



*Supplement of*

## **Atmospheric oxidation of 1,3-butadiene: influence of seed aerosol acidity and relative humidity on SOA composition and the production of air toxic compounds**

**Mohammed Jaoui et al.**

*Correspondence to:* Mohammed Jaoui ([jaoui.mohammed@epa.gov](mailto:jaoui.mohammed@epa.gov)) and Rafal Szmigielski ([ralf@ichf.edu.pl](mailto:ralf@ichf.edu.pl))

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## Section S1

**Authentic/surrogate standards preparation.** A total of 13 commercially-available organic chemicals serving as authentic/surrogate standards were selected in this study (Tables S1). The selected compounds were chosen for their relevance to 13BD SOA species identified previously (Jaoui et al., 2014), and to field study. The standard compounds are associated with functional groups including (-OH), (-COOH) or benzene ring.

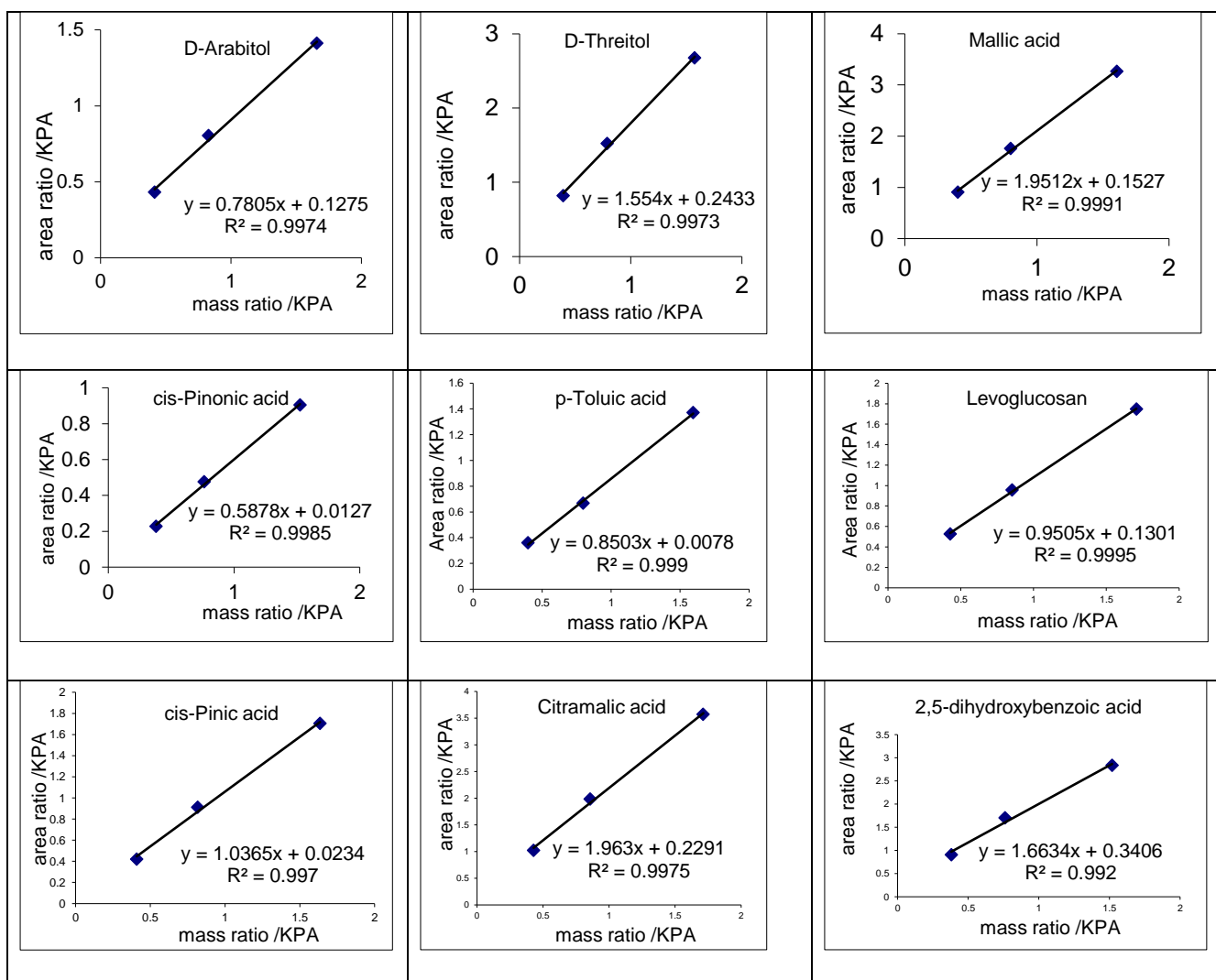
Primary stock solution containing all thirteen analytes were prepared gravimetrically at about 323 – 379  $\mu\text{g/ml}$  in acetonitrile (MS solution: column 4). *cis*-Ketopinic acid (KPA) and  $d_{50}$ -tetracosane (TCS) (internal standards: IS) were prepared separately in a mixture of methanol and acetonitrile (1:1 v/v). The estimated precision for formulating this mixture is 0.1% (Jaoui et al., 2018). The primary mother solution (MS) was used to prepare three external mixtures (ES-mixture 1, ES-mixture 2, and ES-mixture 3: table S1) at concentrations consistent with the sensitivity of the gas chromatograph-mass spectrometer. Thus, inlet injection volumes were selected to give on-column masses from 50 to 250 ng. The filter extraction method optimized previously in our laboratory for samples collected in air was adapted in this study (Jaoui et al., 2018). In the extraction technique, filters underwent sonication for 1 h, followed by evaporation of the extracts under a gentle stream of ultrapure  $\text{N}_2$  using an N-Evap evaporation bath (Organomation Associates, Inc., Berlin, MA), as described in the main paper.

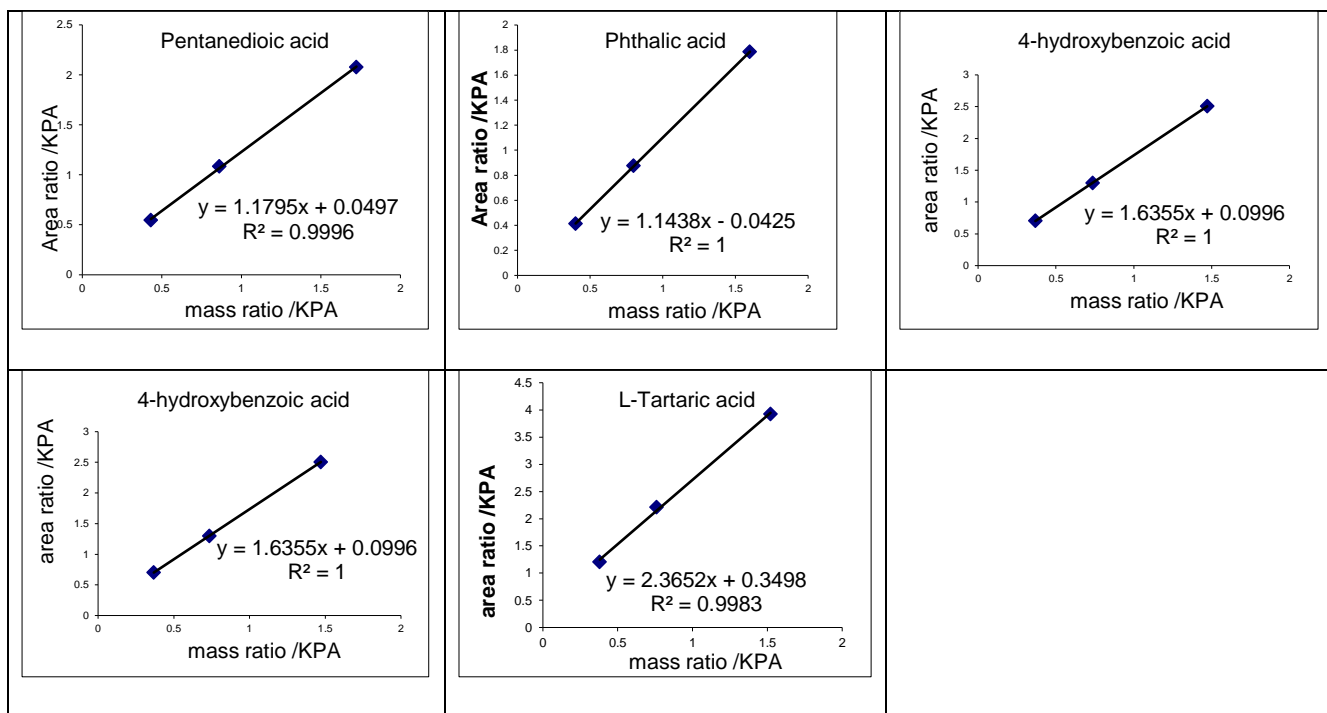
The derivatization of the standard compounds and filter extracts was conducted using a method similar to that found in Jaoui et al. (2018). For the standard mixture ES-mixture 1, a 25  $\mu\text{l}$  aliquot of MS was transferred to a 5-mL conic-bottom tube with a Teflon-lined cap also containing known amount of KPA and TCS giving the concentration reported in Table S1, then evaporated to dryness using dry nitrogen. The procedure was repeated for ES-mixture 2 and ES mixture-3 using 50  $\mu\text{l}$  and 100  $\mu\text{l}$  from MS solution, respectively and the same volume of IS was used. To each dry ES mixture, 200  $\mu\text{L}$  of BSTFA and 100  $\mu\text{L}$  of pyridine were added to start the derivatization. The tubes were air sealed with Teflon caps and Parafilm and allowed to react for 1 h at 70  $^\circ\text{C}$ . After cooling to room temperature, the solutions were transferred to GC-MS vials, and analyzed by GC-MS in the EI and methane-CI modes. Three replicates were injected to check instrumental reproducibility. Note, the two experiments reported in this study were conducted at different time. Since concentrations in ER666 were lower than in ER444, an additional second set of external mixture was prepared similar to ER444 as shown in Table S2.

**Table S1.** Standards compounds used in ER444. MS: mother solution; ES: external calibration solutions.

Compound	MW (g mol <sup>-1</sup> )	MW <sub>bstfa</sub> (g mol <sup>-1</sup> )	MS ( $\mu\text{g/ml}$ )	Rt (min)	Mass (ng) injected in GC-MS		
					ES- mixture 1	ES- mixture 2	ES- mixture 3
D-Arabitol	152.15	136.15	364.70	18.5	60.78	121.57	243.13
D-Threitol	122.12	132.12	346.53	19.4	57.76	115.51	231.02
Malic acid	134.09	148.12	352.47	21.4	58.75	117.49	234.98
<i>cis</i> -Pinonic acid	184.00	134.09	335.20	21.7	55.87	111.73	223.47
<i>p</i> -Toluic acid	136.15	122.12	350.54	22	58.42	116.85	233.69
Levoglucozan	162.10	184.00	375.04	22.7	62.51	125.01	250.03
Pinic acid	186.00	138.12	359.37	25.1	59.90	119.79	239.58
Citramalic acid	148.12	150.09	376.68	25.5	62.78	125.56	251.12
2,5-Dihydroxybenzoic acid	154.12	186.00	333.99	26.1	55.67	111.33	222.66

Pentanedioic acid	132.12	166.13	378.84	26.9	63.14	126.28	252.56
Phthalic acid	166.13	162.10	351.60	27.3	58.60	117.20	234.40
4-Hydroxybenzoic acid	138.12	152.15	323.41	27.6	53.90	107.80	215.61
L-Tartaric acid	150.09	154.12	334.32	28.6	55.72	111.44	222.88
D <sub>50</sub> -Tetracosane (TCS: IS)	182.22	182.22	549.51	22.3	146.54	146.54	146.54
cis-Ketopinic acid (KPA: IS)	386.07	386.07	430.41	36.3	143.47	143.47	143.47





**Figure S1.** Calibration curves associated with all ES standards. cis-Ketopinic acid was used as internal standard.

**Table S2.** Standards compounds used in ER666. MS: mother solution; ES: external calibration solutions.

Compound	Mw (g mol <sup>-1</sup> )	[MS] (μg/ml)	Mass (ng) injected in GC-MS in CI mode		
			ES-solution 1	ES-solution 1	ES-solution 1
p-Toluic acid	136.15	277.20	11.55	23.10	46.20
Pentanedioic acid	132.12	252.80	10.53	21.07	42.13
Citramalic acid	148.12	240.78	10.03	20.06	40.13
Malic acid	134.09	251.32	10.47	20.94	41.89
D-Threitol	122.12	237.62	9.90	19.80	39.60
cis-Pinonic acid	184.00	254.99	10.62	21.25	42.50
4-Hydroxybenzoic acid	138.12	249.17	10.38	20.76	41.53
L-Tartaric acid	150.09	259.37	10.81	21.61	43.23
Pinic acid	186.00	273.37	11.39	22.78	45.56
Phthalic acid	166.13	297.53	12.40	24.79	49.59
Levoglucozan	162.10	246.36	10.26	20.53	41.06
D-Arabitol	152.15	247.69	10.32	20.64	41.28
2,5-Dihydroxybenzoic acid	154.12	245.71	10.24	20.48	40.95
cis-Ketopinic acid (IS)	182.22	195.05	32.51	32.51	32.51
d <sub>50</sub> -Tetracosane (IS)	386.07	487.26	40.60	40.60	40.60

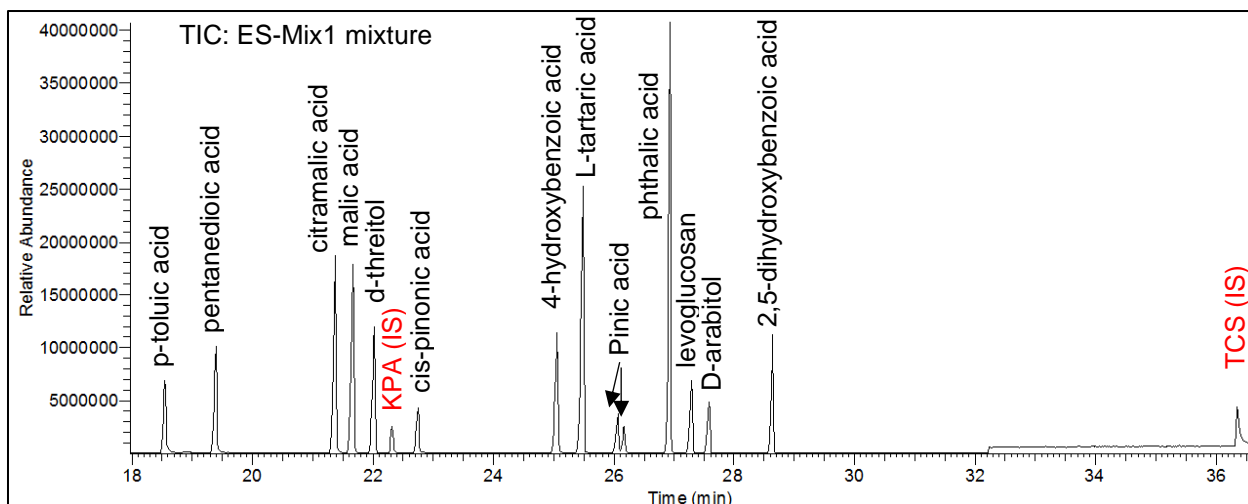
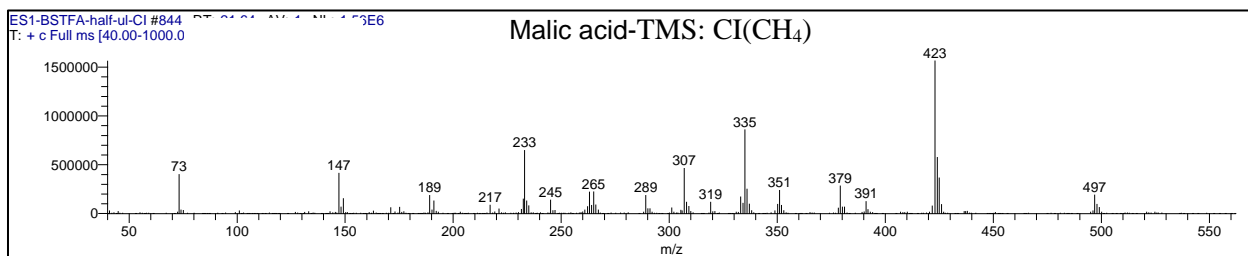
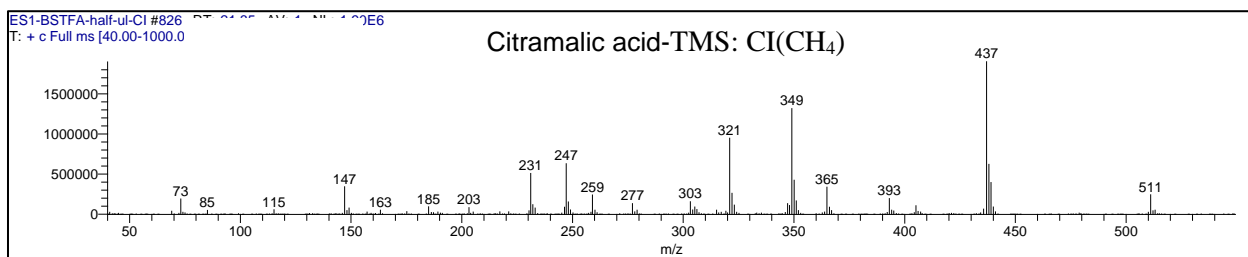
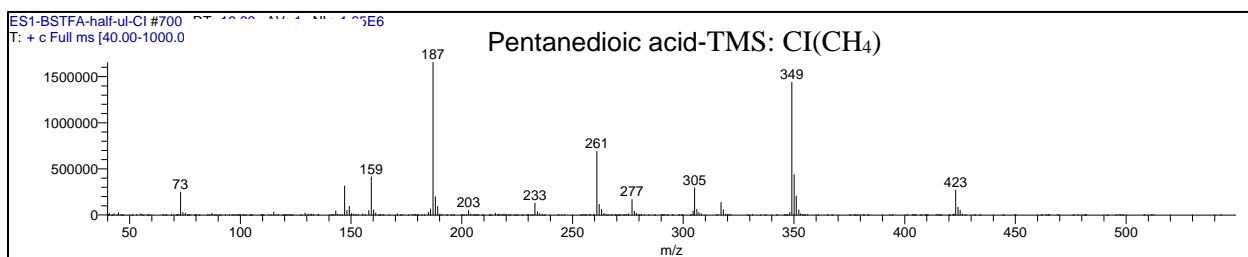
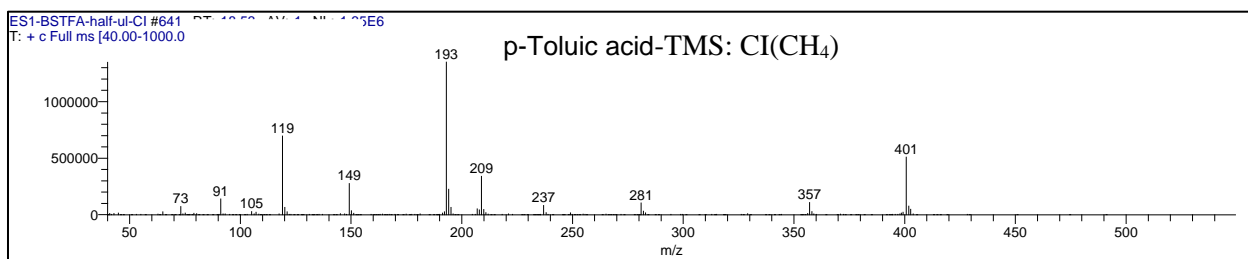
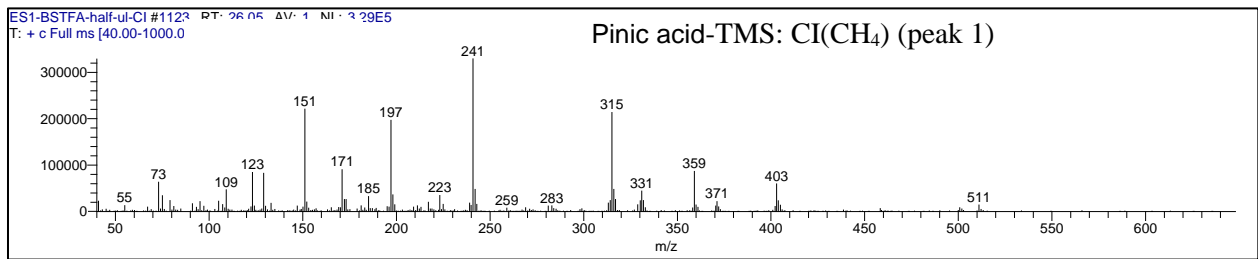
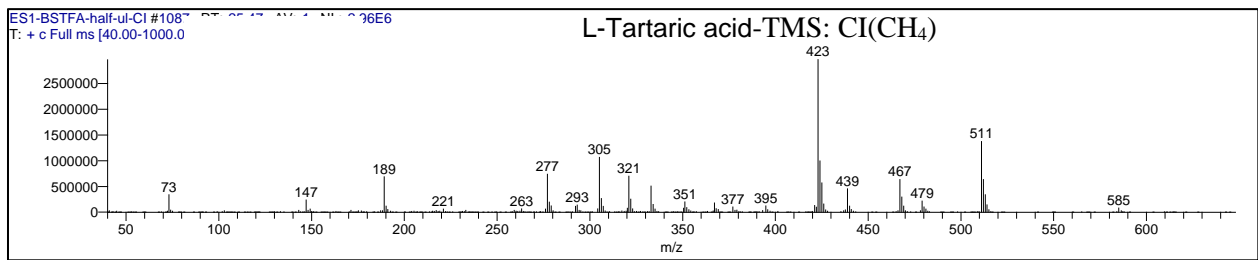
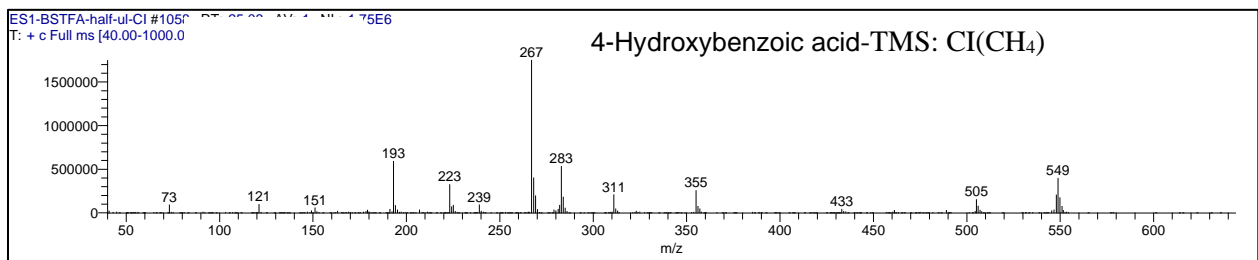
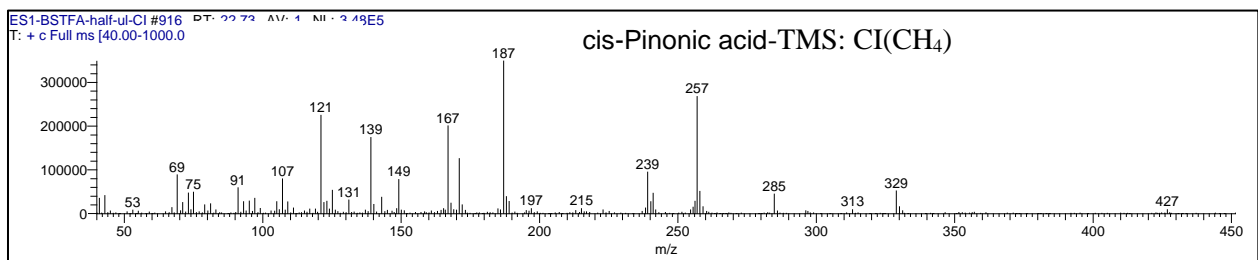
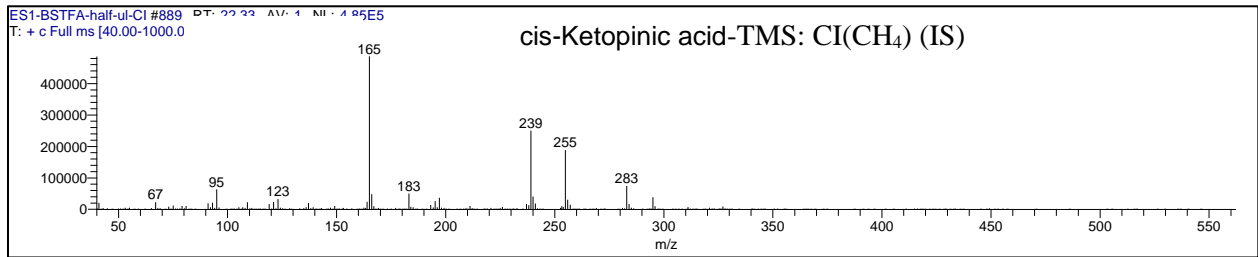
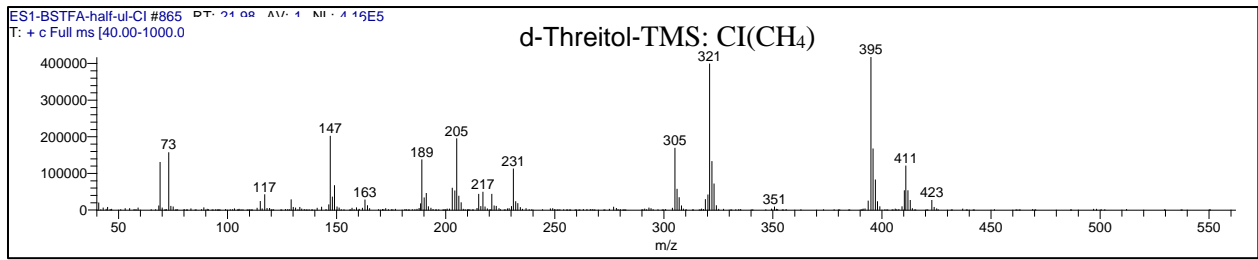
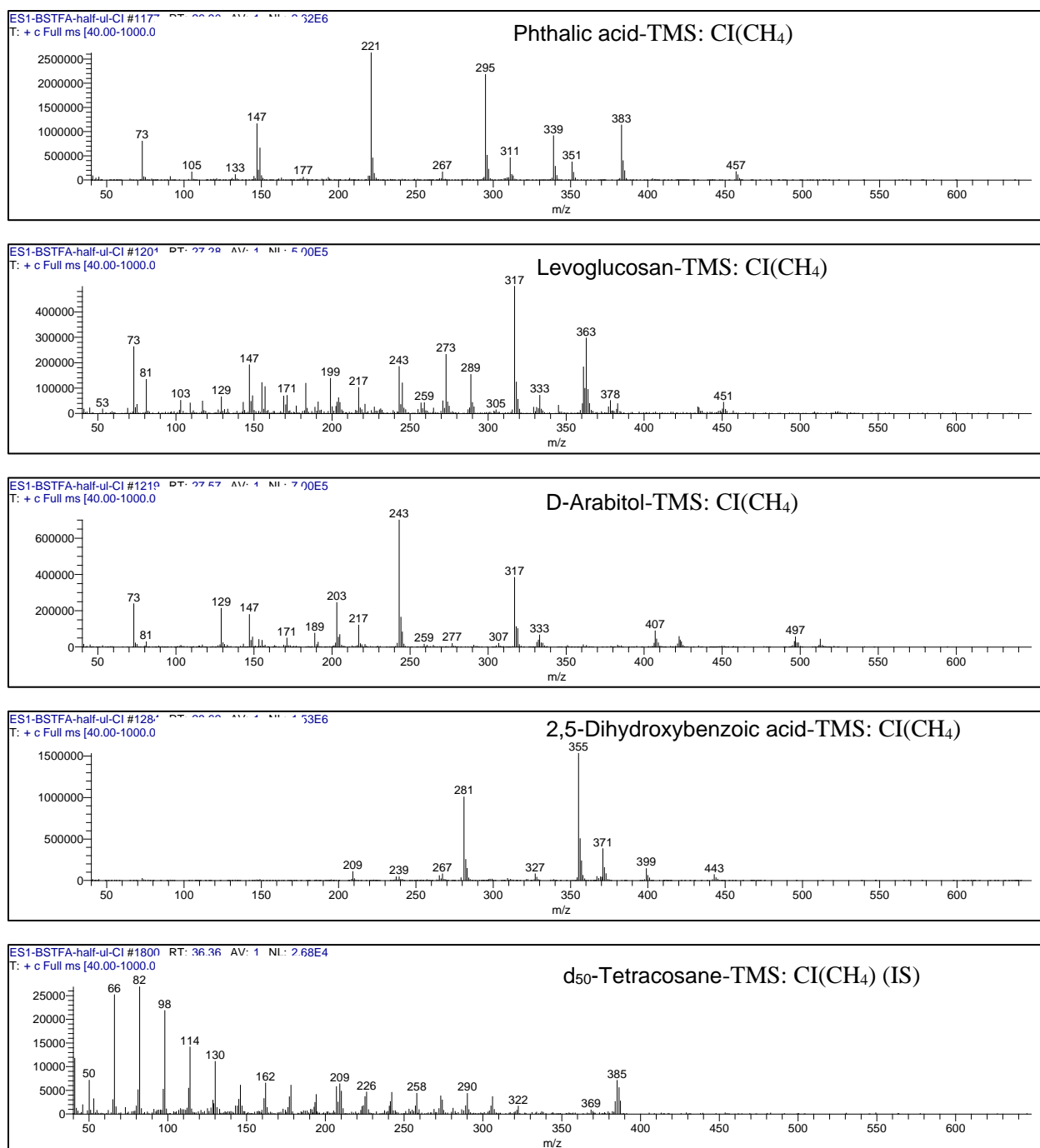


Figure S2. Total ion chromatogram associated with ES-solution 1 from Table S2 as an example.







**Figure S3.** Examples of mass spectra in CI mode recorded for standards used in this study.

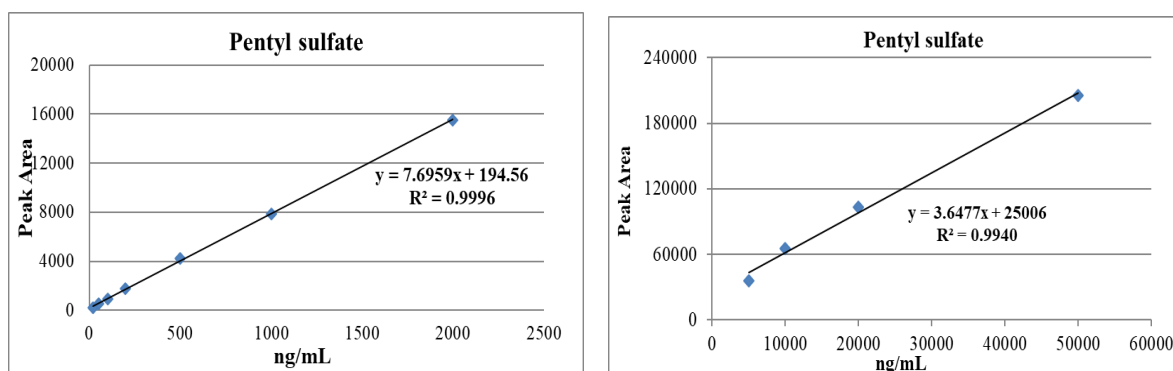
**Table S3.** Mean peak area with standard deviations (SD) obtained for pentyl sulfate calibration curve (mean peak area from three replicates).

Concentration (ng/mL)	Mean peak area	Error (SD)	Error (%SD)
50	507.78	34.52	6.80
100	950.36	46.24	4.87
200	1798.93	117.96	6.56

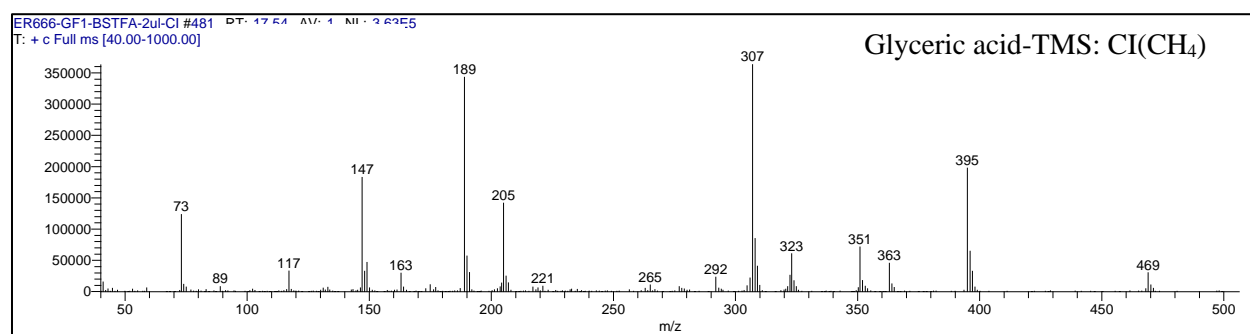
<b>500</b>	4243.87	15.82	0.37
<b>1000</b>	7885.61	91.45	1.16
<b>2000</b>	15535.57	247.47	1.59
<b>5000</b>	36189.08	726.14	2.01
<b>10000</b>	65571.82	628.16	0.96
<b>20000</b>	103093.50	1654.79	1.61
<b>50000</b>	205226.90	4495.42	2.19

**Table S4.** Recovery, LOD and LOQ levels established for sodium 1-pentyl sulfate standard used for LC-MS quantification.

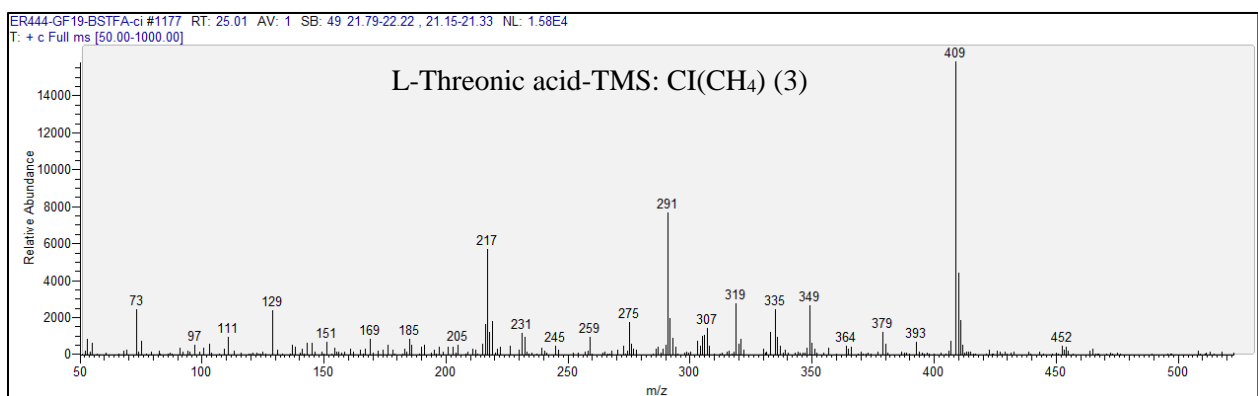
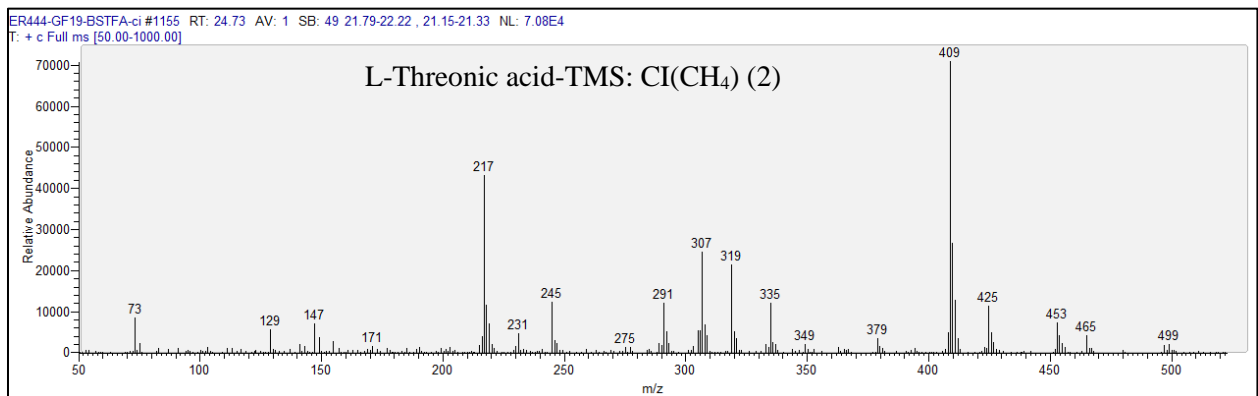
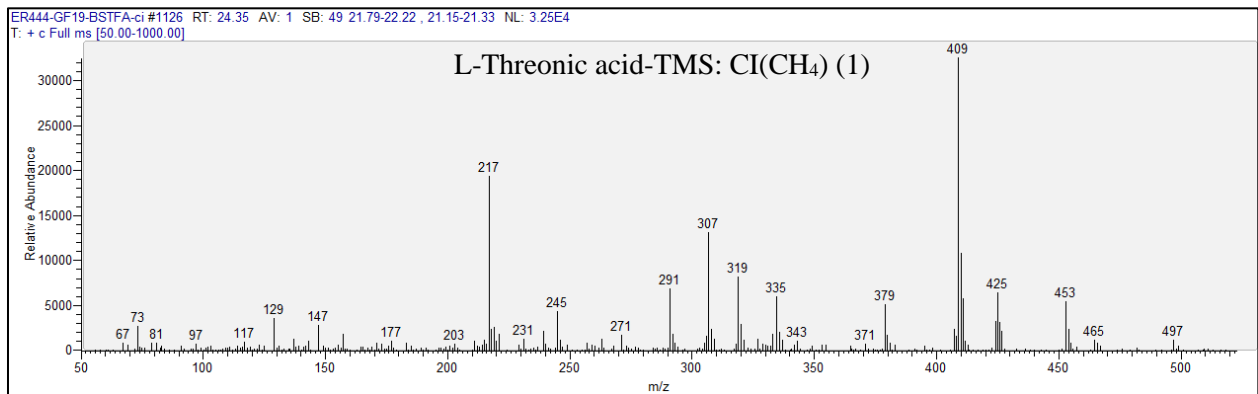
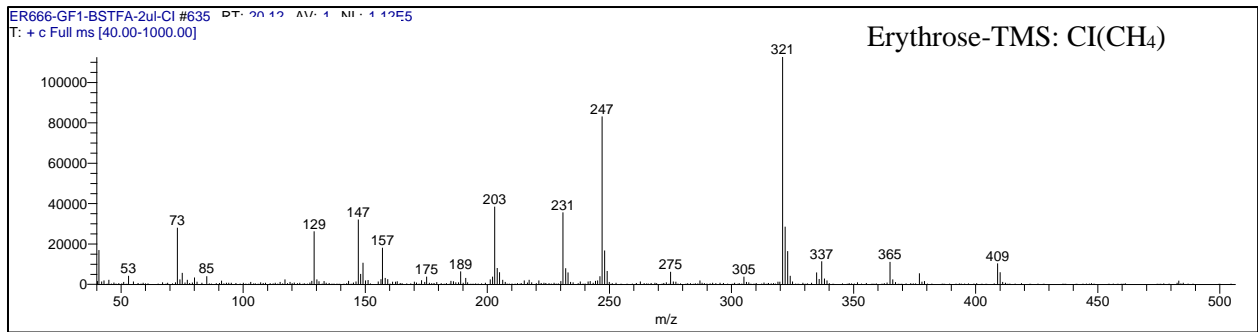
Compound name	Mean recovery [%]	Uncertainty [%]	LOD [ng/sample]	LOQ [ng/sample]
sodium 1-pentyl sulfate	82.1	3.4	14.7	44.7



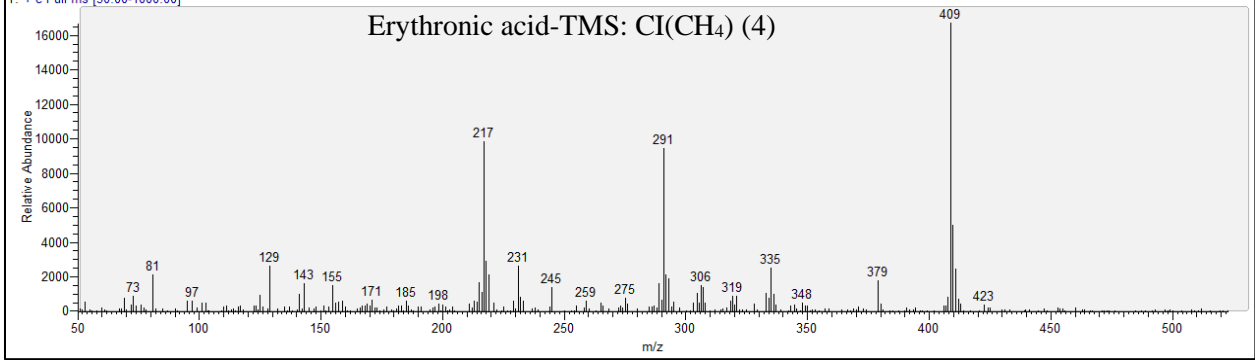
**Figure S4.** Calibration curves associated with pentyl sulfate used as internal standard for OSs and NOSs quantification in the range of 0 – 2000 ng/mL (left) and 5000 – 50000 ng/mL (right).



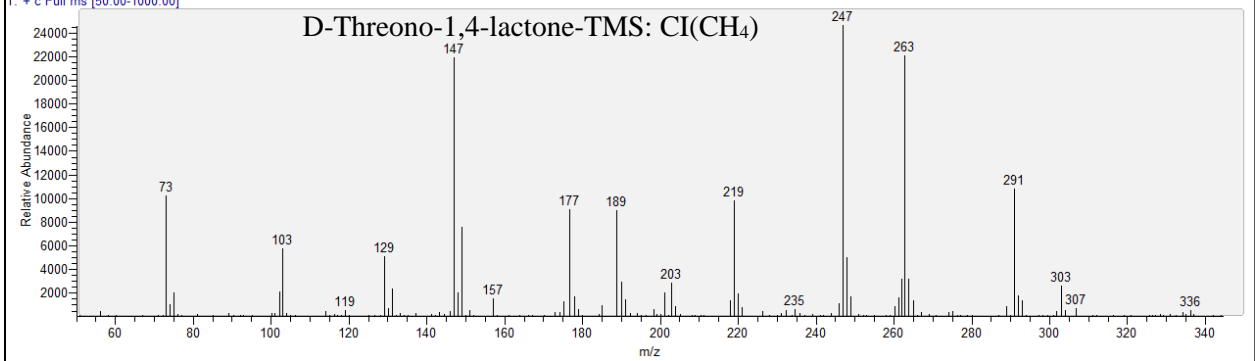




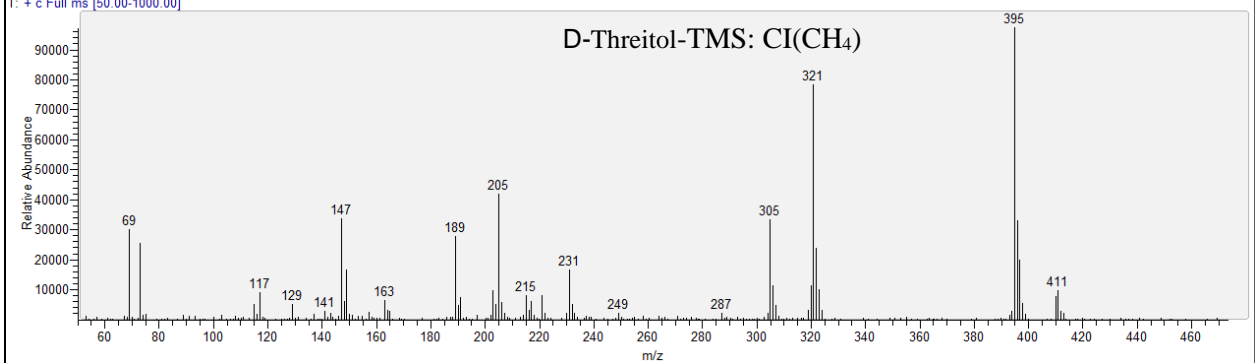
ER444-GF19-BSTFA-ci #1214 RT: 25.50 AV: 1 SB: 49 21.79-22.22 , 21.15-21.33 NL: 1.67E4  
T: + c Full ms [50.00-1000.00]



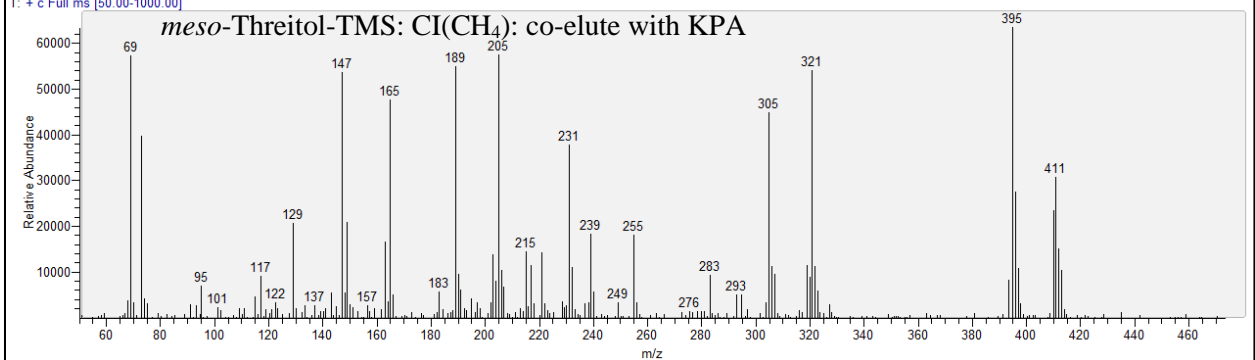
ER444-GF19-BSTFA-ci #917 RT: 21.63 AV: 1 SB: 49 21.79-22.22 , 21.15-21.33 NL: 2.46E4  
T: + c Full ms [50.00-1000.00]



ER444-GF19-BSTFA-ci #1040 RT: 23.24 AV: 1 SB: 49 21.79-22.22 , 21.15-21.33 NL: 9.72E4  
T: + c Full ms [50.00-1000.00]



ER444-GF19-BSTFA-ci #1055 RT: 23.43 AV: 1 SB: 49 21.79-22.22 , 21.15-21.33 NL: 6.34E4  
T: + c Full ms [50.00-1000.00]



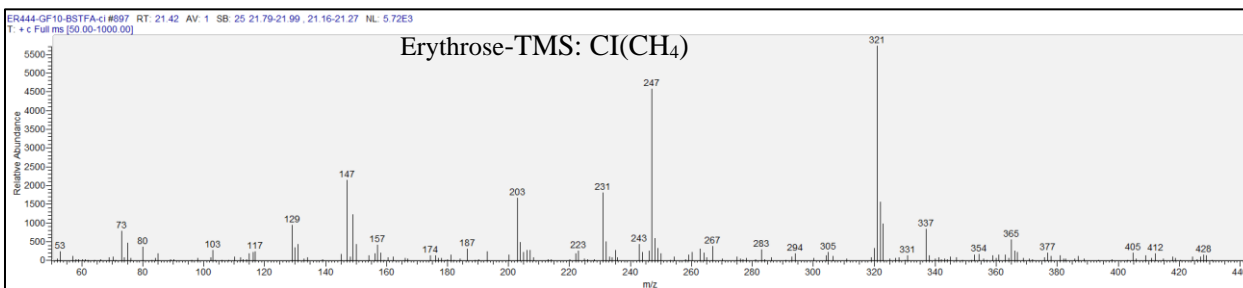
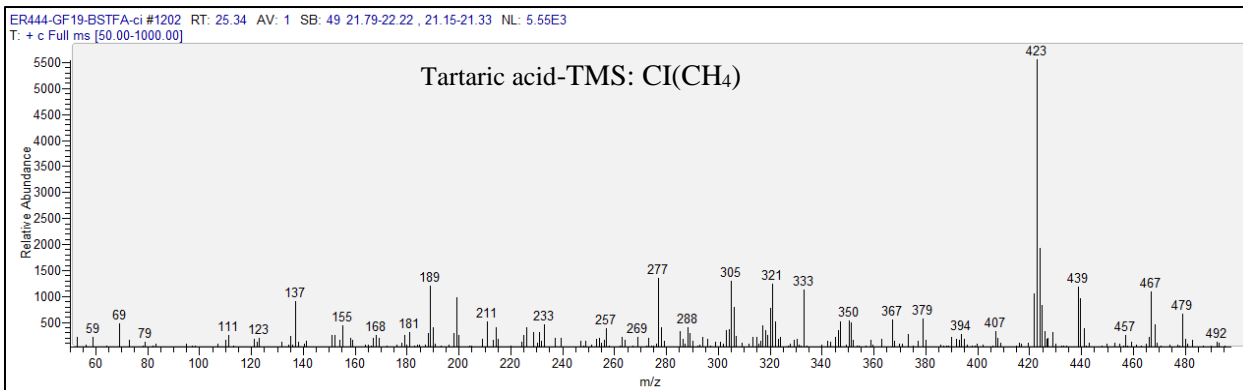
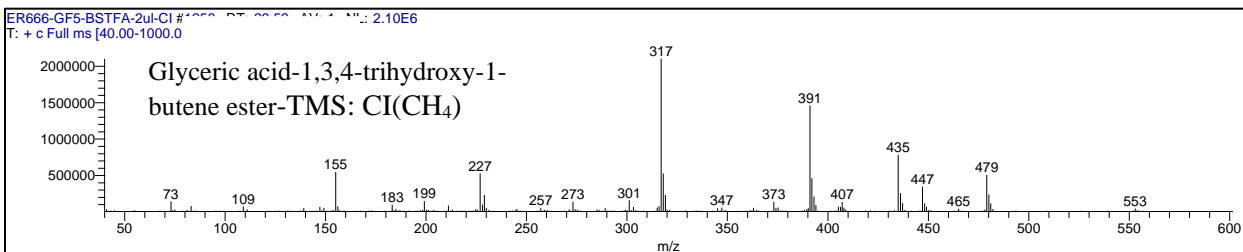
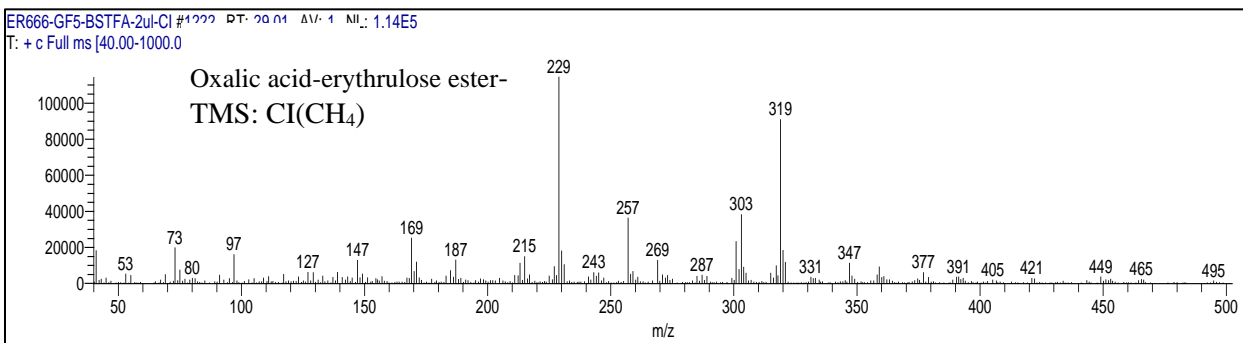
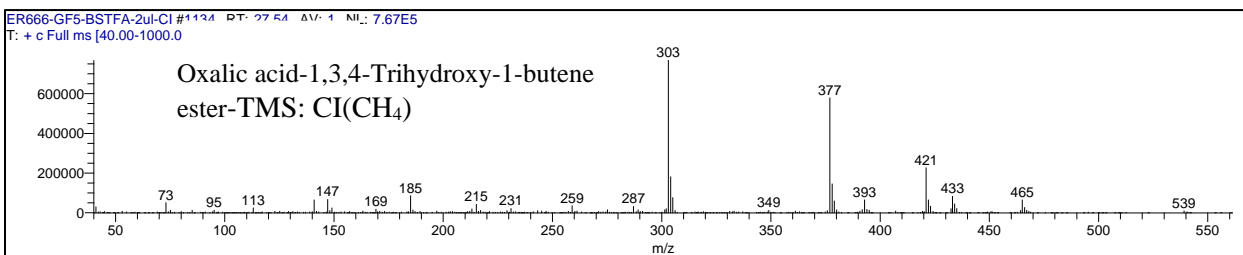
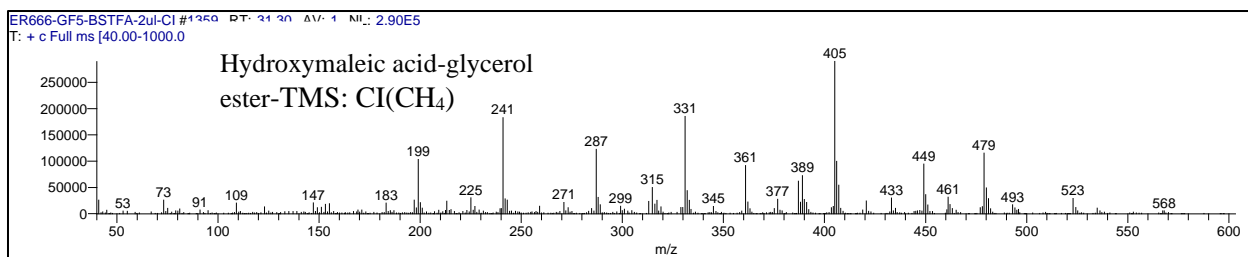
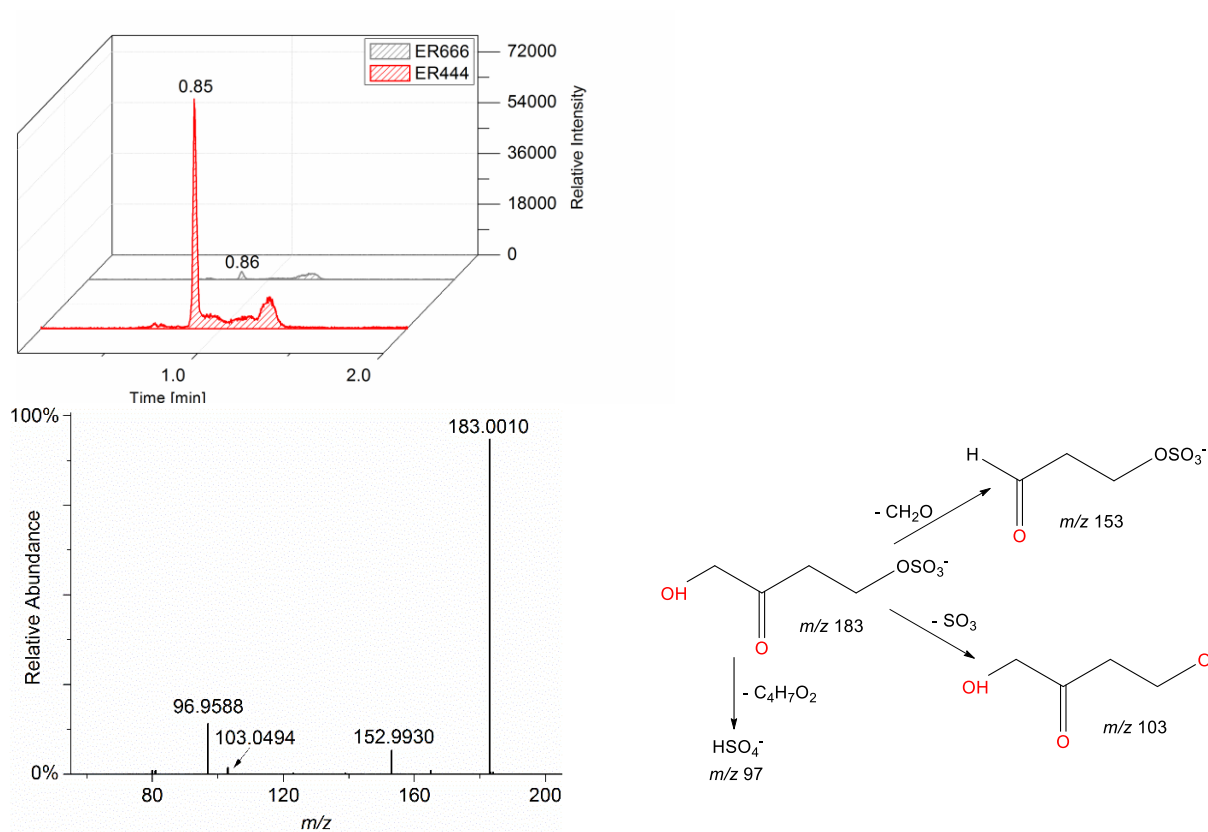


Figure S5. Mass spectra in CI mode recorded in SOA 13BD/NO<sub>x</sub> system (see the main manuscript).

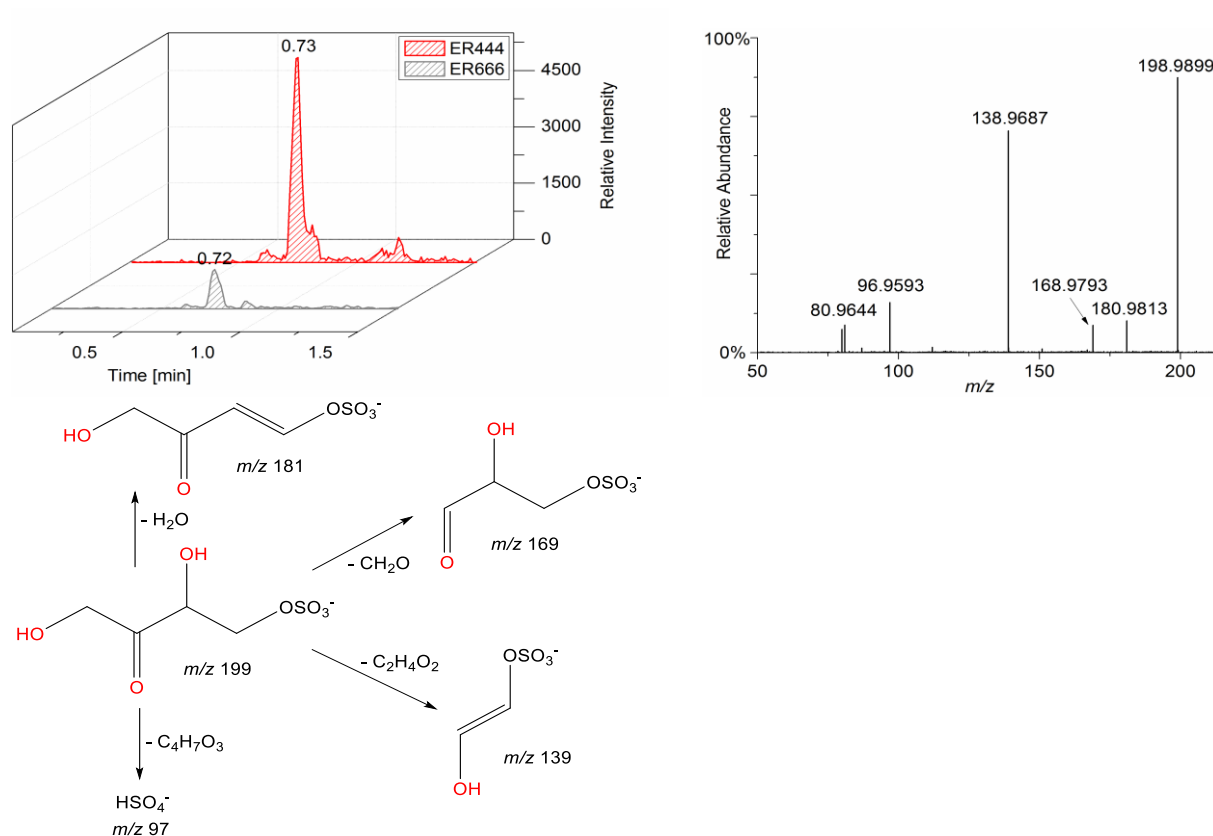




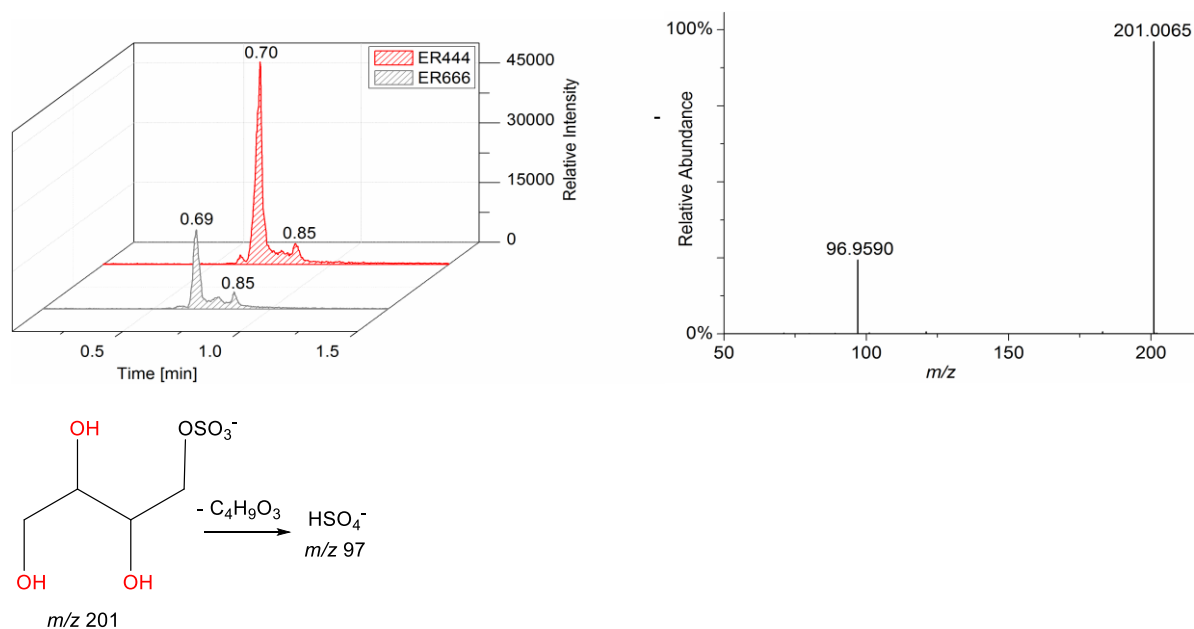
**Figure S6.** Mass spectra of selected reaction products observed in SOA 13BD/NO<sub>x</sub> system (see the main manuscript).



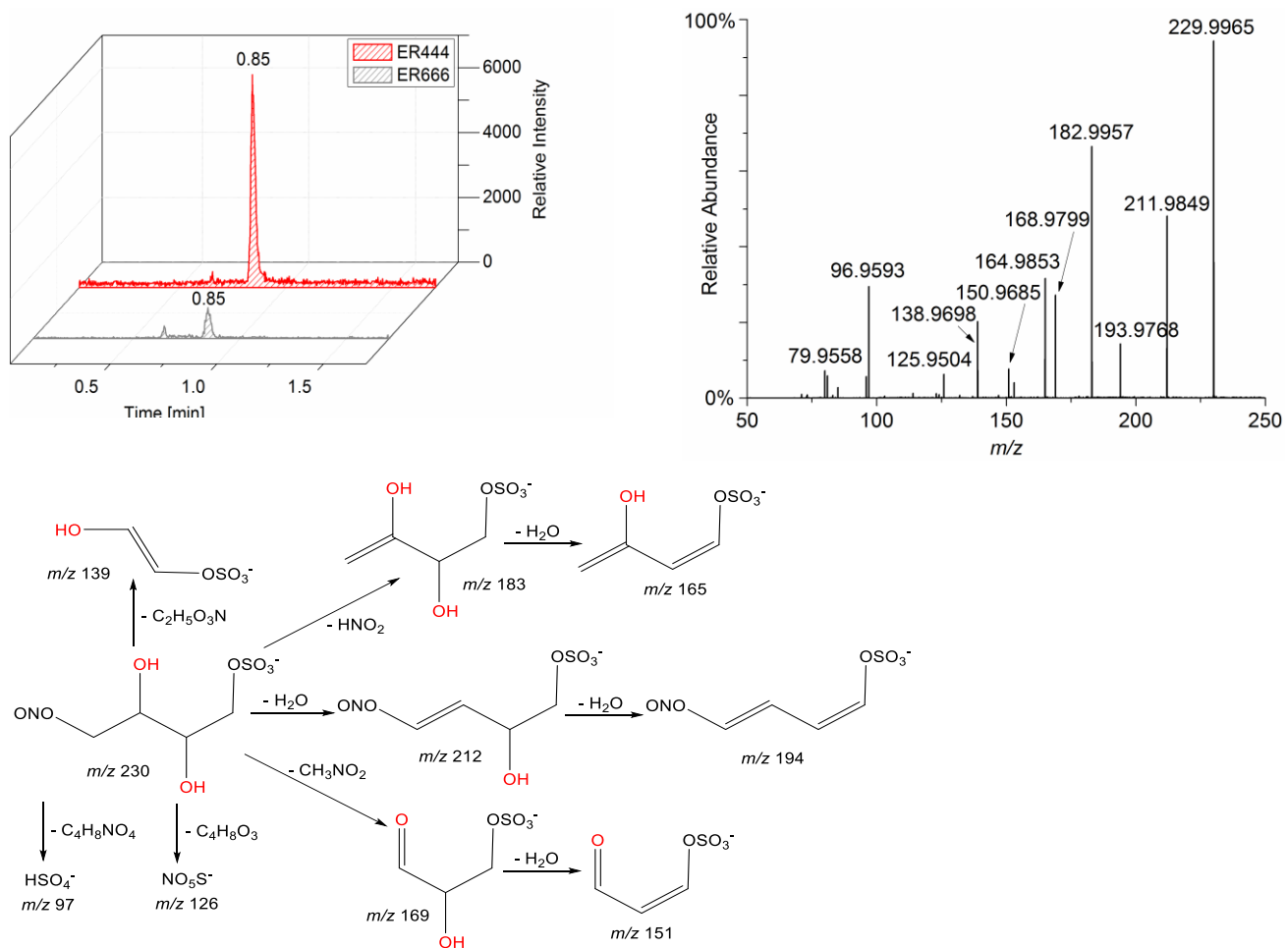
**Figure S7.** Extracted Ion Chromatogram of butanal, 3,4-dihydroxy-organosulfate with MW 184 from smog chamber experiment with ESI(-) product ion mass spectrum recorded for the RT = 0.85 min peak from ER444 sample.



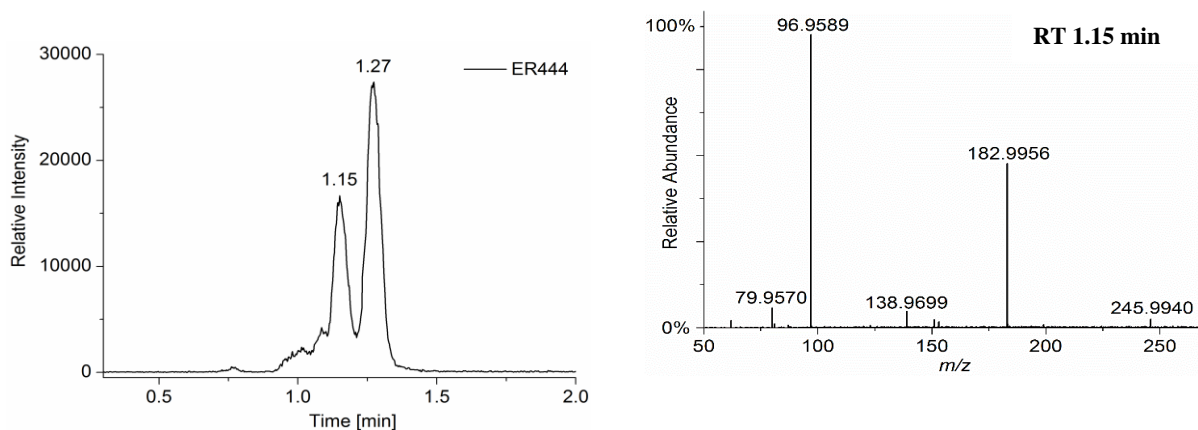
**Figure S8.** Extracted Ion Chromatograms of butanal, 2,3,4-trihydroxy- organosulfate with MW 200 from smog chamber experiments with ESI(-) product ion mass spectrum recorded for the RT = 0.73 min peak from ER444 sample.

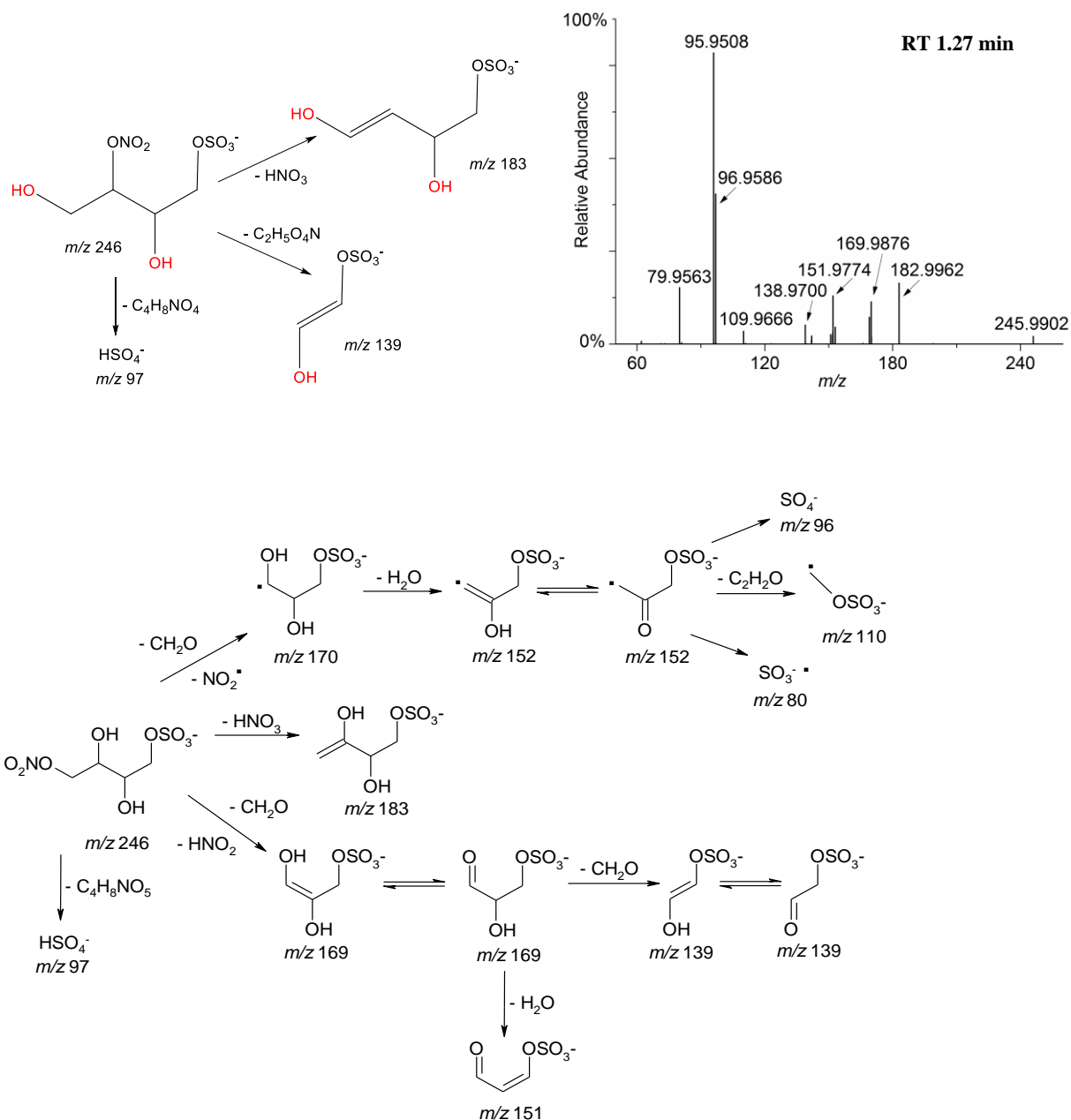


**Figure S9.** Extracted Ion Chromatograms of 1,2,3,4-butanetetrol organosulfate with MW 202 from smog chamber experiments and ambient sample with ESI(-) product ion mass spectrum recorded for the RT = 0.70 min peak from ER444 sample.

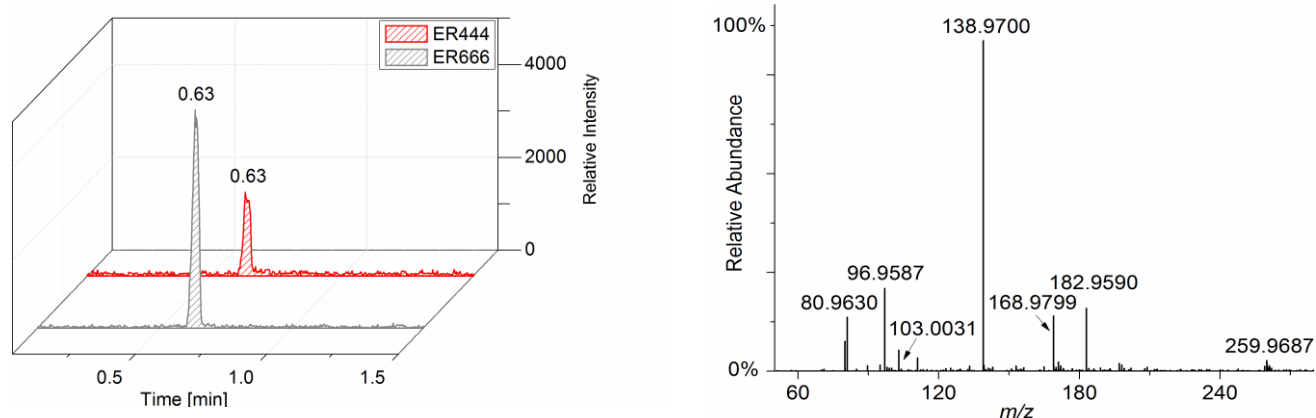


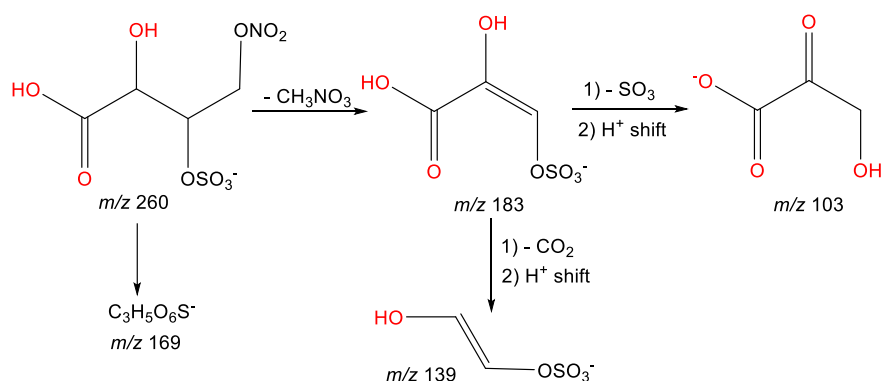
**Figure S10.** Extracted Ion Chromatograms of 1,2,3,4- butanetetrol nitrosoxy-organosulfate with MW 231 from smog chamber experiments with ESI(-) product ion mass spectrum recorded for the RT = 0.85 min peak from ER444 sample.





**Figure S11.** Extracted Ion Chromatogram of 1,2,3,4-butanetetrrol nitroxy-organosulfate with MW 247 from smog chamber experiment with ESI(-) product ion mass spectra recorded for the RT = 1.15 min and RT = 1.27 min peaks from ER444 sample.





**Figure S12.** Extracted Ion Chromatograms of threonic acid nitroxy-organosulfate with MW 261 from smog chamber experiments with ESI(-) product ion mass spectrum recorded for the RT = 0.63 min peak from ER666 sample.

**Table S5.** Estimated concentrations of selected reaction products ( $\text{ng m}^{-3}$ ) from ER666 photooxidation experiments.

	RH (11%)	RH (20%)	RH (29%)	RH (39%)	RH (49%)	RH (60%)
Glyceric acid	187.19	145.65	48.33	91.67	75.04	72.53
D-Threono-1,4-lactone	5.92	10.46	5.71	2.46	1.97	3.57
1,3,4-Trihydroxy-1-butene	41.71	26.58	16.06	13.86	9.59	9.41
Hydroxymaleic acid	24.37	13.64	5.24	5.40	4.15	5.13
Erythrose	54.90	5.16	10.24	3.61	2.90	3.05
Malic acid	57.75	73.20	58.51	70.95	37.25	50.44
Threitol	114.56	66.78	56.27	18.20	18.37	14.31
<i>meso</i> -Erythritol	128.20	60.01	56.15	19.81	19.03	15.18
D-Threonic acid	132.64	104.03	90.42	80.39	79.94	80.18
Threonic acid isomer	11.51	5.69	9.12	2.31	3.39	0.00
<i>meso</i> -Threonic acid	207.24	195.04	180.80	108.36	88.02	82.55
Dihydroxymaleic acid	59.40	34.21	26.47	22.44	16.94	16.22
Tartaric acid	4.80	3.73	3.19	2.85	1.59	1.49
Tartaric acid isomer	6.73	7.71	8.35	6.51	3.64	3.62
<b>Oligomers: non-acidified seed aerosol</b>						
Oxalic acid-1,3,4-Trihydroxy-1-butene ester	136.83	178.21	153.60	150.01	80.69	85.99
Oxalic acid-erythrose ester	34.38	21.73	27.80	20.31	11.35	16.23
Glyceric acid-1,3,4-trihydroxy-1-butene ester	798.43	572.05	566.02	332.40	159.39	142.91
Hydroxymaleic acid-glycerol	86.77	89.38	89.36	84.34	41.62	45.42
<b>Unknowns: non-acidified seed aerosol</b>						
U-3	28.42	35.29	48.32	30.34	18.06	26.19
U-6	43.71	44.37	43.22	0.00	7.68	8.68
U-7	46.90	40.77	45.66	0.00	7.22	6.64



**Table S6.** Estimated concentrations of selected reaction products (ng m<sup>-3</sup>) from ER444 photooxidation experiments.

	RH (10%)	RH (31%)	RH (50%)	RH (62%)
Glyceric acid	833.18	1064.74	429.63	130.95
D-Threono-1,4-lactone	124.09	89.42	75.51	51.04
1,3,4-Trihydroxy-1-butene	133.44	180.53	56.93	71.68
Hydroxymaleic acid	74.98	27.24	12.76	0.00
Erythrose	16.10	12.66	0.00	0.00
Malic acid	0.00	42.76	17.89	0.00
<i>Threitol</i>	283.56	203.46	91.16	55.35
meso-erythritol	325.46	259.07	120.82	69.89
D-Threonic acid	74.39	70.09	63.14	41.67
Threonic acid isomer	178.32	120.60	77.96	51.13
meso-Threonic acid	36.35	19.98	29.10	9.94
Dihydroxymaleic acid	22.31	0.00	0.00	0.00
Tartaric acid	43.51	19.19	9.07	6.44
Tartaric acid isomer	79.37	24.84	8.75	9.30
<b>Oligomers: acidified seed aerosol</b>				
Oxalic acid-1,3,4-Trihydroxy-1-butene ester	334.00	226.52	90.84	118.83
Oxalic acid-erythrulose ester	307.57	86.69	100.26	93.45
Glyceric acid-1,3,4-trihydroxy-1-butene ester	348.69	497.35	157.48	218.42
Hydroxymaleic acid-glycerol	203.54	151.78	184.64	26.77
<b>Unknowns: acidified seed aerosol</b>				
U-1	220.45	26.18	18.29	12.15
U-2	174.87	169.71	56.21	6.05
U-3	260.50	267.88	106.15	93.80
U-4	544.69	105.25	92.73	83.68
U-5	293.90	70.08	39.24	40.36
U-6	554.89	571.70	493.35	440.39
U-7	203.54	156.60	88.65	54.69

**Table S7.** Estimated concentrations of selected reaction products (ng m<sup>-3</sup>) from ER666 photooxidation experiments

	RH 9	RH 19	RH 30	RH 39	RH 49	RH 60
<b>LC-MS data **</b>						
<i>m/z</i> [M – H] <sup>-</sup>						
183	3.01 ± 0.49	< LOD	< LOD	< LOD	< LOD	< LOD

185	64.87 ± 2.88	70.87 ± 5.84	74.83 ± 4.92	85.91 ± 3.24	82.82 ± 2.00	59.36 ± 2.50
199	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
201	11.97 ± 1.50	7.81 ± 0.84	2.91 ± 0.43	1.95 ± 0.65	2.72 ± 0.28	< LOD
213	1.78 ± 0.45	2.76 ± 0.58	2.14 ± 0.35	4.47 ± 0.87	4.27 ± 0.65	1.67 ± 0.28
215	2.22 ± 0.45	1.15 ± 0.38	< LOD	< LOD	2.18 ± 1.21	< LOD
230	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
246	455.07 ± 6.06	444.47 ± 2.82	349.36 ± 2.02	291.88 ± 1.68	361.16 ± 2.44	186.02 ± 4.90
260	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

\*\* concentrations were estimated based on selected [M-H]<sup>-</sup> ions

**Table S8.** Estimated concentrations of reaction products (ng m<sup>-3</sup>) from ER444 photooxidation experiments

	<b>RH 10</b>	<b>RH 31</b>	<b>RH 50</b>	<b>RH 62</b>
<b>LC-MS data **</b>				
<i>m/z</i> [M - H] <sup>-</sup>				
183	133.74 ± 3.23	80.31 ± 5.41	48.73 ± 2.21	35.46 ± 1.41
185	106.26 ± 4.14	90.31 ± 3.77	52.93 ± 2.86	34.79 ± 1.87
197	27.19 ± 0.47	20.81 ± 1.94	4.75 ± 0.08	9.38 ± 1.64
199	27.72 ± 0.46	12.75 ± 0.92	7.19 ± 0.60	8.03 ± 0.83
201	230.69 ± 6.08	112.61 ± 5.65	56.97 ± 2.28	51.17 ± 3.08
213	7.22 ± 0.96	6.77 ± 2.87	5.19 ± 1.95	< LOD
215	11.29 ± 2.08	5.71 ± 5.71	2.67 ± 0.76	< LOD
230	75.55 ± 4.30	37.66 ± 2.81	25.89 ± 3.60	25.16 ± 1.56
246	3251.52 ± 29.98	1969.09 ± 113.47	1293.69 ± 24.36	957.31 ± 26.68
260	< LOD	< LOD	< LOD	< LOD

\*\* concentrations were estimated based on selected [M-H]<sup>-</sup>

## Section S2. Input data for EAIM modelling of particle acidity

### *Non-acidified seed experiments*

$1\mu\text{g m}^{-3} (\text{NH}_4)_2\text{SO}_4$                        $M=132.14 \text{ g/mol}$

$[\text{NH}_4^+] = 2 \times 1 \times 10^{-6} \text{ g m}^{-3} / 132.14 \text{ g/mol} = 1.5135 \times 10^{-8} \text{ mol m}^{-3}$

$[\text{SO}_4^{2-}] = 1 \times 10^{-6} \text{ g m}^{-3} / 132.14 \text{ g/mol} = 7.5677 \times 10^{-9} \text{ mol m}^{-3}$

RH /temp.      11 %, 25.3 °C;  
                    20 %, 25.3 °C;  
                    29 %, 25.1 °C;  
                    39 %, 24.7 °C;  
                    49 %, 25.0 °C;  
                    60 %, 24.7 °C.

### *Acidified seed experiments*

$\sim 35 \mu\text{g m}^{-3} \text{ SO}_4^{2-}$                        $M = 96.07 \text{ g/mol}$

1/3 as  $(\text{NH}_4)_2\text{SO}_4$  and 2/3 as  $\text{H}_2\text{SO}_4$

$11.67 \mu\text{g SO}_4^{2-} \text{ m}^{-3}$  as  $(\text{NH}_4)_2\text{SO}_4$

that is  $11.67 \times 10^{-6} \text{ g m}^{-3} / 96.07 \text{ g mol}^{-1} \text{ SO}_4^{2-} = 1.2147 \times 10^{-7} \text{ mol SO}_4^{2-} \text{ m}^{-3}$

and  $2 \times 1.2147 \times 10^{-7} = 2.4294 \times 10^{-7} \text{ mol NH}_4^+ \text{ m}^{-3}$

$23.33 \mu\text{g SO}_4^{2-} \text{ m}^{-3}$  as  $\text{H}_2\text{SO}_4$

that is  $23.33 \times 10^{-6} \text{ g m}^{-3} / 96.07 \text{ g mol}^{-1} \text{ SO}_4^{2-} = 2.4284 \times 10^{-7} \text{ mol SO}_4^{2-} \text{ m}^{-3}$

and  $2 \times 2.4284 \times 10^{-7} = 4.8568 \times 10^{-7} \text{ mol H}^+ \text{ m}^{-3}$

Together,  $\text{SO}_4^{2-} = 1.2147 \times 10^{-7} + 2.4284 \times 10^{-7} = 3.6431 \times 10^{-7} \text{ mol SO}_4^{2-} \text{ m}^{-3}$

Check  $35 \times 10^{-6} / 96.07 = 3.6432 \times 10^{-7} \text{ mol SO}_4^{2-} \text{ m}^{-3}$       OK

Thus,

$[\text{NH}_4^+] = 2.4294 \times 10^{-7} \text{ mol m}^{-3}$

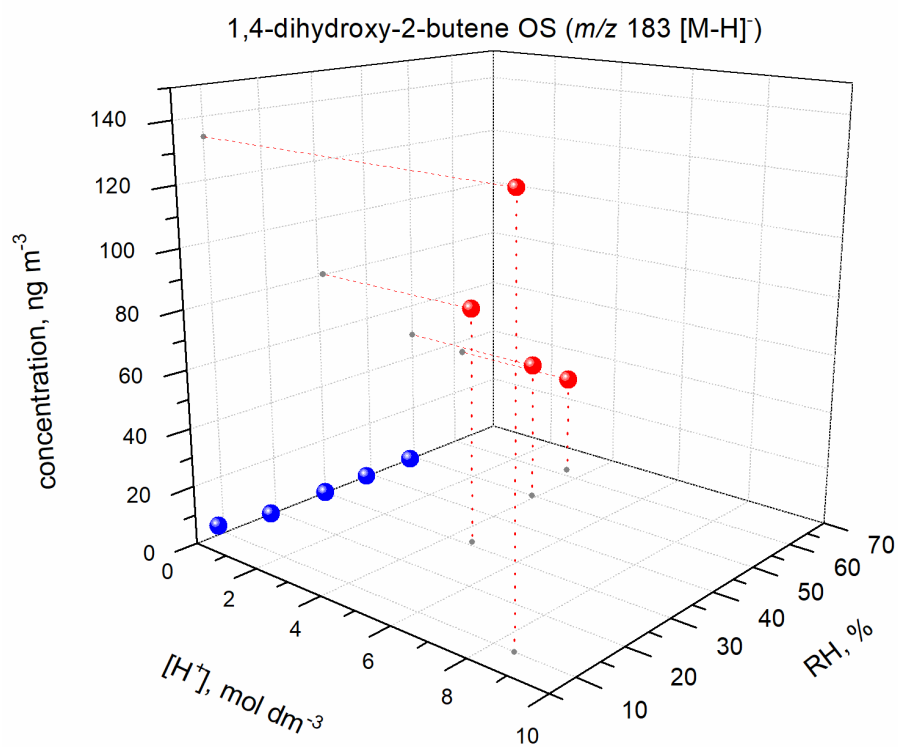
$$[\text{SO}_4^{2-}] = 3.6431 \times 10^{-7} \text{ mol m}^{-3}$$

$$[\text{H}^+] = 4.8568 \times 10^{-7} \text{ mol m}^{-3}$$

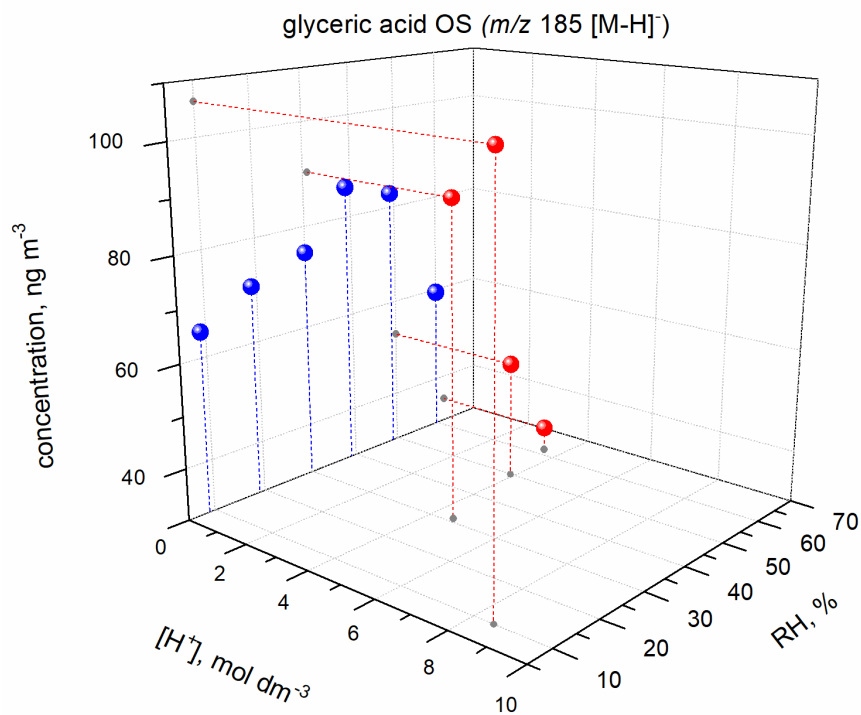
RH /temp.    10 %, 22.4 °C;  
                  31 %, 22.6 °C;  
                  50 %, 22.2 °C;  
                  62 %, 22.2 °C.

### Influence of RH and acidity on the product yields

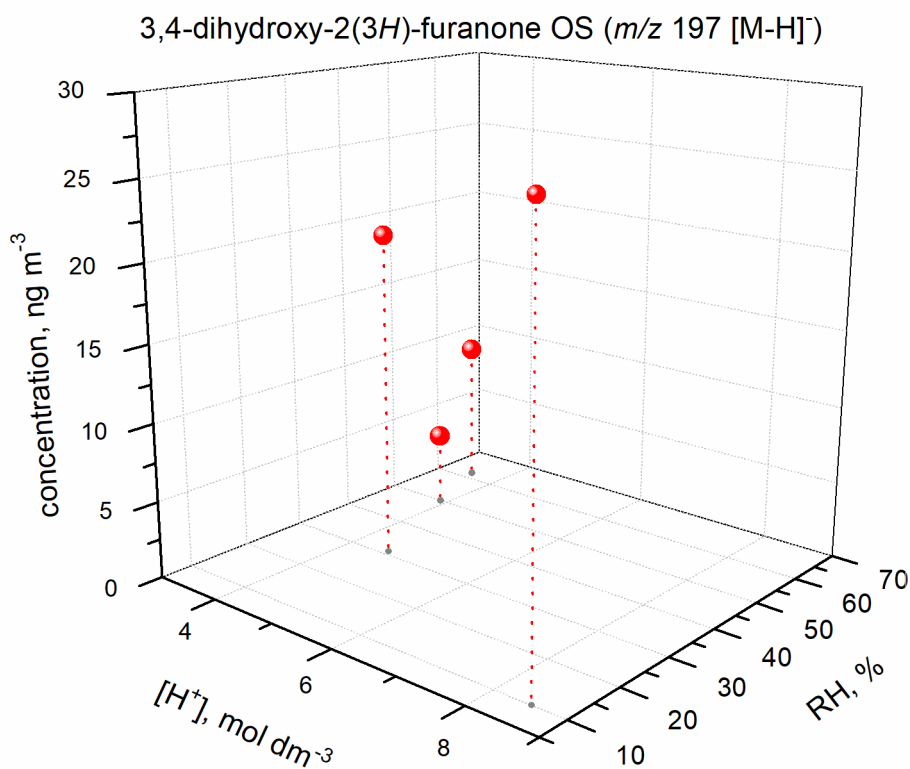
#### Organosulfates



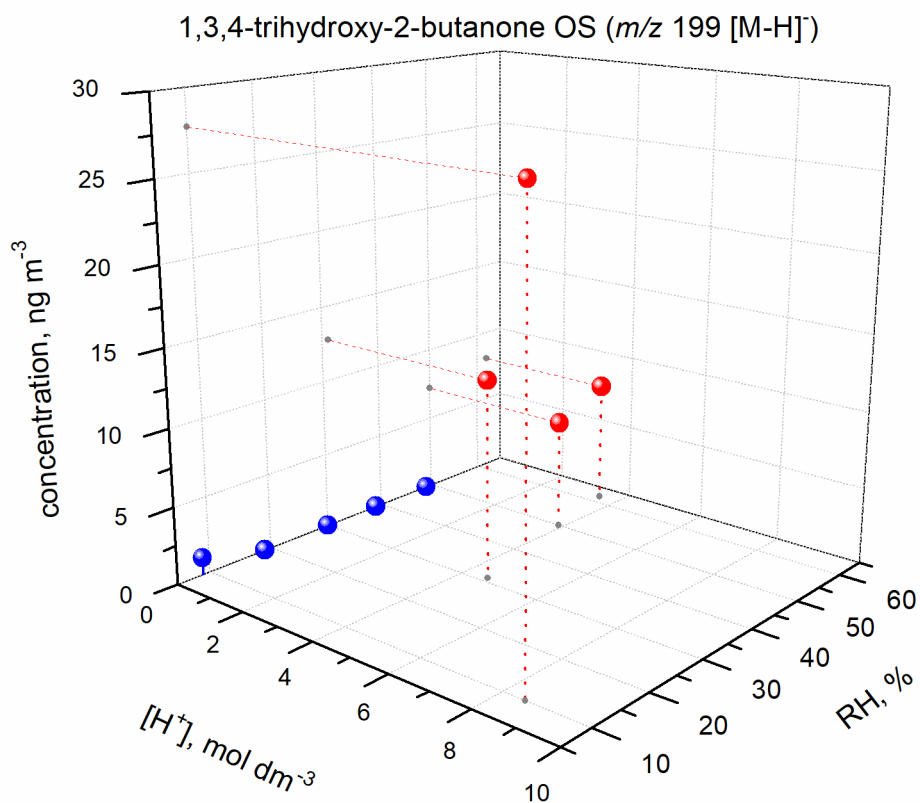
**Figure S13.** Concentrations of 1,4-dihydroxy-2-butene organosulfate ( $m/z$  183 [M-H]<sup>-</sup>) in non-acidified (blue) and acidified (red) experiments.



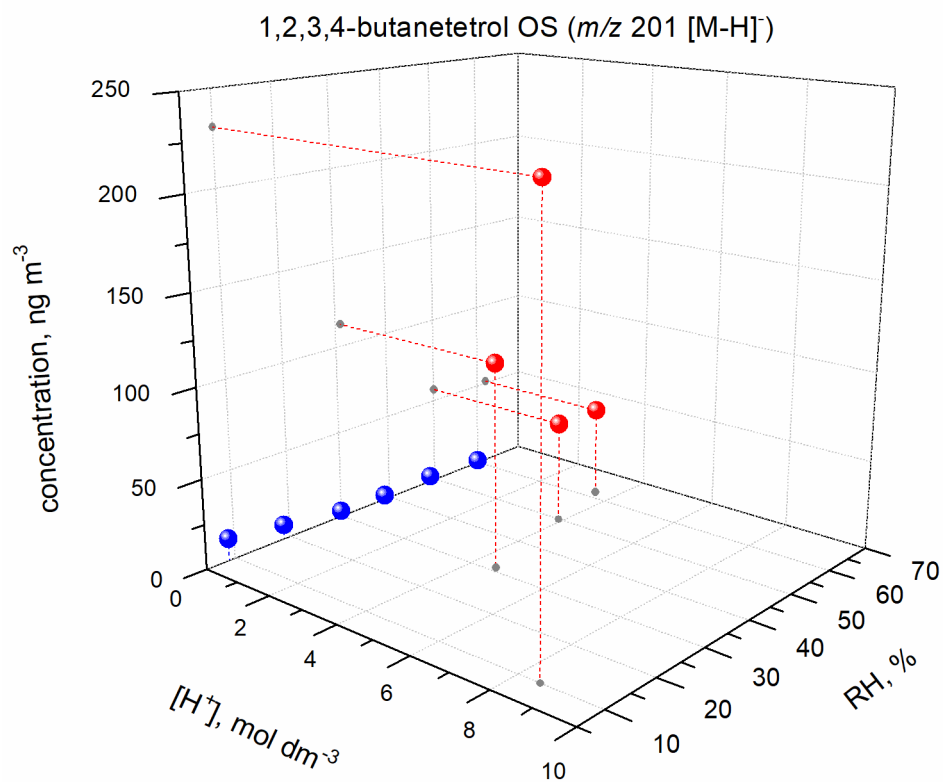
**Figure S14.** Concentrations of glyceric acid organosulfate ( $m/z$  185 [M-H]<sup>-</sup>) in non-acidified (blue) and acidified (red) experiments.



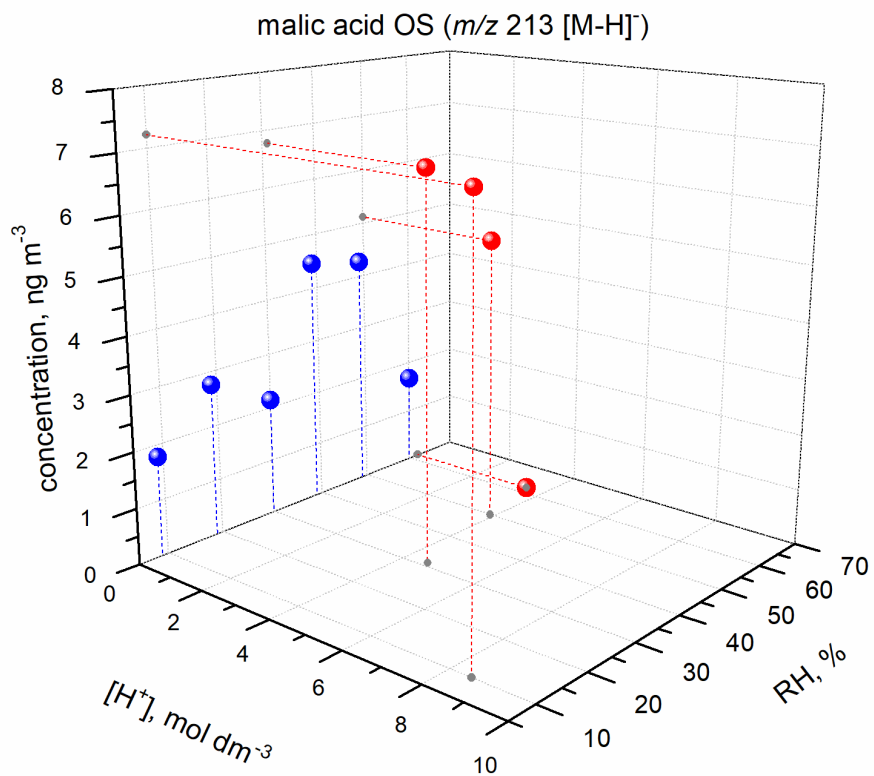
**Figure S15.** Concentrations of 3,4-dihydroxy-2(3*H*)-furanone organosulfate ( $m/z$  197) in non-acidified (blue) and acidified (red) experiments.



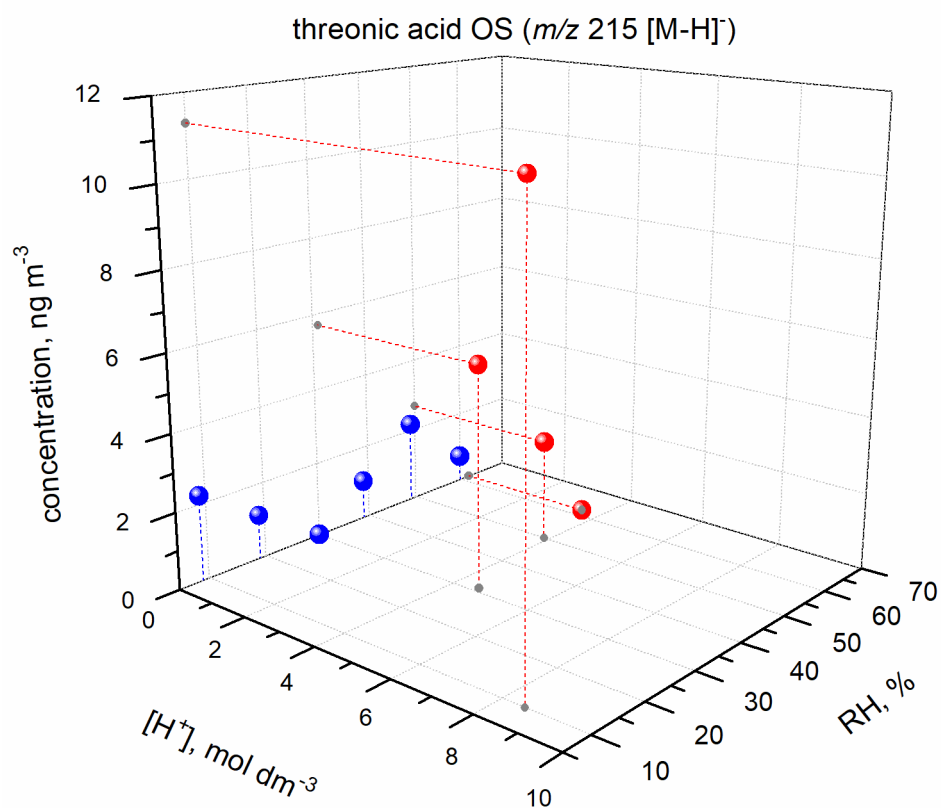
**Figure S16.** Concentrations of 1,3,4-trihydroxy-2-butanone organosulfate ( $m/z$  199 [M-H]<sup>-</sup>) in non-acidified (blue) and acidified (red) experiments.



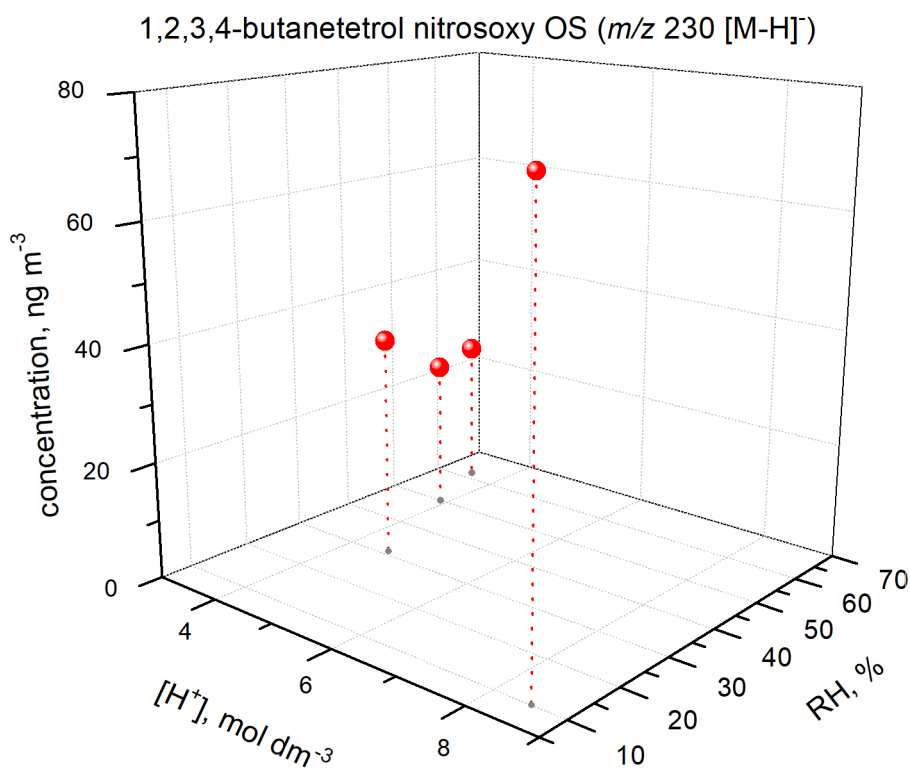
**Figure S17.** Concentrations of 1,2,3,4-butanetetrol OS ( $m/z$  201 [M-H]<sup>-</sup>) in non-acidified (blue) and acidified (red) experiments.



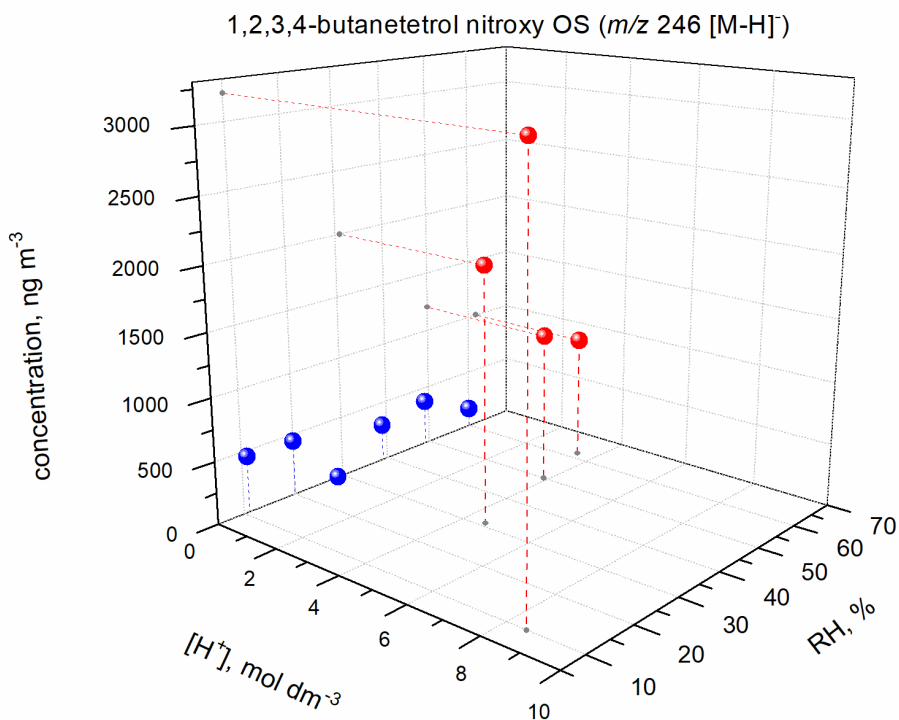
**Figure S18.** Concentrations of malic acid organosulfate ( $m/z$  213 [M-H]<sup>-</sup>) in non-acidified (blue) and acidified (red) experiments.



**Figure S19.** Concentrations of threonic acid organosulfate ( $m/z$  215 [M-H]<sup>-</sup>) in non-acidified (blue) and acidified (red) experiments.



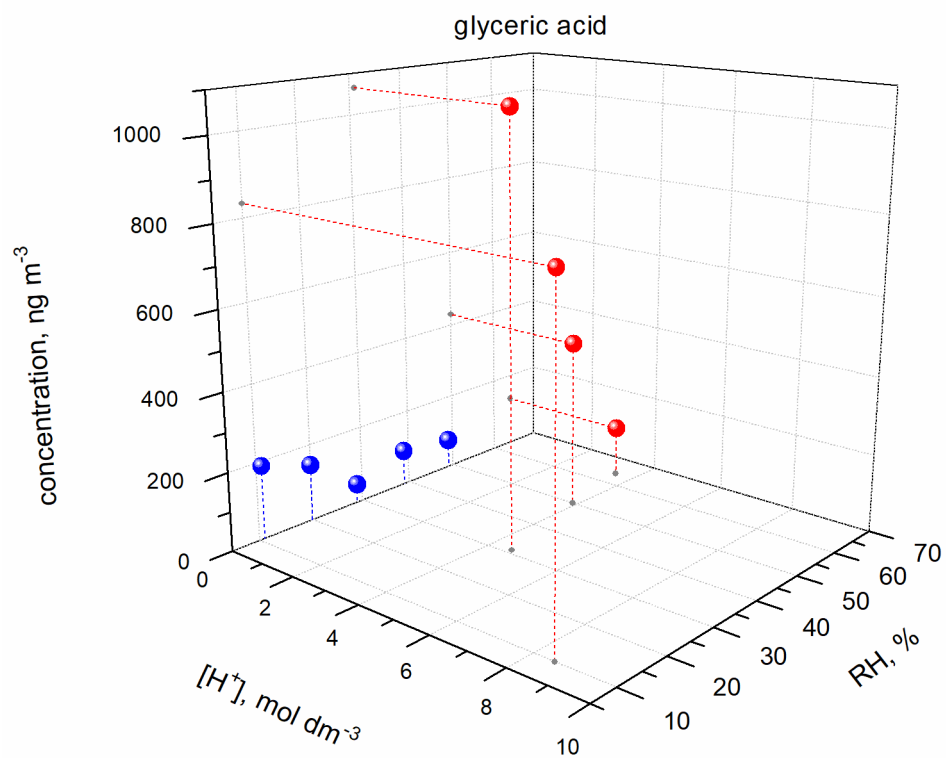
**Figure S20.** Concentrations of 1,2,3,4-butanetetrol nitrosoxy organosulfate ( $m/z$  230 [M-H]<sup>-</sup>) in non-acidified (blue) and acidified (red) experiments.



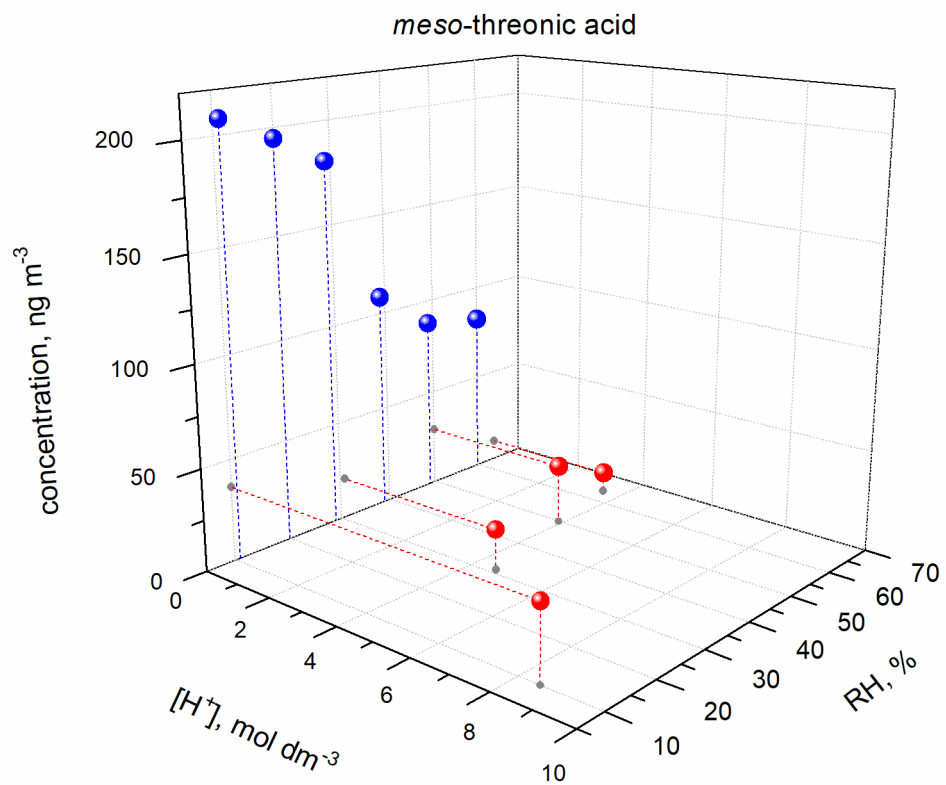
**Figure S21.** Concentrations of 1,2,3,4-butanetetrol nitrosoxy-organosulfate ( $m/z$  246 [M-H]<sup>-</sup>) in non-acidified (blue) and acidified (red) experiments.



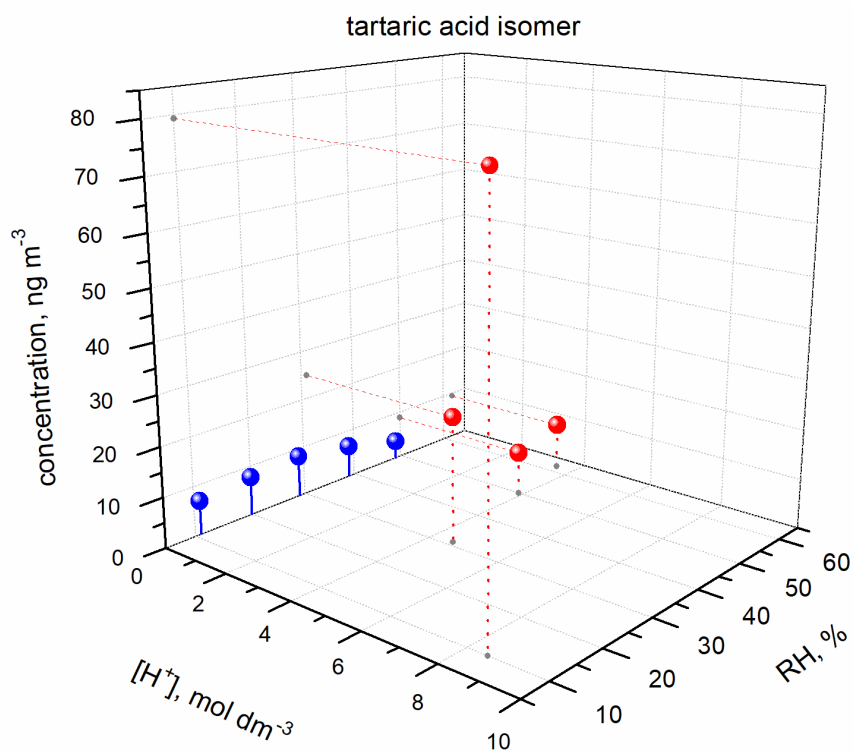
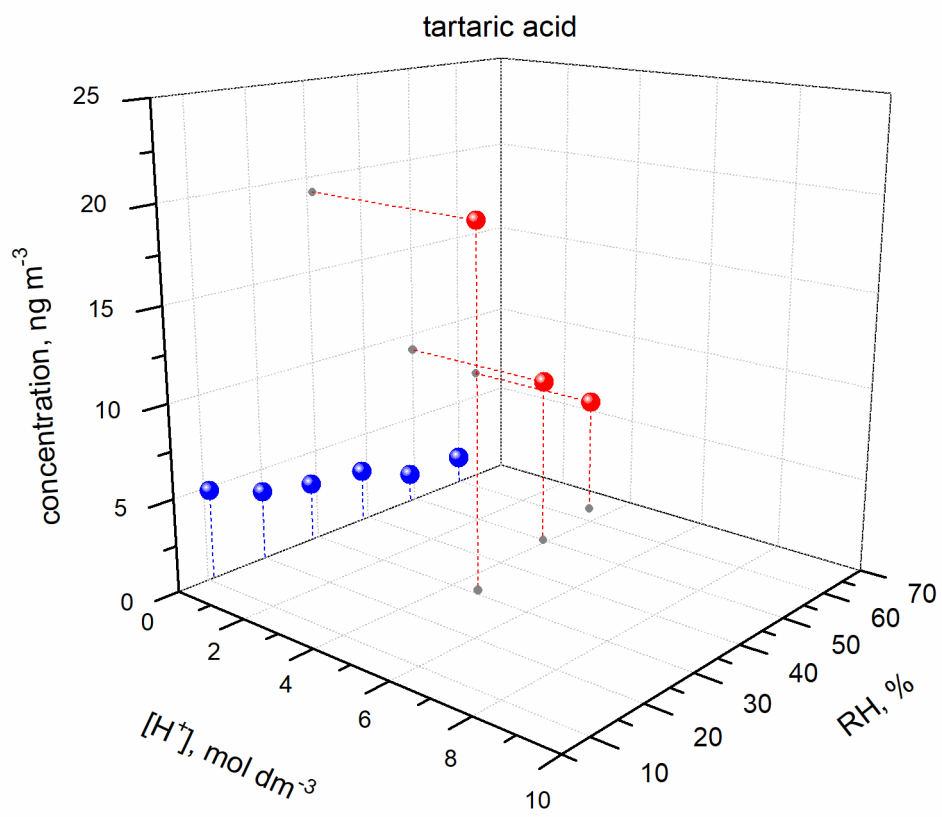
**Organic acids, sugar alcohols and lactones**



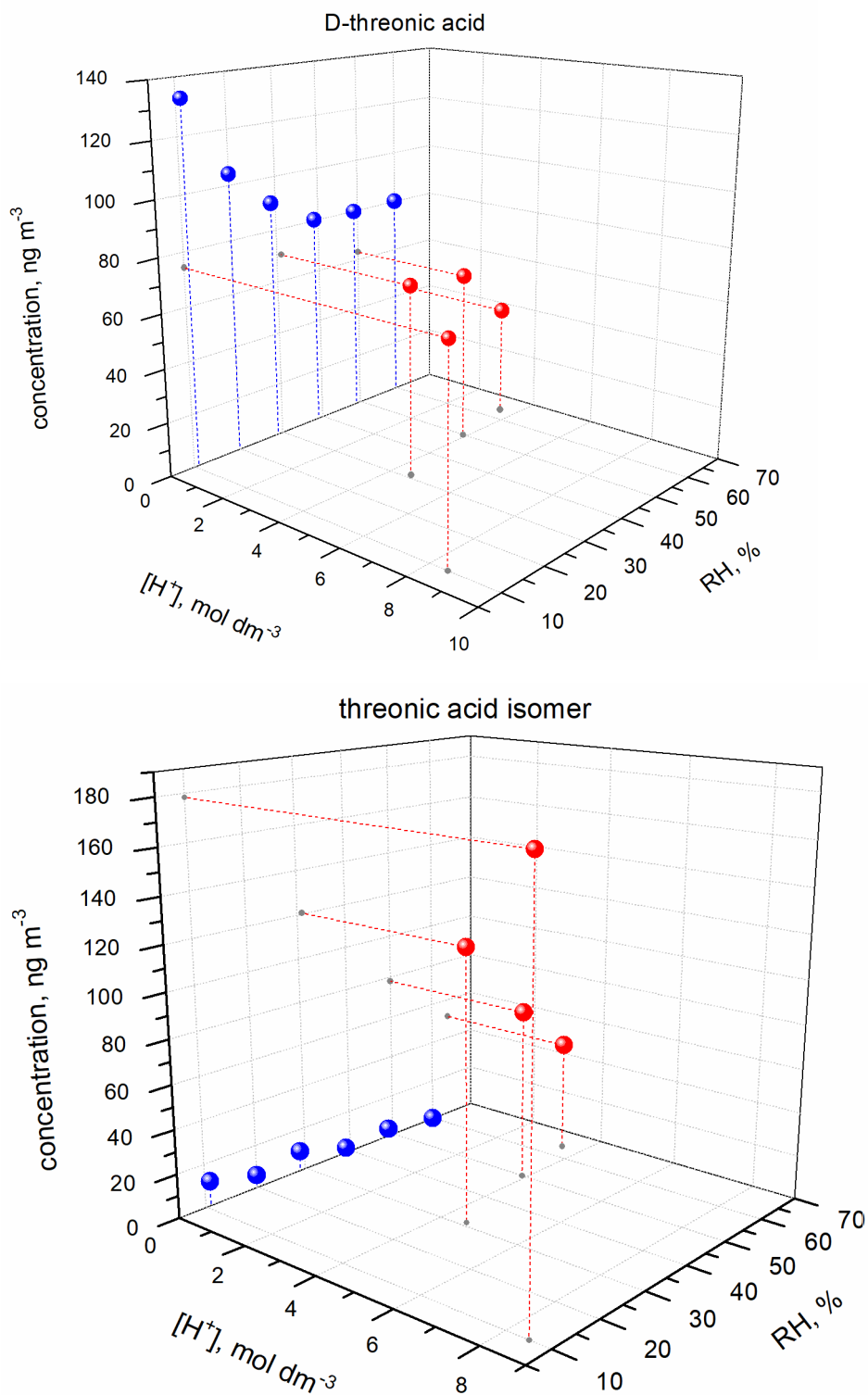
**Figure S22.** Concentrations of glyceric acid in non-acidified (blue) and acidified (red) experiments.



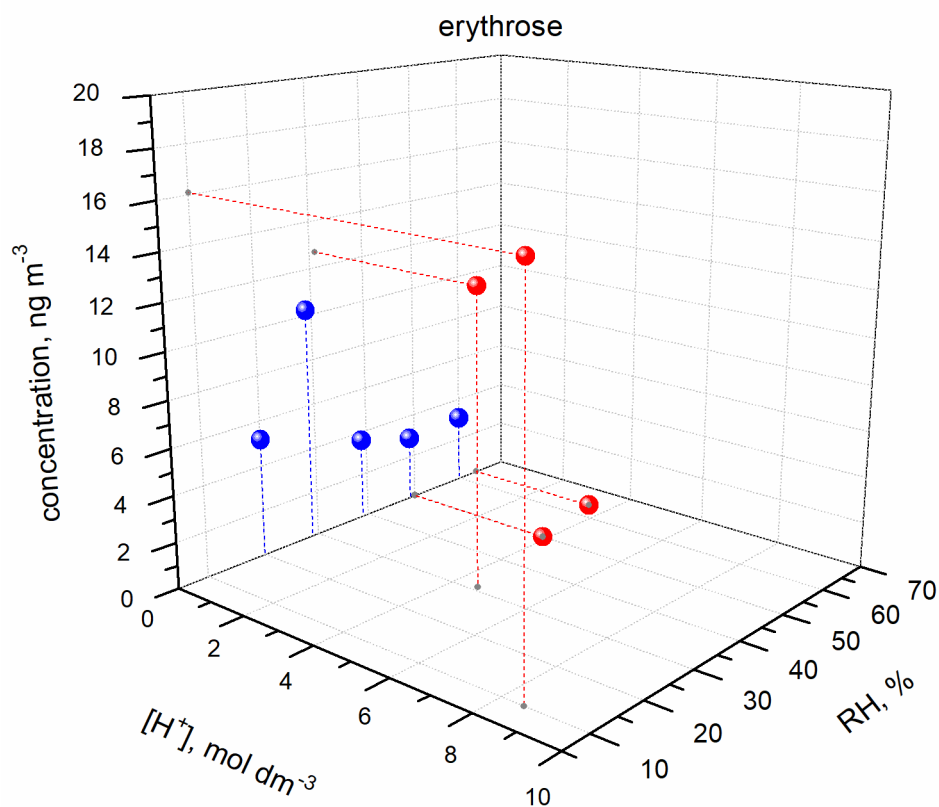
**Figure S23.** Concentrations of *meso*-threonic acid in non-acidified (blue) and acidified (red) experiments.



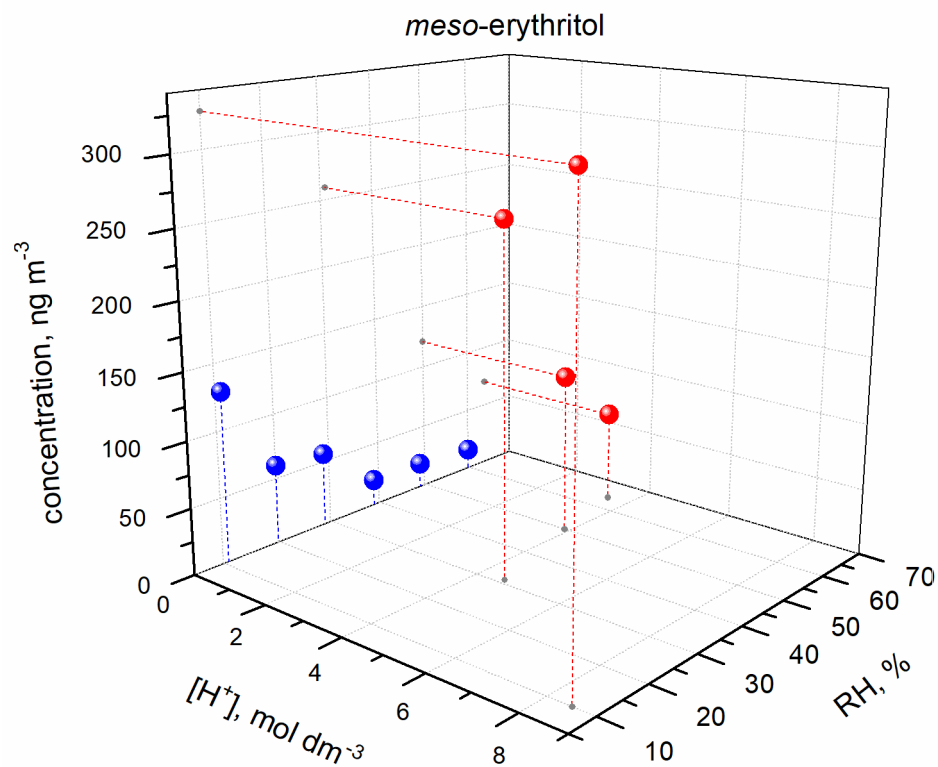
**Figure S24.** Concentrations of tartaric acid isomers in non-acidified (blue) and acidified (red) experiments.



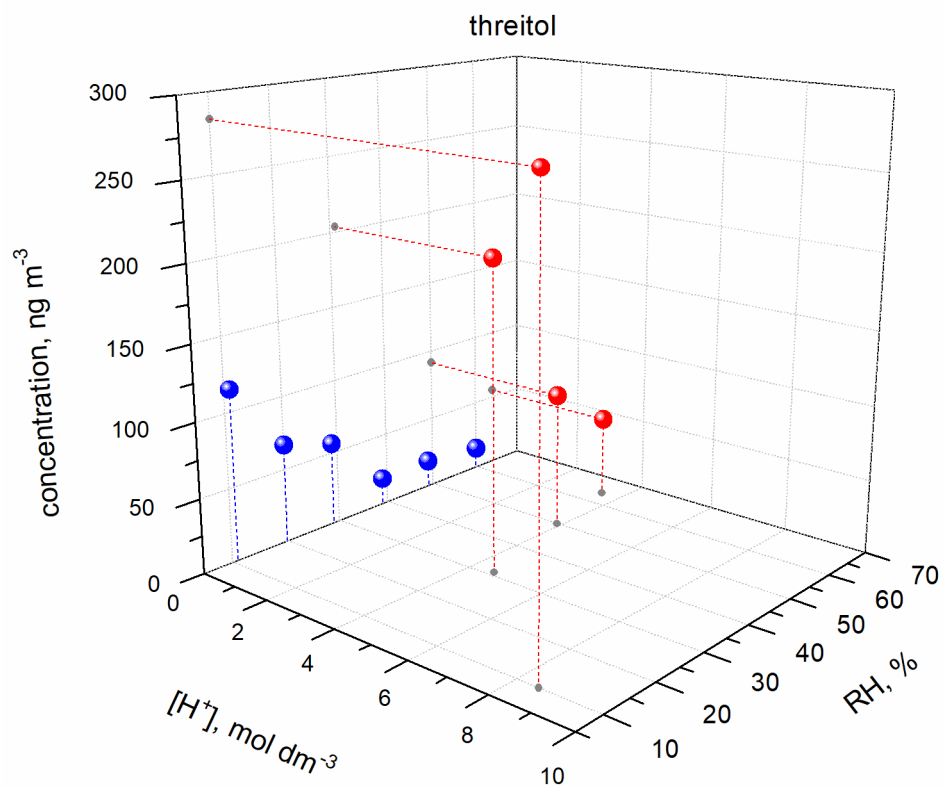
**Figure S25.** Concentrations of threonic acid isomers in non-acidified (blue) and acidified (red) experiments.



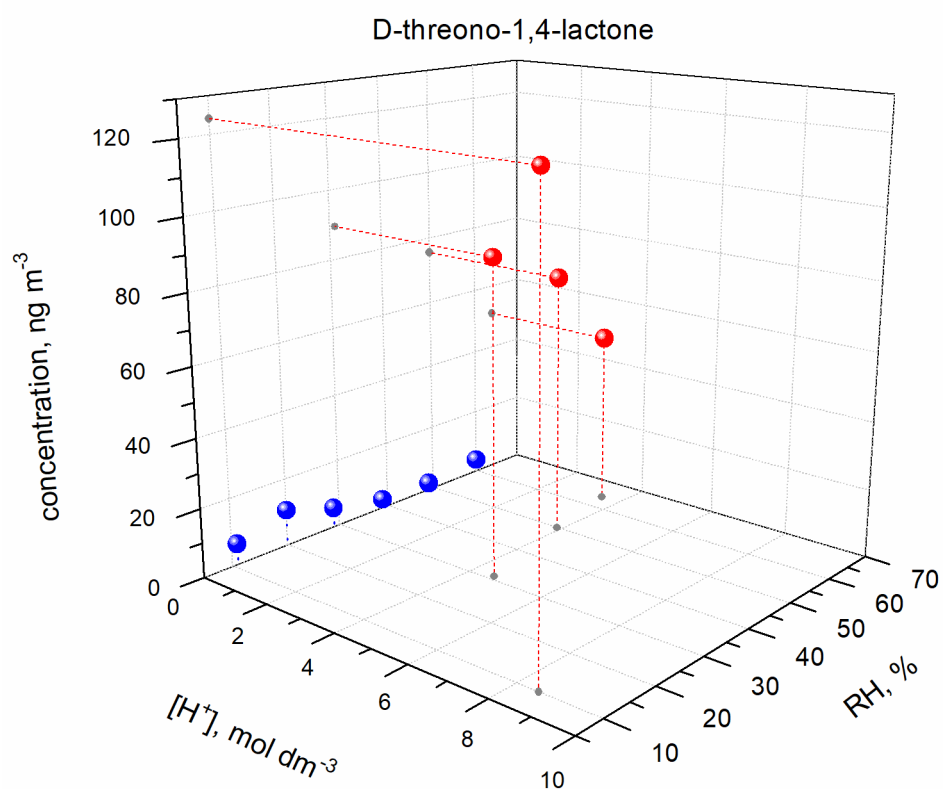
**Figure S26.** Concentrations of erythrose in non-acidified (blue) and acidified (red) experiments.



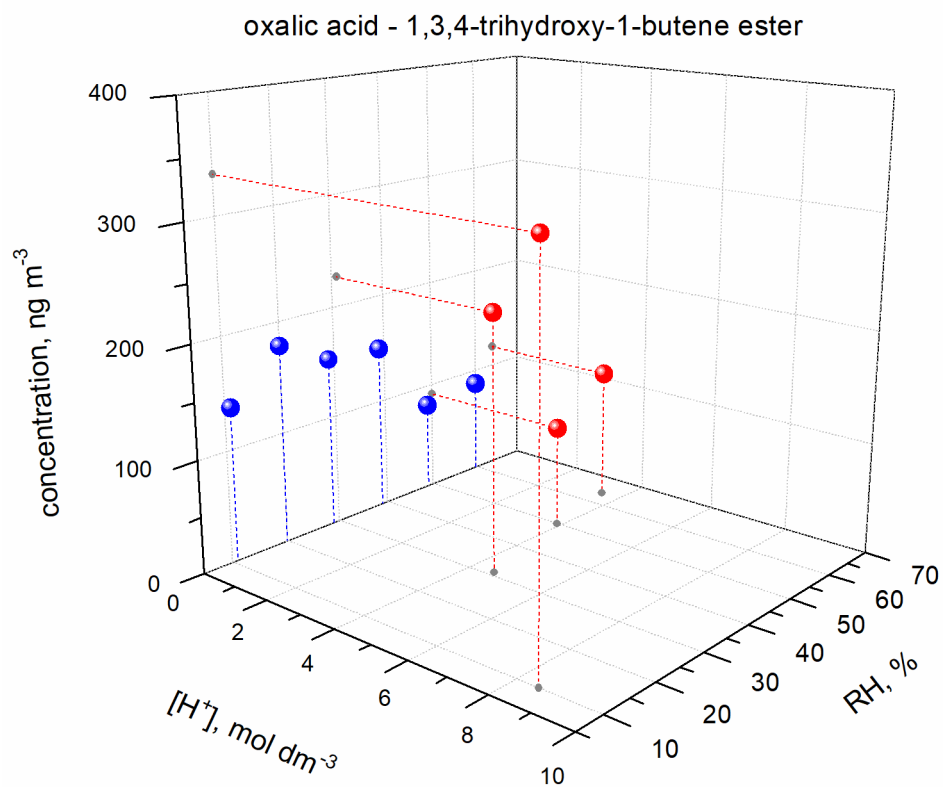
**Figure S27.** Concentrations of *meso*-erythritol in non-acidified (blue) and acidified (red) experiments.



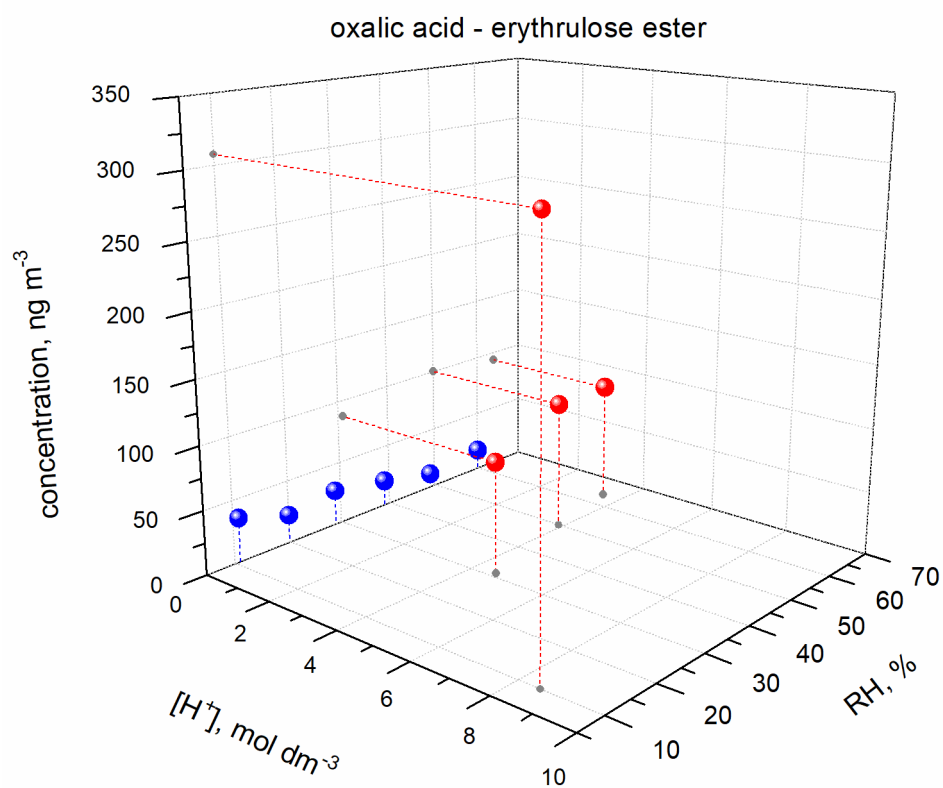
**Figure S28.** Concentrations of threitol in non-acidified (blue) and acidified (red) experiments.



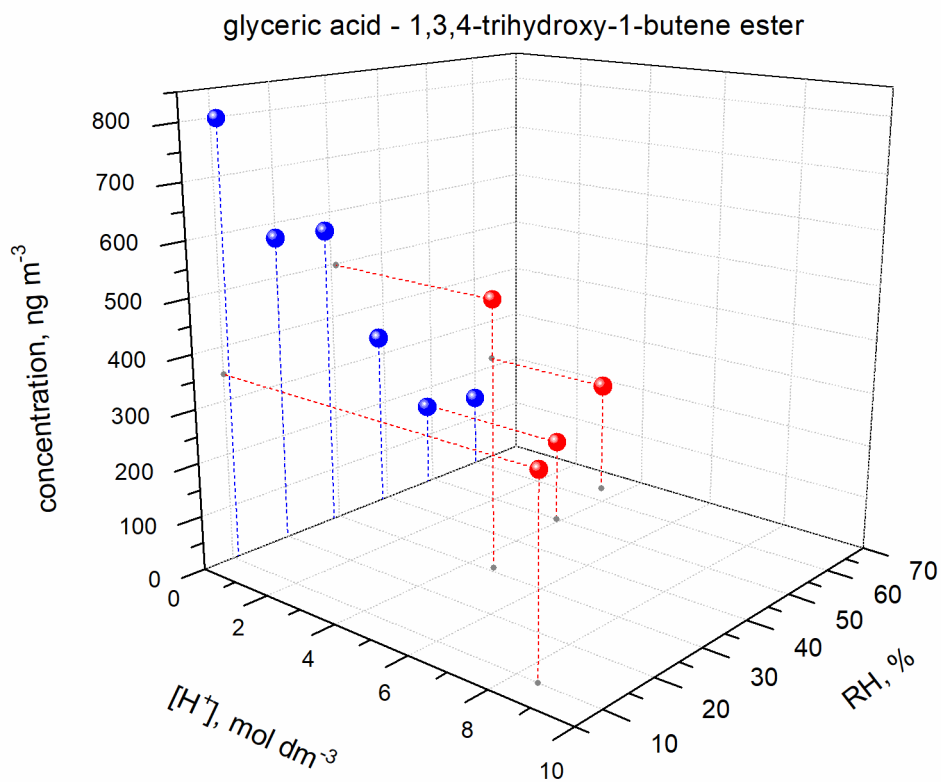
**Figure S29.** Concentrations of D-threono-1,4-lactone in non-acidified (blue) and acidified (red) experiments.



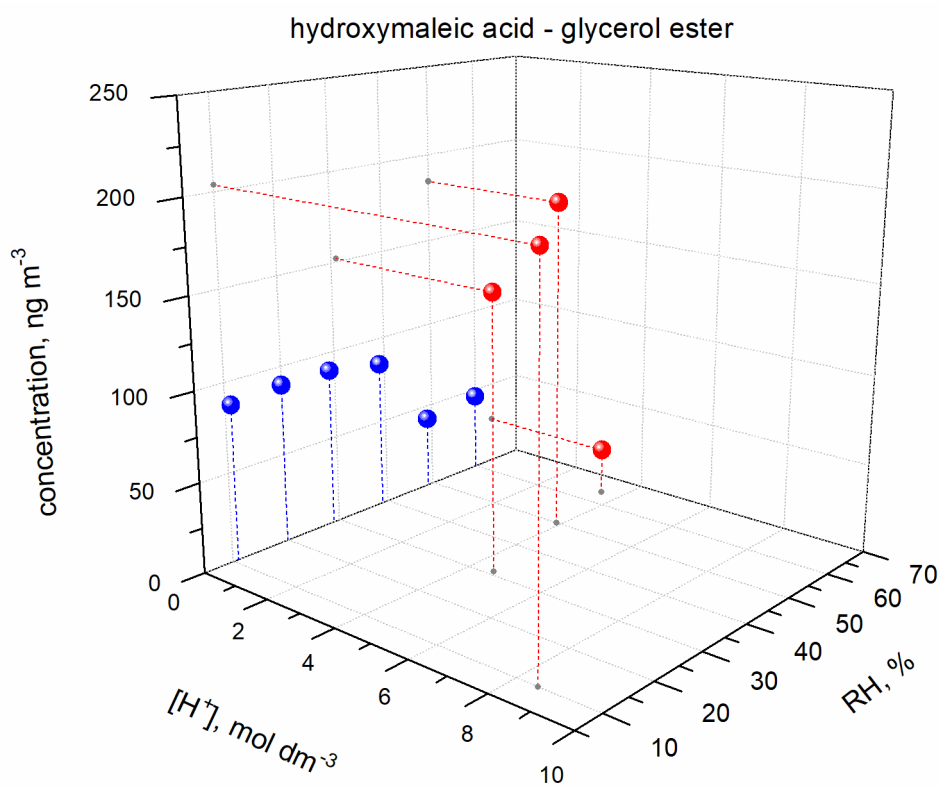
**Figure S30.** Concentrations of oxalic acid – 1,3,4-trihydroxy-1-butene ester in non-acidified (blue) and acidified (red) experiments.



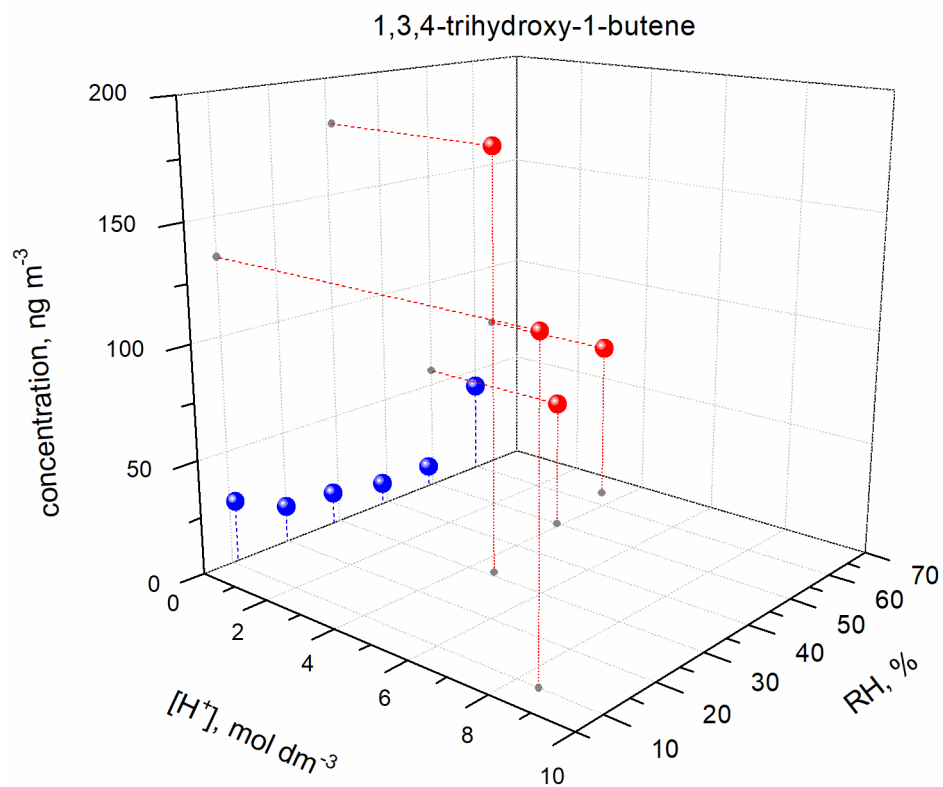
**Figure S31.** Concentrations of oxalic acid – erythulose ester in non-acidified (blue) and acidified (red) experiments.



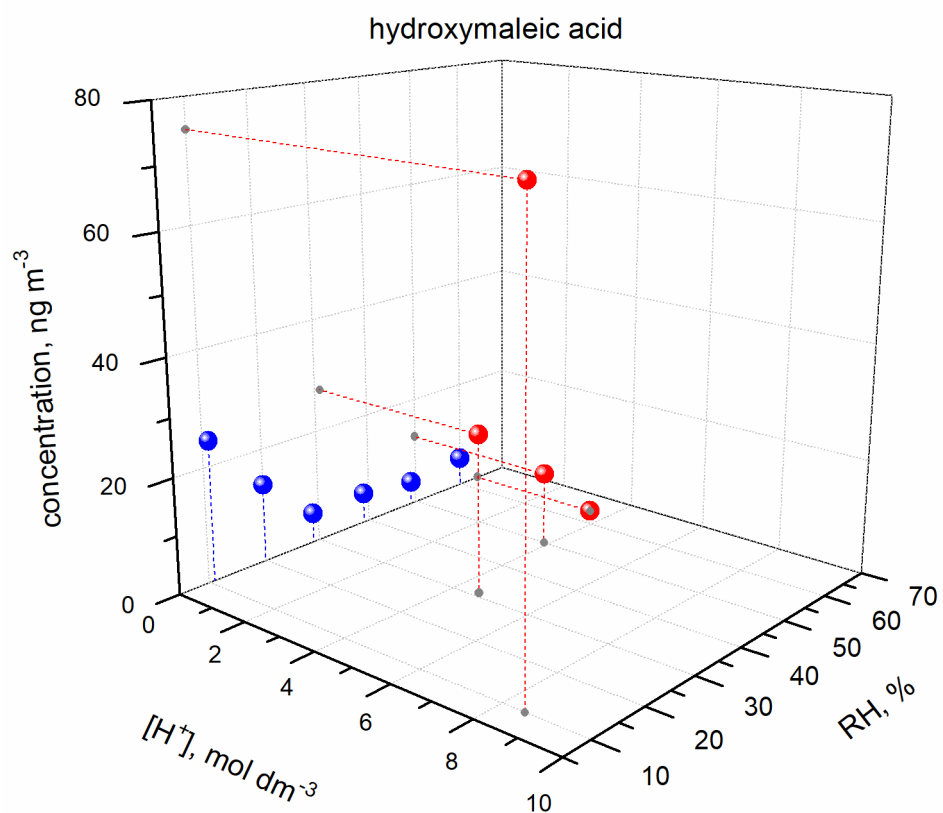
**Figure S32.** Concentrations of glyceric acid – 1,3,4-trihydroxy-1-butene ester in non-acidified (blue) and acidified (red) experiments.



**Figure S33.** Concentrations of hydroxymaleic acid – glycerol ester in non-acidified (blue) and acidified (red) experiments.

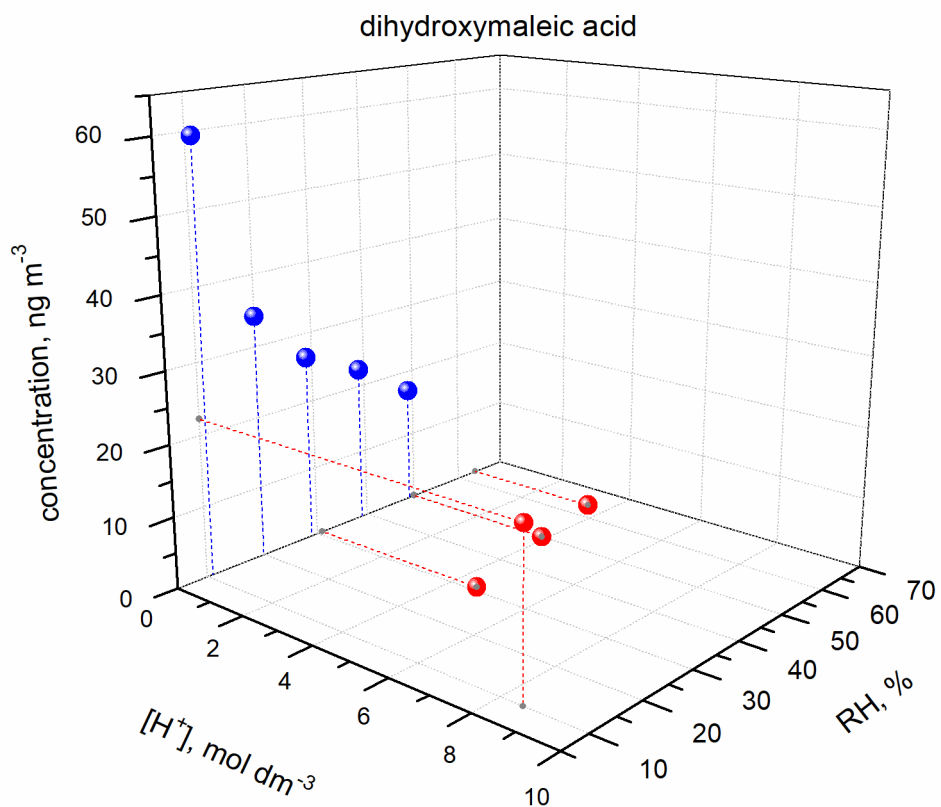


**Figure S34.** Concentrations of 1,3,4-trihydroxy-1-butene in non-acidified (blue) and acidified (red) experiments.



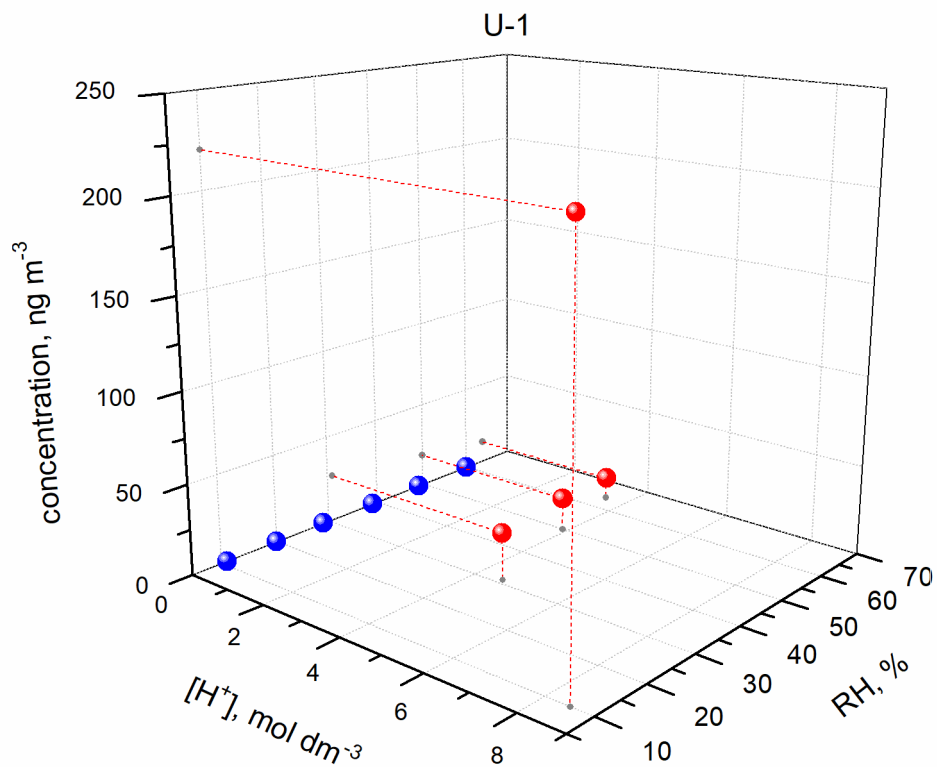
**Figure S35.** Concentrations of hydroxymaleic acid in non-acidified (blue) and acidified (red) experiments.



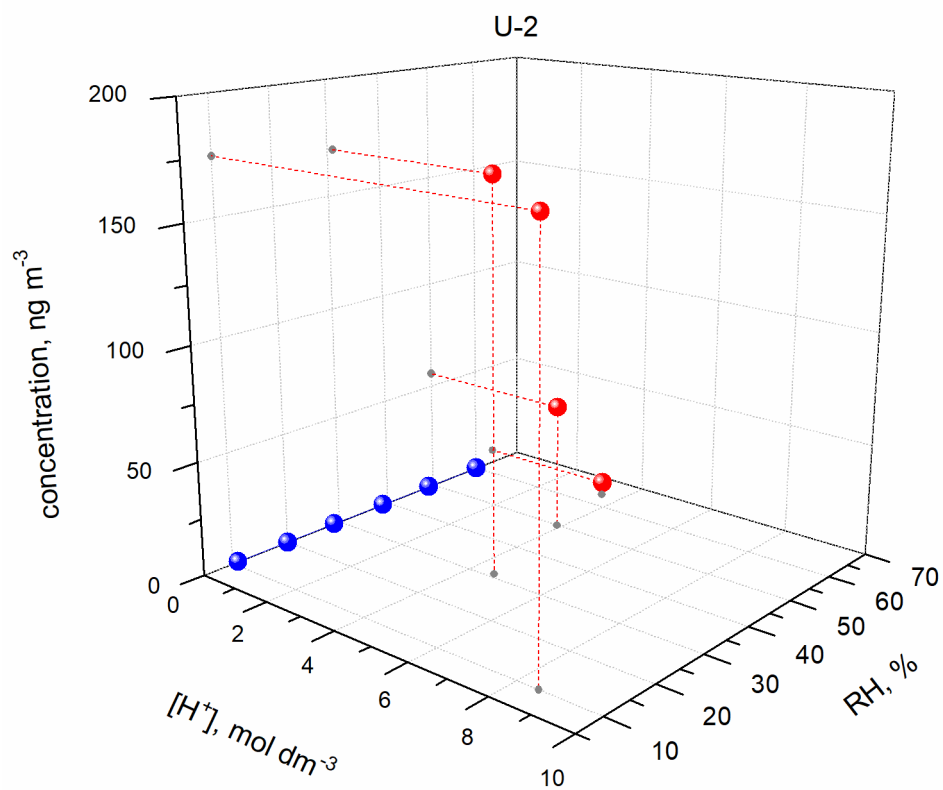


**Figure S36.** Concentrations of dihydroxymaleic acid in non-acidified (blue) and acidified (red) experiments.

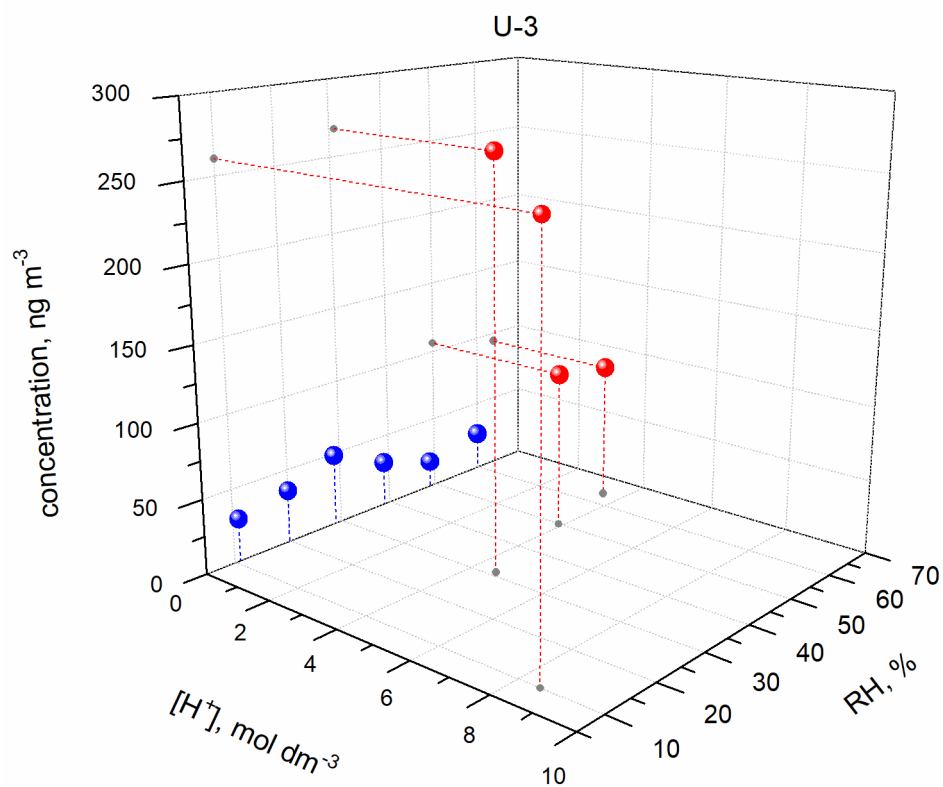
*Unknown compounds*



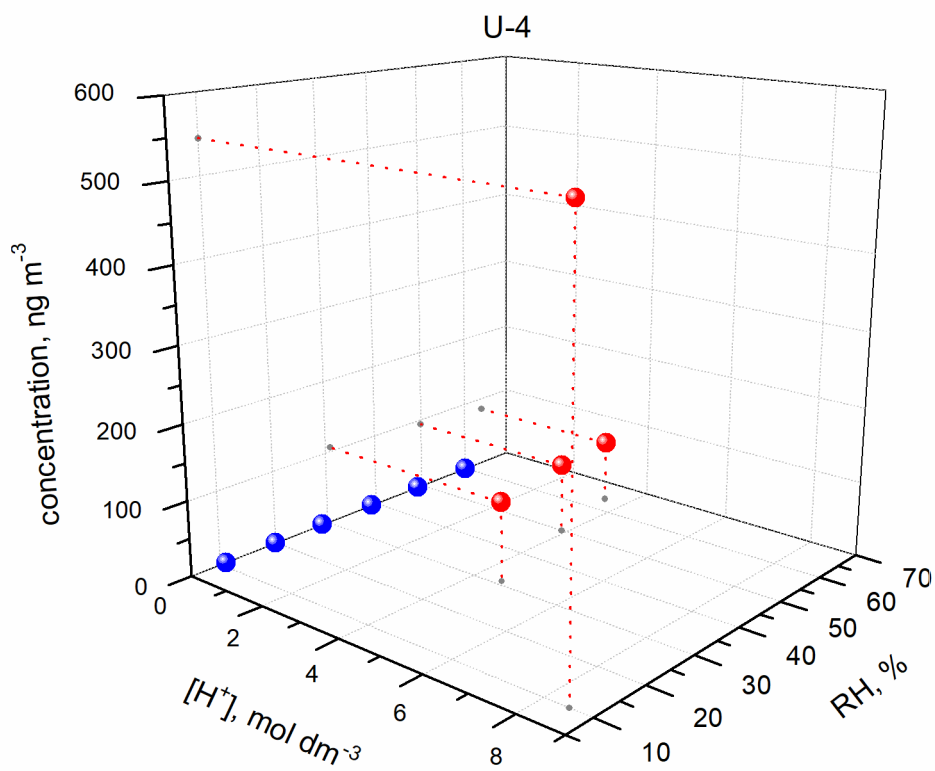
**Figure S37.** Concentrations of U-1 product in non-acidified (blue) and acidified (red) experiments.

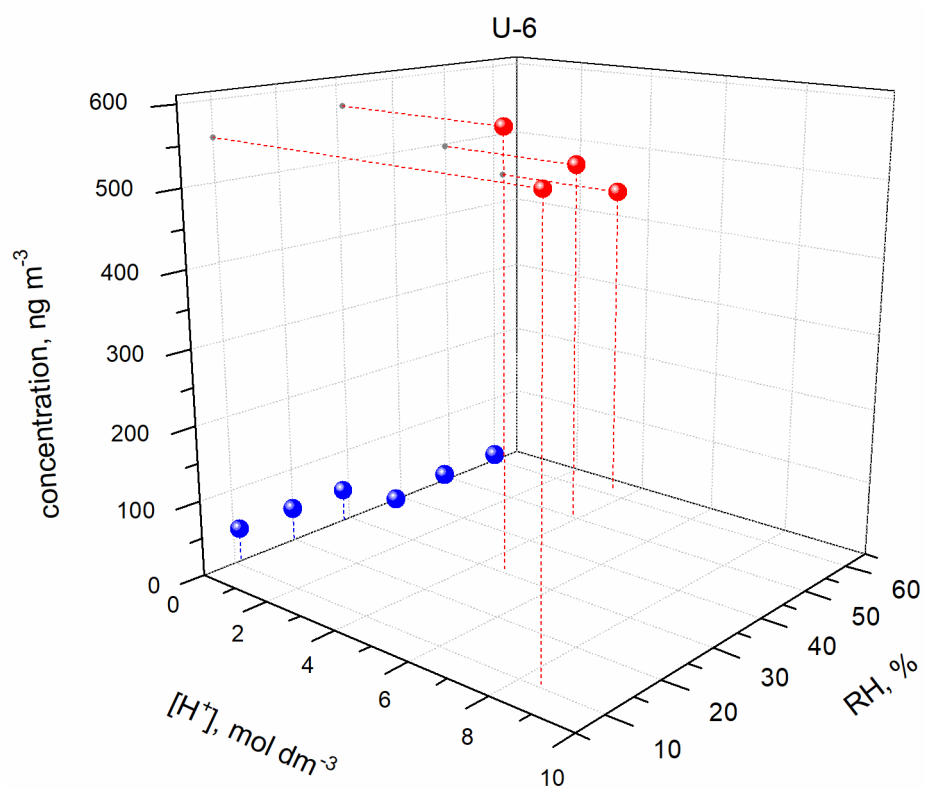


**Figure S38.** Concentrations of U-2 product in non-acidified (blue) and acidified (red) experiments.

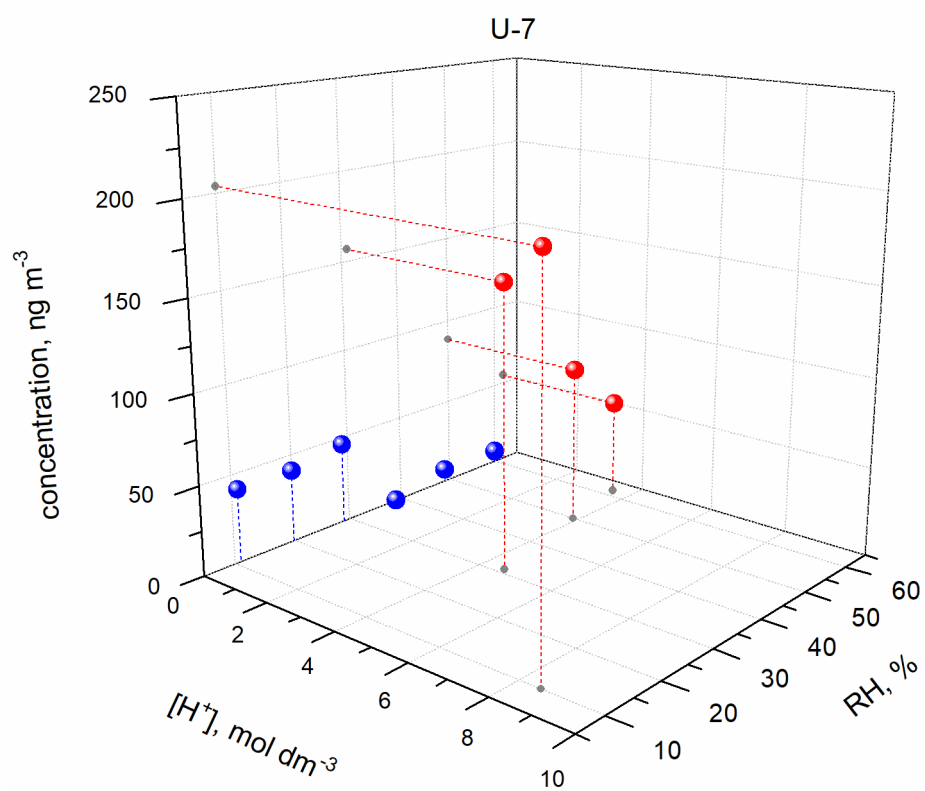


**Figure S39.** Concentrations of U-3 product in non-acidified (blue) and acidified (red) experiments.





**Figure S42.** Concentrations of U-6 product in non-acidified (blue) and acidified (red) experiments.



**Figure S43.** Concentrations of U-7 product in non-acidified (blue) and acidified (red) experiments.

## References.

Jaoui, M., Lewandowski, M., Docherty, K., Offenberg, J. H., and Kleindienst, T. E.: Atmospheric oxidation of 1,3-butadiene: characterization of gas and aerosol reaction products and implications for PM<sub>2.5</sub>, *Atmos. Chem. Phys.*, 14, 13681–13704, doi:10.5194/acp-14-13681-2014, 2014.

Jaoui, M., Lewandowski, M., Offenberg, J. H., Colon, M., Docherty, K., and Kleindienst, T. E.: Characterization of aerosol nitroaromatic compounds: Validation of an experimental method, *J. Mass Spectrom.*, 53, 680-692, 2018.

Jaoui, M., Kleindienst, T. E., Lewandowski, M., and Edney, E. O.: Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic or hydroxyl groups, 1. Method development, *Anal. Chem.*, 76, 4765–4778, 2004.