-nitrilotris-,1,1',1''-tris(dihydrogen phosphate), sodium salt	68171-29-9		0.00120%
Diammonium peroxidisulphate	7727-54-0	0.00601	0.00074%
Polymer of 2-acrylamido-2-methylpropanesulfonic acid sodium salt and methyl acrylate	136793-29-8	0.00541	0.00067%
Alkyl(c12-16) dimethylbenzyl ammonium chloride	68424-85-1	0.00506	0.00062%
Sodium erythorbate	6381-77-7	0.00436	0.00054%
Trisodium ortho phosphate	7601-54-9	0.00427	0.00053%
Urea	57-13-6	0.00332	0.00041%
Polypropylene glycol	25322-69-4	0.00294	0.00036%
Methanol	67-56-1	0.00252	0.00031%
Fatty acids, tall-oil	61790-12-3	0.00156	0.00019%
Thiourea, polymer with formaldehyde and 1- phenylethanone	68527-49-1	0.00129	0.00016%
Ethylene Glycol	107-21-1	0.00121	0.00015%
Non-crystalline silica (impurity)	7631-86-9	0.00084	0.00010%
Vinylidene chloride/methylacrylate copolymer	25038-72-6	0.0008	0.00010%
Sodium sulfate	7757-82-6	0.00078	0.00010%

Alcohols, C14-15, ethoxylated (7EO)	68951-67-7	0.00061	0.00008%
Ethanol	64-17-5	0.00061	0.00007%
Propargyl alcohol	107-19-7	0.00041	0.00005%
2-Propenamid (impurity)	79-06-1	0.00017	0.00002%
Hexadec-1-ene	629-73-2	0.00014	0.00002%
1-Octadecene (C18)	112-88-9	0.00007	0.00001%
Dimethyl siloxanes and silicones	63148-62-9	0.00005	0.00001%
Tetrasodium ethylenediaminetetraacetate	64-02-8	0.00009	0.00001%
Dodecamethylcyclohexasiloxane	540-97-6		
Siloxanes and silicones, dimethyl, reaction products with silica	67762-90-7	0.00001	
Octamethylcyclotetrasiloxane	556-67-2		
poly(tetrafluoroethylene)	9002-84-0	0.00001	
Formaldehyde	50-00-0	0.00001	
Copper(II) sulfate	7758-98-7		
Decamethyl cyclopentasiloxane	541-02-6		
Magnesium silicate hydrate (talc)	14807-96-6	0.00002	

Table ESI13. FracFocus disclosure for well MIP 3H. FR Pro 150, Supplier – ECM, Purpose – Friction Reduction.

Ingredients	CAS #	Max Conc in Additive (% by mass)	Max Conc in HF Fluid (% by mass)
Water	7732-18-5	50.0000	0.01575%
Polyacrylamide-co-acrylic acid	2594478	32.0000	0.01008%
Sodium Chloride	7647-14-5	15.0000	0.00472%
Alcohol Ethoxylate Surfactants	Trade	5.0000	0.00157%
Petroleum Distillate	64742-47-8	25.0000	0.00008%

Table ESI14. FracFocus disclosure for well MIP 5H – Basic Information.

Job Start Date:	10/28/2015
Job End Date:	11/05/2015
State:	West Virginia
County:	Monongalia
API Number:	47-061-01699-00-00
Operator Name:	Northeast Natural Energy LLC
Well Name and Number:	MIP 5H
Longitude:	-79.97615200
Latitude:	39.60183300
Datum:	NAD83
Federal/Tribal Well:	NO
True Vertical Depth:	7,530
Total Base Water Volume (gal):	9,961,350
Total Base Non Water Volume:	0

Table ESI15. FracFocus disclosure for well MIP 5H. Proppant Transport, Supplier – Schlumberger, Purpose - Corrosion Inhibitor, Scale Inhibitor, Biocide, Acid, Breaker, Gelling Agent, Friction Reducer, Iron Control Agent, Fluid Loss Additive , Propping Age.

Ingredients	CAS #	Max Conc in Additive (% by mass)	Max Conc in HF Fluid (% by mass)
Water (Including Mix Water Supplied by Client)*	NA		87.58016
Quartz, Crystalline silica	14808-60-7	98.77034	12.26228
Hydrochloric acid	7647-01-0	0.90405	0.11223
Ammonium sulfate	7783-20-2	0.12127	0.01506
Acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, sodium salt polymer	38193-60-1	0.08951	0.01111
Glutaraldehyde	111-30-8	0.03083	0.00383
Guar gum	9000-30-0	0.02213	0.00275
Polymer of 2-acrylamido-2-methylpropanesulfonic acid sodium salt and methyl acrylate	136793-29-8	0.00959	0.00119
Ethanol, 2,2',2''-nitrilotris-,1,1',1''-tris(dihydrogen phosphate), sodium salt	68171-29-9	0.00943	0.00117
Sodium erythorbate	6381-77-7	0.00589	0.00073
Urea	57-13-6	0.00589	0.00073
Alkyl(c12-16) dimethylbenzyl ammonium chloride	68424-85-1	0.00551	0.00068
Trisodium ortho phosphate	7601-54-9	0.00415	0.00051
Methanol	67-56-1	0.00332	0.00041
Fatty acids, tall-oil	61790-12-3	0.0021	0.00026
Thiourea, polymer with formaldehyde and 1- phenylethanone	68527-49-1	0.00174	0.00022
Sodium sulfate	7757-82-6	0.00137	0.00017
Non-crystalline silica (impurity)	7631-86-9	0.00128	0.00016
Ethylene Glycol	107-21-1	0.00118	0.00015
Alcohols, C14-15, ethoxylated (7EO)	68951-67-7	0.00082	0.0001
Ethanol	64-17-5	0.00066	0.00008
Propargyl alcohol	107-19-7	0.00055	0.00007
2-Propenamid (impurity)	65532	0.00029	0.00004
Hexadec-1-ene	629-73-2	0.00018	0.00002
Tetrasodium ethylenediaminetetraacetate	59940	0.00015	0.00002
Diammonium peroxidisulphate	7727-54-0	0.00008	0.00001
1-Octadecene (C18)	112-88-9	0.00009	0.00001
Dimethyl siloxanes and silicones	63148-62-9	0.00008	0.00001

Decamethyl cyclopentasiloxane	541-02-6	0.00001	
Siloxanes and silicones, dimethyl, reaction products with silica	67762-90-7	0.00001	
Octamethylcyclotetrasiloxane	556-67-2	0.00001	
Formaldehyde	50-00-0	0.00001	
Dodecamethylcyclohexasiloxane	540-97-6		
Copper(II) sulfate	7758-98-7		

Table ESI16. FracFocus disclosure for well MIP 5H. FR Pro 150, Supplier – ECM, Purpose – Friction reducer.

Ingredients	CAS #	Max Conc in Additive (% by mass)	Max Conc in HF Fluid (% by mass)
Water	7732-18-5	50.0000	0.0024
Polyacrylamide-co-acrylic acid	2594478	32.0000	0.00154
Sodium Chloride	7647-14-5	15.0000	0.00072
Alcohol Ethoxylate Surfactants	Trade	5.0000	0.00024
Hydrotreated Petroleum Distillate	64742-47-8	25.0000	

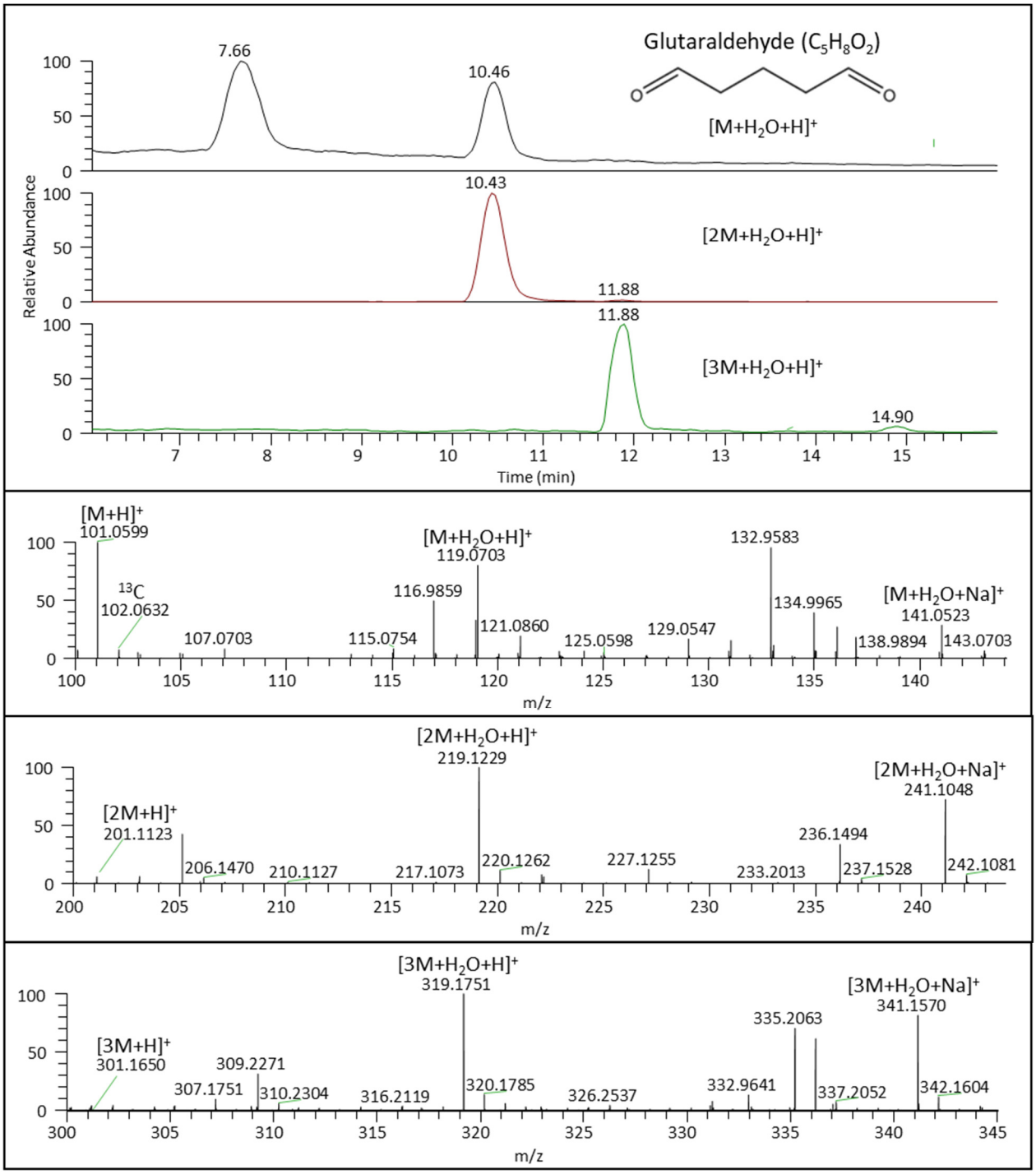


Figure ESI2. Confirmation of glutaraldehyde in HFF 3H. The protonated adduct, a hydrated and protonated adduct and a hydrated and sodiated adduct were observed of the parent compound as well as its dimer and trimer. This is in line with previous findings.[3] Retention times matched those of the analytical standards, but due to the small *m/z* value of the parent compound, distinct fragments had *m/z* values out of the range of detection.

Table ESI17. Kendrick Mass Analysis of ADBAC in HFF 5H. ADBAC-C12, ADBAC-C14 and ADBAC-C16 were the dominant peaks, but trace levels of other ADBAC homologues were detected. The Kendrick Mass scaling factor for ADBAC is 0.998903.

			[M^+]				
	Molecular Formula	Calculated Neutral Mass	Accurate Mass	Error (ppm)	Kendrick Mass	Kendrick Mass Defect	RT (min)
ADBAC-C6	$C_{15}H_{26}N^+$	220.2060	220.2060	0.2	219.9644	0.9644	11.0
ADBAC-C8	$C_{17}H_{30}N^+$	248.2373	248.2373	0.3	247.9650	0.9650	13.1
ADBAC-C10	$C_{19}H_{34}N^+$	276.2686	276.2686	0.2	275.9655	0.9655	15.8
ADBAC-C12	$C_{21}H_{38}N^+$	304.2999	304.2998	-0.1	303.9660	0.9660	18.0
ADBAC-C14	$C_{23}H_{42}N^+$	332.3312	332.3309	-0.7	331.9663	0.9663	19.9
ADBAC-C16	$C_{25}H_{46}N^+$	360.3625	360.3624	-0.3	359.9671	0.9671	21.3
ADBAC-C18	$C_{27}H_{50}N^+$	388.3938	388.3936	-0.4	387.9675	0.9675	22.4

Table ESI18. Kendrick Mass Analysis of PEG in FW 5H. Only PEG homologues present in the reference standard are included in this analysis because isomeric structures could be present in the sample. The Kendrick Mass scaling factor for PEG is 0.998903. The dominant observed mass for each homologue is marked in ***bold***.

		$[M+H]^+$					$[M+NH_4]^+$					$[M+Na]^+$					
	Molecular Formula	Calculated Mass	Accurate Mass	Error	Kendrick Mass	Kendrick Mass Defect	Calculated Mass	Accurate Mass	Error	Kendrick Mass	Kendrick Mass Defect	Calculated Mass	Accurate Mass	Error	Kendrick Mass	Kendrick Mass Defect	RT (min)
PEG-EO5	$C_{10}H_{22}O_6$	239.1489	239.1490	0.5	239.007	0.007	256.1755	256.1756	0.4	256.023	0.023	261.1309	***261.1310***	0.5	260.976	0.976	8.4
PEG-EO6	$C_{12}H_{26}O_7$	283.1751	283.1753	0.7	283.007	0.007	300.2017	***300.2018***	0.3	300.023	0.023	305.1571	305.1572	0.4	304.975	0.975	8.8
PEG-EO7	$C_{14}H_{30}O_8$	327.2013	327.2015	0.5	327.007	0.007	344.2279	***344.2280***	0.3	344.023	0.023	349.1833	349.1833	0.2	348.975	0.975	9.2
PEG-EO8	$C_{16}H_{34}O_9$	371.2276	371.2278	0.7	371.007	0.007	388.2541	***388.2543***	0.5	388.023	0.023	393.2095	393.2095	0.0	392.975	0.975	9.5
PEG-EO9	$C_{18}H_{38}O_{10}$	415.2538	415.2542	1.1	415.007	0.007	432.2803	***432.2808***	1.2	432.023	0.023	437.2357	437.2360	0.7	436.976	0.976	9.6
PEG-EO10	$C_{20}H_{42}O_{11}$	459.2800	459.2802	0.4	459.007	0.007	476.3065	***476.3069***	0.8	476.023	0.023	481.2619	481.2621	0.3	480.976	0.976	9.8
PEG-EO11	$C_{22}H_{46}O_{12}$	503.3062	503.3068	1.2	503.007	0.007	520.3328	***520.3334***	1.2	520.024	0.024	525.2881	525.2887	1.1	524.976	0.976	10
PEG-EO12	$C_{24}H_{50}O_{13}$	547.3324	547.333	1.1	547.007	0.007	564.3590	***564.3596***	1.1	564.024	0.024	569.3144	569.3149	0.9	568.976	0.976	10.2
PEG-EO13	$C_{26}H_{54}O_{14}$	591.3586	591.359	0.6	591.007	0.007	608.3852	***608.3857***	0.8	608.023	0.023	613.3406	613.3409	0.6	612.976	0.976	10.3
PEG-EO14	$C_{28}H_{58}O_{15}$	635.3848	635.3854	0.9	635.007	0.007	652.4114	***652.4119***	0.8	652.023	0.023	657.3668	657.3672	0.7	656.976	0.976	10.4

Table ESI19. Kendrick Mass Analysis of polypropylene glycol (PPG) in FW 5H. Only PPG homologues present in the reference standard are included in this analysis because isomeric structures could be present in the sample. The Kendrick Mass scaling factor for PPG is 0.999279. The dominant observed mass for each homologue is marked in ***bold***.

		$[M+H]^+$					$[M+NH_4]^+$					$[M+Na]^+$					
	Molecular Formula	Calculated Mass	Accurate Mass	Error	Kendrick Mass	Kendrick Mass Defect	Calculated Mass	Accurate Mass	Error	Kendrick Mass	Kendrick Mass Defect	Calculated Mass	Accurate Mass	Error	Kendrick Mass	Kendrick Mass Defect	RT (min)
PPG-PO4	$C_{12}H_{26}O_5$	251.1853	251.1855	0.8	251.004	0.0043	268.2118	268.2121	1.1	268.019	0.0186	273.1672	***273.1674***	0.6	272.970	0.9704	10.9
PPG-PO5	$C_{15}H_{32}O_6$	309.2272	309.2271	-0.2	309.004	0.0041	326.2537	326.2537	0.0	326.018	0.0184	331.2091	***331.2090***	-0.3	330.970	0.9701	11.9
PPG-PO6	$C_{18}H_{38}O_7$	367.2690	367.2689	-0.4	367.004	0.0040	384.2956	384.2955	-0.3	384.018	0.0183	389.2510	***389.2508***	-0.4	388.970	0.9700	13.0
PPG-PO7	$C_{21}H_{44}O_8$	425.3109	425.3110	0.2	425.004	0.0042	442.3374	442.3378	0.9	442.019	0.0187	447.2928	***447.2929***	0.1	446.970	0.9703	14.3
PPG-PO8	$C_{24}H_{50}O_9$	483.3528	***483.3529***	0.3	483.004	0.0043	500.3793	500.3796	0.6	500.019	0.0187	505.3347	505.3347	0.0	504.970	0.9702	15.4
PPG-PO9	$C_{27}H_{56}O_{10}$	541.3946	***541.3950***	0.7	541.004	0.0045	558.4212	558.4216	0.7	558.019	0.0188	563.3766	563.3768	0.4	562.970	0.9704	16.6
PPG-PO10	$C_{30}H_{62}O_{11}$	599.4365	***599.4370***	0.9	599.005	0.0046	616.4630	616.4637	1.1	616.019	0.0191	621.4184	621.4188	0.6	620.971	0.9706	17.5
PPG-PO11	$C_{33}H_{68}O_{12}$	657.4784	***657.4791***	1.1	657.005	0.0049	674.5049	674.5057	1.2	674.019	0.0192	679.4603	679.4607	0.6	678.971	0.9706	18.3

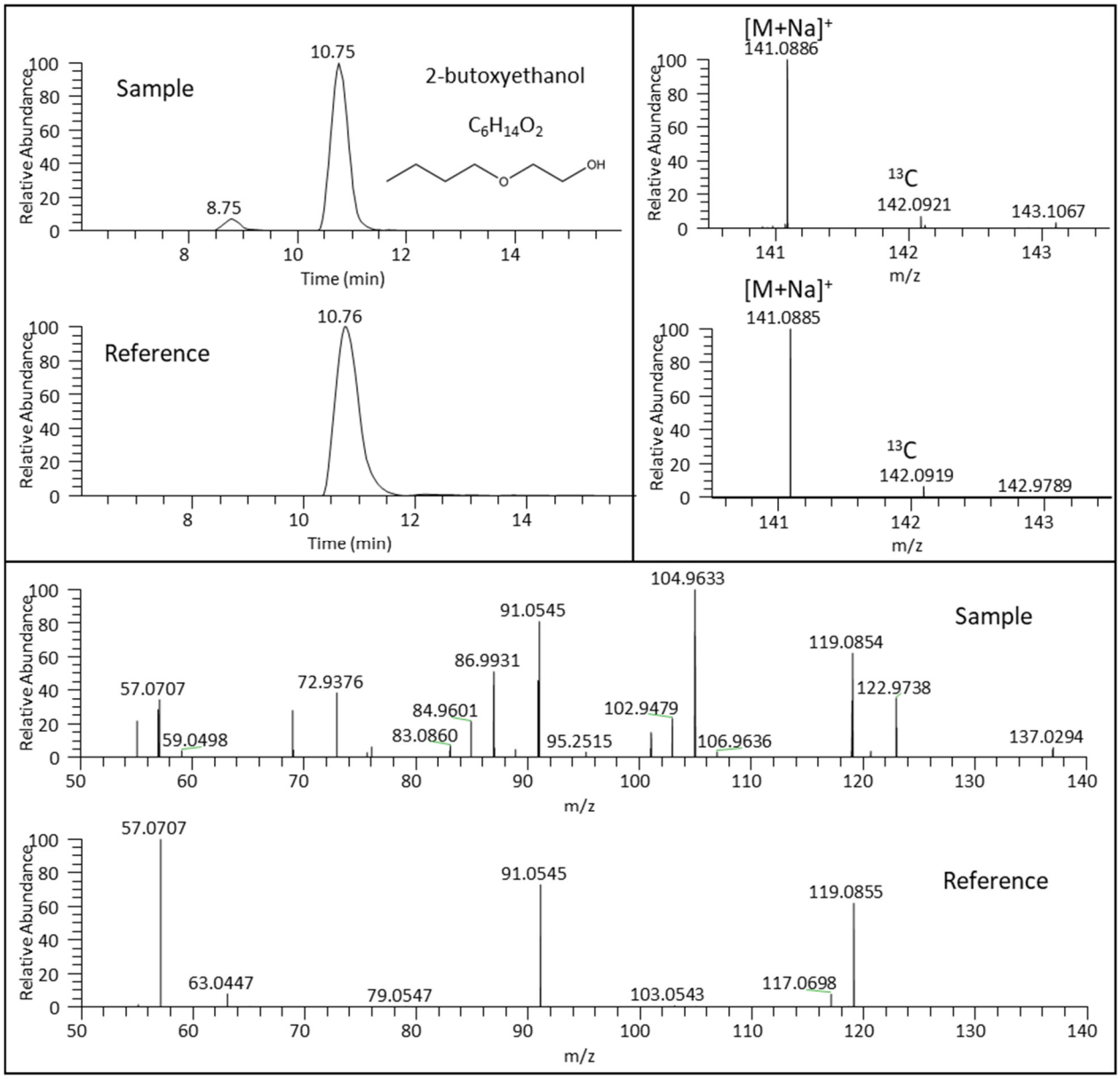


Figure ESI3. Confirmation of 2-butoxyethanol (2-BE). RT of 10.7 and the exact mass of the sodiated adduct (m/z = 141.0667, Δm = 0.92 ppm) matched between reference standard and sample. The MS/MS fragments with m/z values of 57.0707 and 105.0034 (overshadowed by the 104.9635 value in this image) match those obtained in compound tuning (see Table ESI8). The MS/MS fragment with an m/z value of 91.0545 matches a dominant fragment observed in a reference standard run in the same sequence as the sample.

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