1 **Trace Analysis of Anionic and Nonionic Surfactants from Oil Dispersants in Gulf of**
2 **Mexico Seawater Using Large Volume Injection Liquid Chromatography with Tandem**
3 **Mass Spectrometry**
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5 Benjamin J. Place[1], Matt J. Perkins[2], Adam Barsamian[1], Paul Blakemore[1], Jennifer A. Field[2]
6 [1] Department of Chemistry, Oregon State University, Corvallis, OR
7 [2] Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis,
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EXPERIMENTAL METHODS
LVI-LC-MS/MS Method Details
A single MRM transition was identified and scanned for α-/β-EHSS (m/z 309 > 81), while two MRM transitions were scanned for DOSS (quantitative: m/z 421 > 81, qualitative: m/z 421 > 227). The negatively ionized analytes were detected during the first 17 min. Span 80 was detected in positive mode with two MRM transitions (quantitative: m/z 429 > 411, qualitative: m/z 446 > 429). The qualitative transitions for DOSS and Span 80 were monitored to verify presence, although there were no ratio requirements due to poor sensitivity of the qualitative transitions. The positively ionized analytes were detected for the latter 16 min of the analytical run. A timeline is illustrated in shown in **Figure S8** and the MS Parameters is shown in **Table S1**.

Salt Elution Timeline.
In order to determine the required time for the complete elution of the salts in the seawater samples, an eluent precipitation experiment was developed. A sample of 1,800 µL (25% Isopropanol, 75% Instant Ocean sample) was injected using the developed analytical HPLC parameters except with the post-column eluent collected instead of injected into the MS. After the injection, 30 s (0.25 mL) fractions of eluent were collected over the first 10 min of the analytical run.
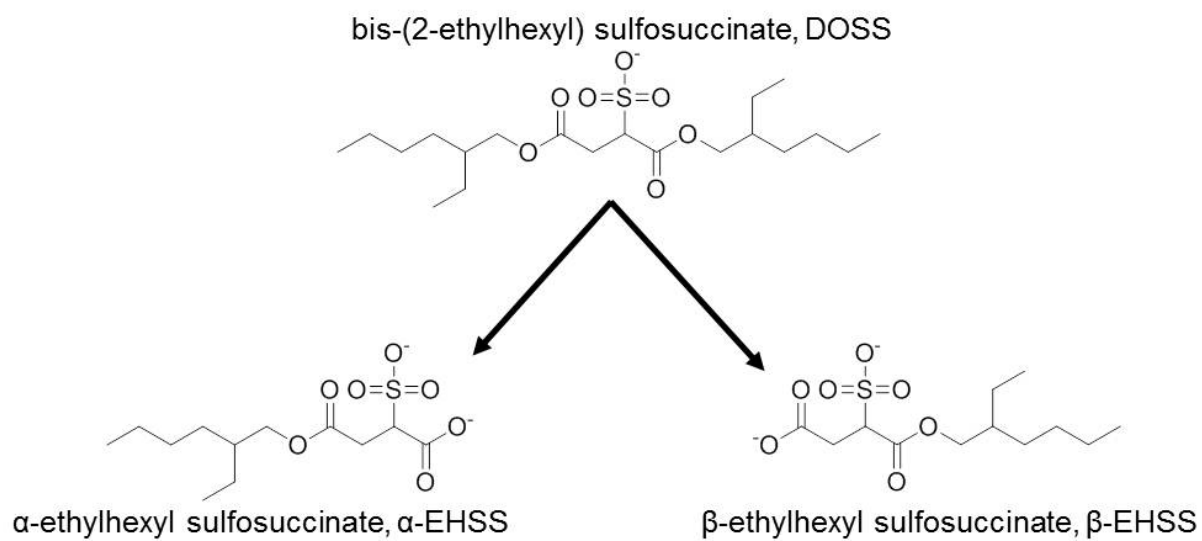
A solution of 1 M $AgNO_3$/0.6 M HNO_3 was made in deionized water for the precipitation of solid AgCl (Cl^- as a broad indicator of seawater). Preliminary experiments found samples containing > 0.1% seawater showed visible AgCl precipitate. A 100-µL aliquot of the $AgNO_3$ solution was added to each eluent and the samples were briefly shaken.

## RESULTS AND DISCUSSION

Salt Elution Timeline.
AgCl precipitate was observed for samples from 1 min to 7.5 min, suggesting majority of the salts eluted during this time. The post-column divert valve was set to divert the eluent flow to the mass spectrometer only after 9.5 min, which verified that no high concentrations of salt would be directed to the MS (**Figure S1**).

63 **Figure S1.** Hydrolysis transformation pathway for DOSS to α- and β-EHSS.

bis-(2-ethylhexyl) sulfosuccinate, DOSS

α-ethylhexyl sulfosuccinate, α-EHSS

β-ethylhexyl sulfosuccinate, β-EHSS

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65 **Figure S2.** Visual demonstration of salt elution from the analytical column using $AgNO_3$ as a
66 precipitation indicator of Cl^- ions.
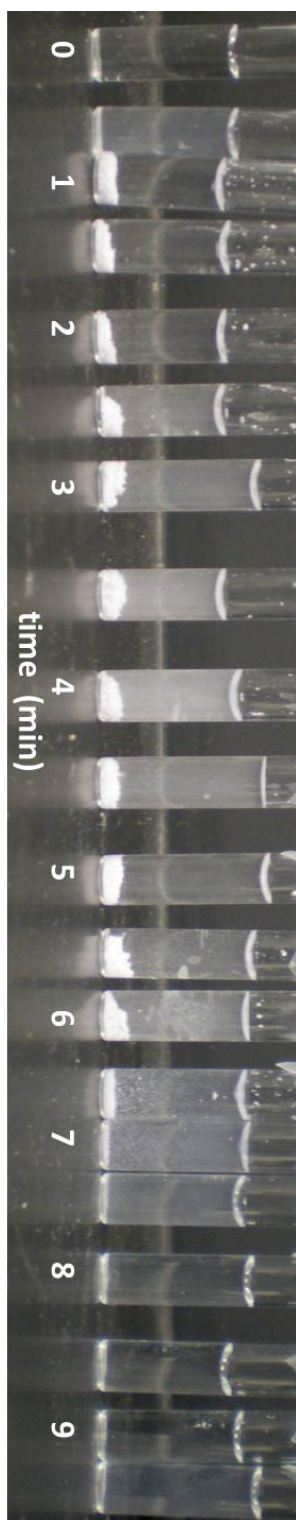
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69　**Figure S3**. Stability of analytes in parent stock standards prepared in methanol (DOSS) and
70　isopropanol (Span 80, Tween 80, Tween 85).

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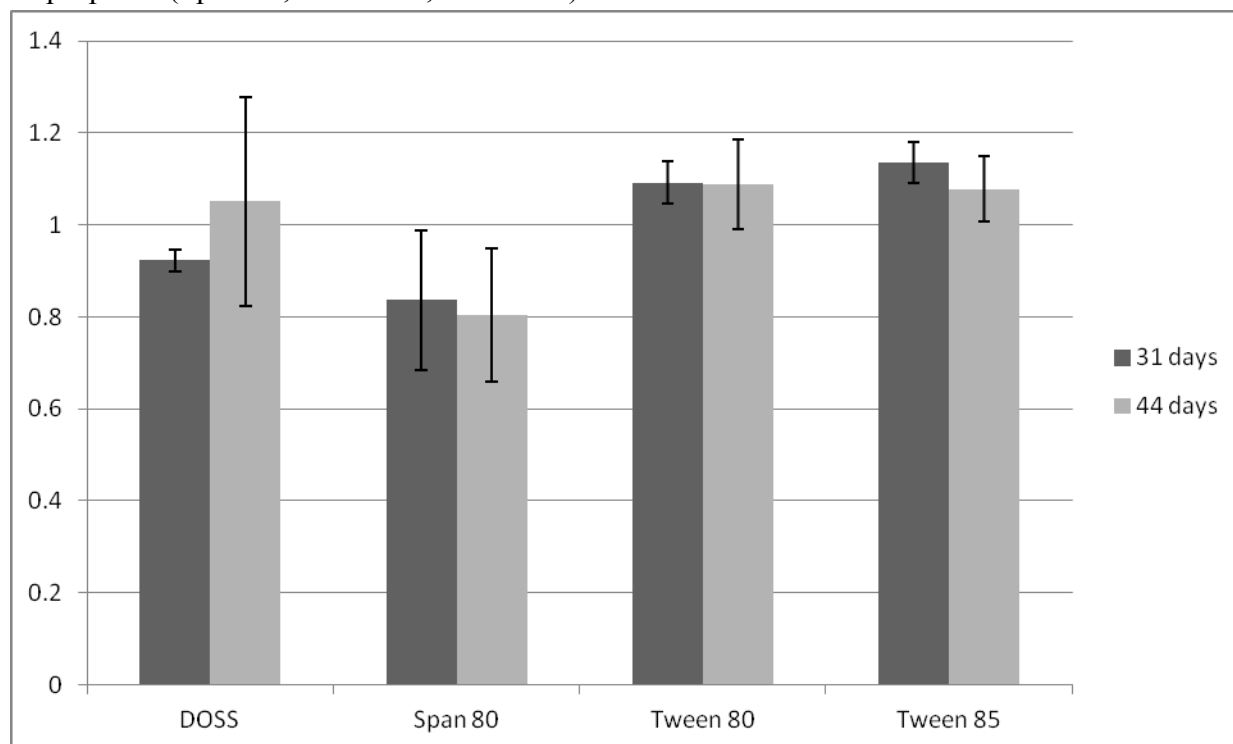
73 **Figure S4**. Stability of analytical standards in HPLC autosampler vials with/without 25%
74 isopropanol. Normalized area was calculated by dividing the resultant area counts by the largest
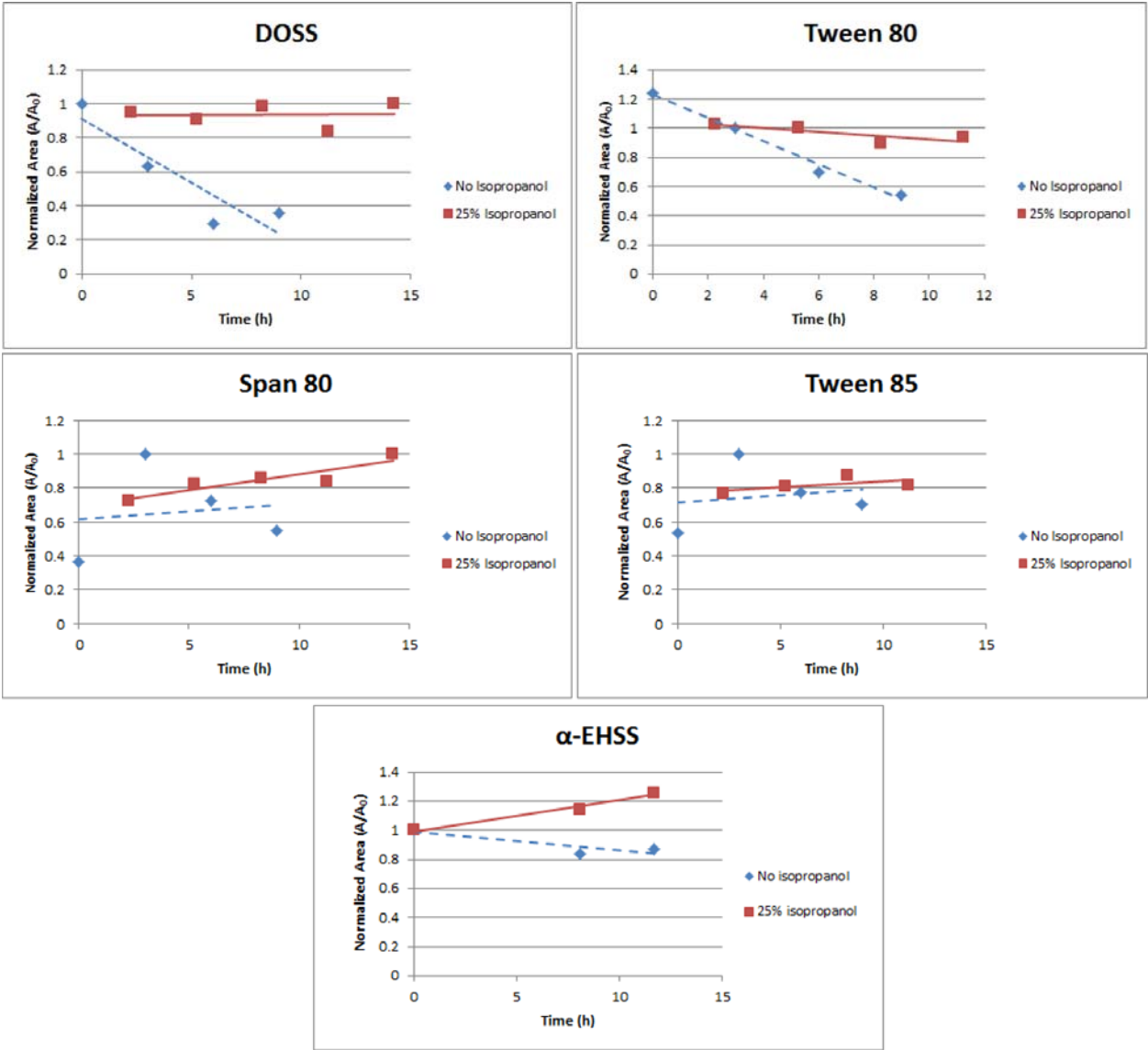75 area counts for that compound.

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78 **Figure S5.** Matrix effects, as indicated by normalized peak area counts, of nonionic analytes
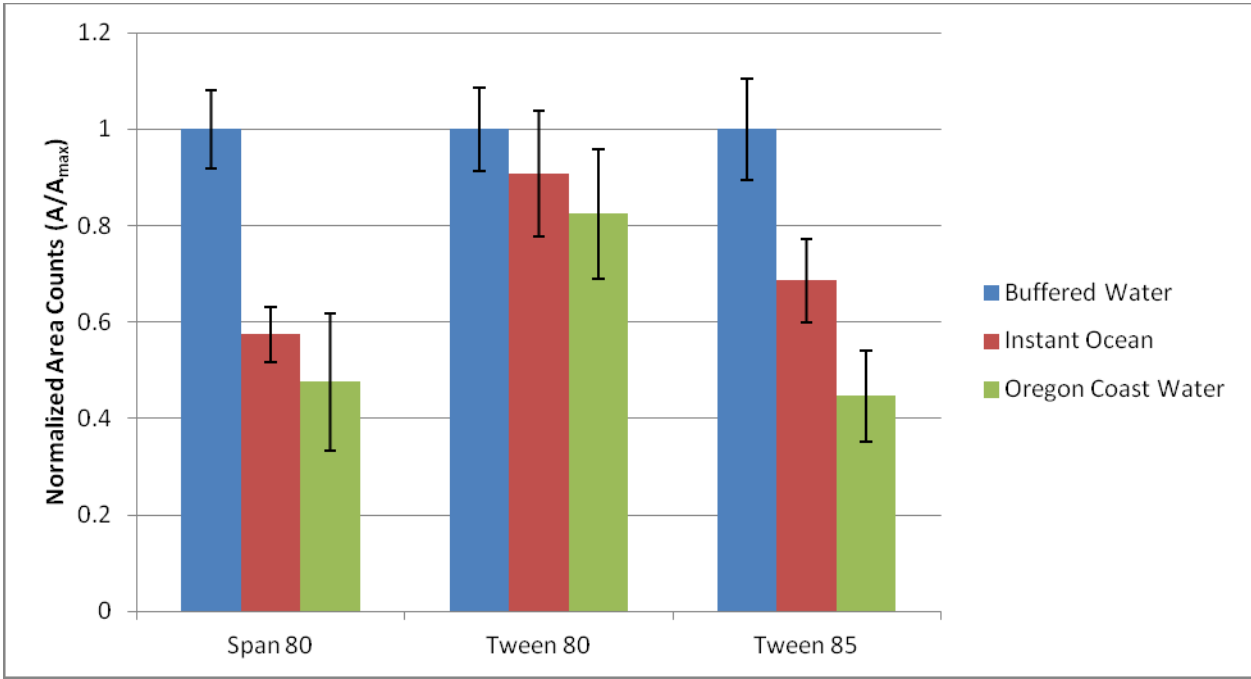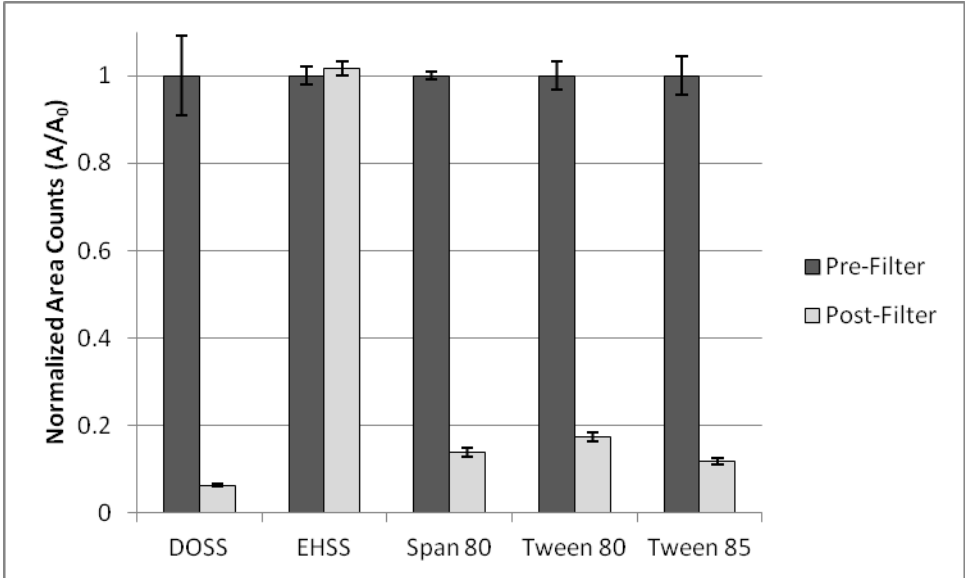79 prepared in buffered water (0.5 mM ammonium acetate), Instant Ocean, and Oregon Coast
80 water.

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83   **Figure S6**. Recovery of all analytes before and after filtration through a Sterivex 0.2-µm
84   sterilization filter.

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87   **Figure S7**. Chromatographic separation of DOSS analyte in sample (A) and the system
88   background contamination (B) using a guard column placed after the pump mixer, but before the
89   autosampler.

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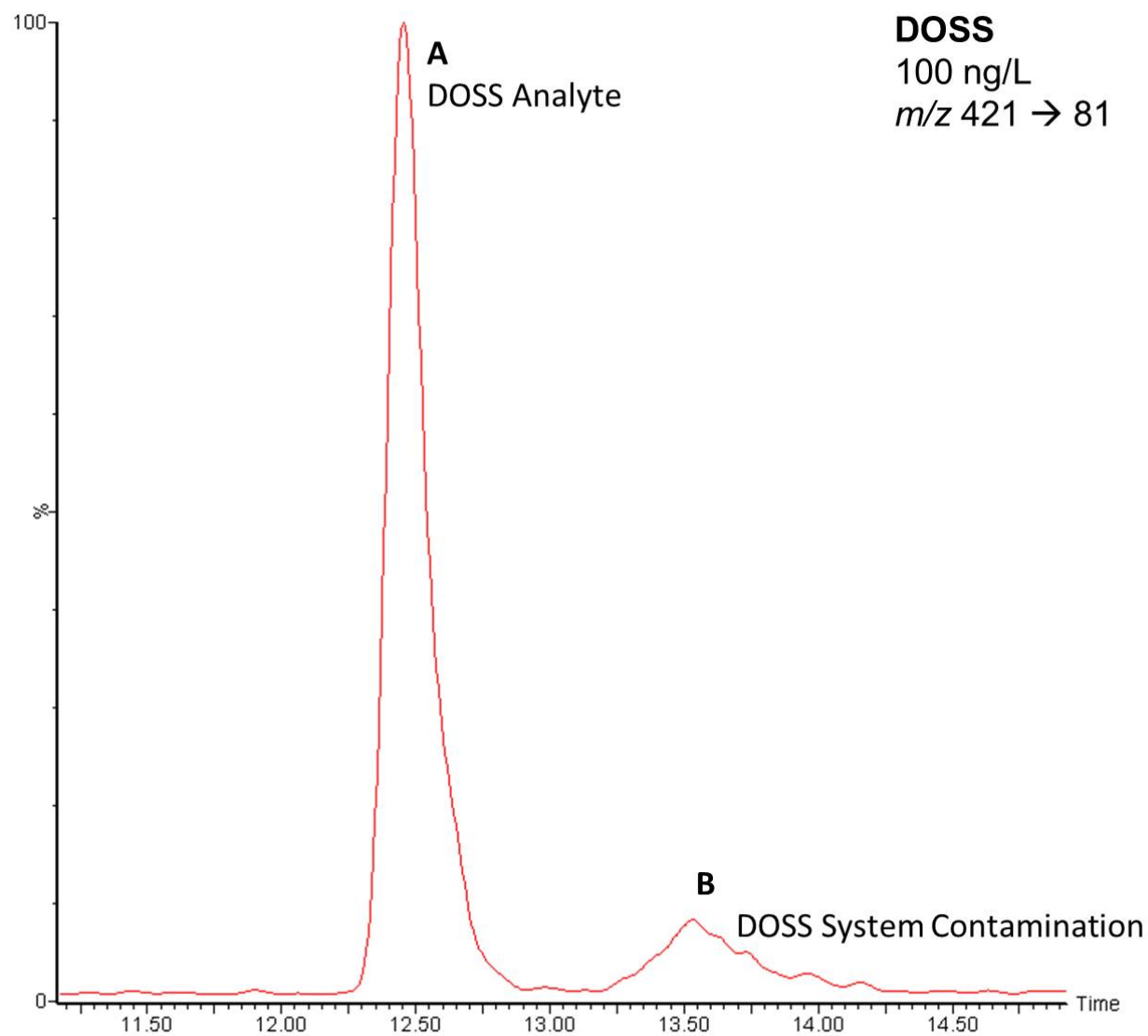
91 **Table S1**. MS Parameters for the detection of all analytes. * indicates secondary MRM
92 transitions used for analyte verification.

Analyte	Retention Time (min)	MS Ionization	Scan Mode	Parent Ion (*m/z*)	Daughter Ion (*m/z*)	Cone Voltage (V)	Collision Energy (V)
DOSS	12.7	Negative	MRM	421	81	44	26
		Negative	MRM	421	227*	42	18
$^{13}C_4$-DOSS	12.7	Negative	MRM	425	81	44	26
α-/β-EHSS	10.1	Negative	MRM	309	81	44	26
Span 80	26.8	Positive	MRM	429	411	40	13
		Positive	MRM	446	429*	40	13
Tween 80	26.0	Positive	Parent Ion	400 - 1300	309	30	40
Tween 85	28.2	Positive	Parent Ion	400 - 1300	309	30	40

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94 **Figure S8**. Timeline of LC-MS/MS Parameters.
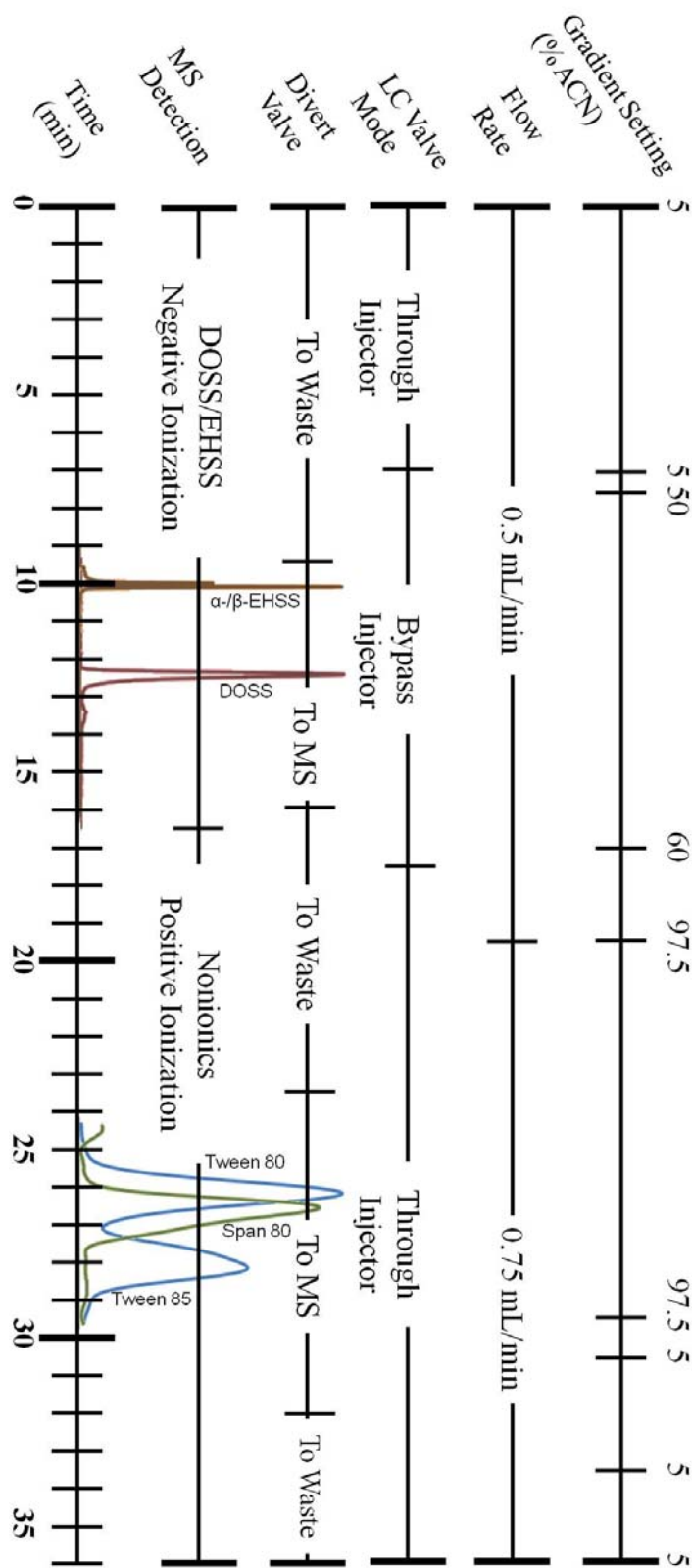

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97 **Figure S9**. Schematic of LC/MS design. Top figure is the LC/MS in main pass LC mode and
98 post-column solvent flow is diverted to the waste (column wash step). Bottom figure is the
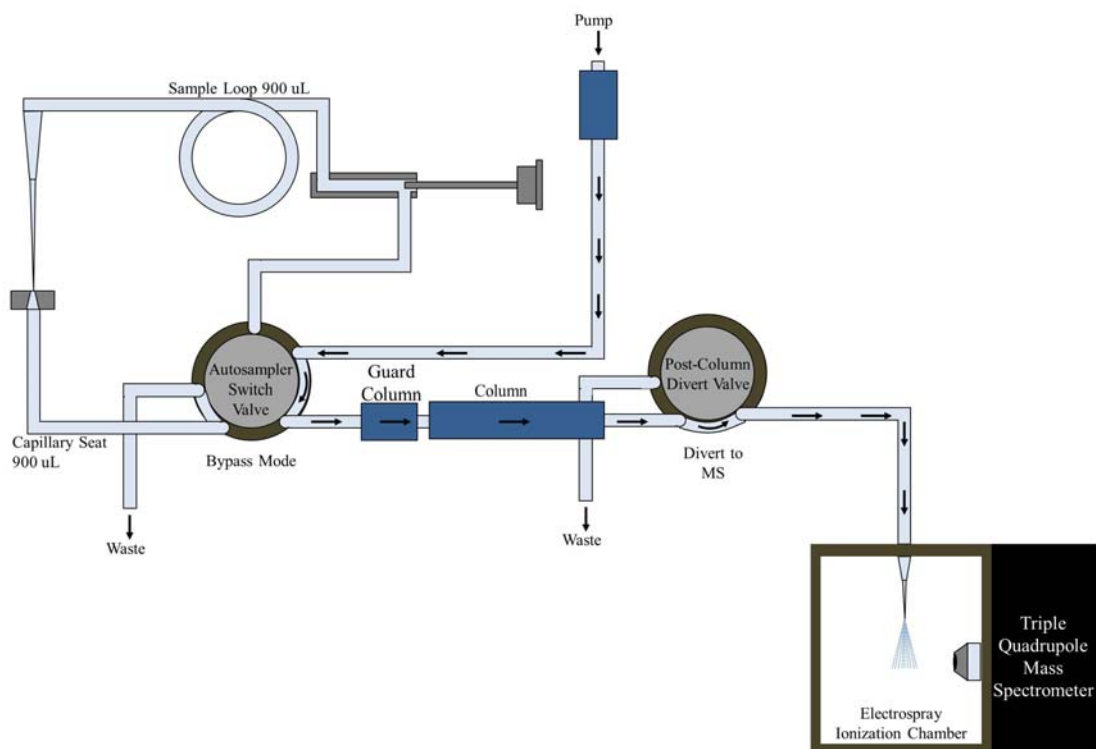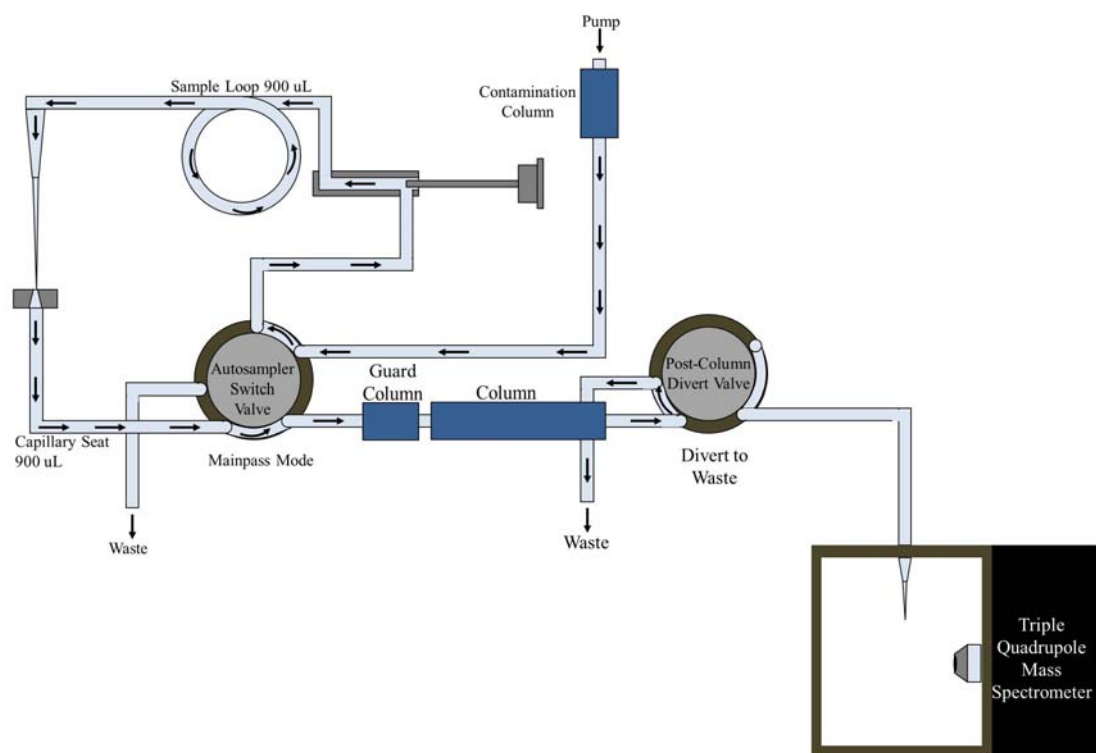99 LC/MS in bypass LC mode with post-column solvent flow diverted to the MS (analyte elution
100 step)
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104   **Figure S10**. Top: Chromatogram of the parent ion scanning for *m/z* 309, Tween 80 and Tween
105   85 are designated as peaks A and B, respectively. Middle: Parent ions of product ion *m/z* 309 for
106   peak A. Bottom: Parent ions of product ion *m/z* 309 for peak B.

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