



*Supplement of*

**Measurements of volatile organic compounds in ambient air by gas-chromatography and real-time Vocus PTR-TOF-MS: calibrations, instrument background corrections, and introducing a PTR Data Toolkit**

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## Supplemental Tables

**Table S1: Summary of VOC standards calibrated routinely before, during, and after the field measurements. For each standard, the summary includes the quantitative ion, observed  $m/Q$ , fraction of the standard's total signal attributed to the quantitative ion ( $f$ ) averaged over all field standard chromatograms, the ions used to calculate  $f$  in addition to the quantitative ion, molecular polarizability ( $\alpha$ ), permanent dipole moment ( $D$ ), calculated proton-transfer reaction rate constant ( $k_{PTR}$ ), average ( $\pm 1$  standard deviation, SD) of all fast calibration field sensitivities except periods where the source malfunctioned, and the 5 s averaging limit of detection (LOD; defined as three times the standard deviation of the instrument background divided by the sensitivity) averaged across all catalyst measurements.**

Standard	Quantitative Ion	$m/Q$ (Th)	$f$	Ions Included in Calculating $f$	$\alpha$ ( $10^{-24}$ cm <sup>3</sup> )	$D$ (Debye)	$k_{PTR}$ (E/N = 160 Td) ( $10^{-9}$ cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	Sensitivity $\pm 1$ SD (cps ppbv <sup>-1</sup> )	LOD (5 s) (pptv)
Methanol	CH <sub>4</sub> OH <sup>+</sup> + CH <sub>4</sub> O(H <sub>2</sub> O)H <sup>+</sup>	33.0335	-	-	3.28 <sup>a</sup>	1.70 <sup>a</sup>	2.08	3 $\pm$ 2	2000
Acetonitrile	C <sub>2</sub> H <sub>3</sub> NH <sup>+</sup>	42.0338	0.967 $\pm$ 0.002	C <sub>2</sub> H <sub>3</sub> N(H <sub>2</sub> O)H <sup>+</sup>	4.44 <sup>a</sup>	3.93 <sup>a</sup>	3.61	2000 $\pm$ 300	14
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> OH <sup>+</sup>	45.0335	-	-	4.60 <sup>a</sup>	2.75 <sup>a</sup>	2.84	2000 $\pm$ 300	60
Acrylonitrile	C <sub>3</sub> H <sub>3</sub> NH <sup>+</sup>	54.0338	0.957 $\pm$ 0.003	C <sub>3</sub> H <sub>3</sub> N(H <sub>2</sub> O)H <sup>+</sup>	8.05 <sup>a</sup>	3.92 <sup>a</sup>	3.82	4800 $\pm$ 700	4
Acetone	C <sub>3</sub> H <sub>6</sub> OH <sup>+</sup>	59.0491	0.89 $\pm$ 0.02	C <sub>3</sub> H <sub>6</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> O(H <sub>2</sub> O) <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>	6.37 <sup>a</sup>	2.88 <sup>a</sup>	2.94	4300 $\pm$ 700	14
Isoprene	C <sub>5</sub> H <sub>8</sub> H <sup>+</sup>	69.0699	0.39 $\pm$ 0.02*	C <sub>5</sub> H <sub>8</sub> (H <sub>2</sub> O)H <sup>+</sup> , C <sub>5</sub> H <sub>7</sub> <sup>+</sup> , C <sub>4</sub> H <sub>5</sub> <sup>+</sup> , C <sub>3</sub> H <sub>5</sub> <sup>+</sup> , C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	9.99 <sup>a</sup>	0.25 <sup>a</sup>	1.92	1300 $\pm$ 100	13
Methyl Ethyl Ketone	C <sub>4</sub> H <sub>8</sub> OH <sup>+</sup>	73.0648	0.838 $\pm$ 0.007	C <sub>4</sub> H <sub>8</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>4</sub> H <sub>7</sub> <sup>+</sup> , C <sub>3</sub> H <sub>5</sub> O <sup>+</sup>	8.13 <sup>a</sup>	2.78 <sup>a</sup>	2.85	400 $\pm$ 500	6
Benzene	C <sub>6</sub> H <sub>6</sub> H <sup>+</sup>	79.0542	0.877 $\pm$ 0.008	C <sub>6</sub> H <sub>7</sub> O <sup>+</sup>	10.4 <sup>a</sup>	0 <sup>b</sup>	1.93	2300 $\pm$ 400	9
Toluene	C <sub>7</sub> H <sub>8</sub> H <sup>+</sup>	93.0699	0.74 $\pm$ 0.02	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> , C <sub>6</sub> H <sub>7</sub> O <sup>+</sup>	12.1 <sup>a</sup>	0.375 <sup>a</sup>	2.06	3200 $\pm$ 500	4
m-Xylene	C <sub>8</sub> H <sub>10</sub> H <sup>+</sup>	107.0855	0.79 $\pm$ 0.02	C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	14.2 <sup>a</sup>	0.27 <sup>b</sup>	2.20	3100 $\pm$ 400	5
1,2,4-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub> H <sup>+</sup>	121.1012	0.82 $\pm$ 0.02	C <sub>8</sub> H <sub>9</sub> <sup>+</sup>	17.2 <sup>b</sup>	0.29 <sup>b</sup>	2.40	3100 $\pm$ 400	6
$\alpha$ -Pinene	C <sub>10</sub> H <sub>16</sub> H <sup>+</sup>	137.1325	0.36 $\pm$ 0.02	C <sub>7</sub> H <sub>11</sub> <sup>+</sup> , C <sub>7</sub> H <sub>9</sub> <sup>+</sup> , C <sub>7</sub> H <sub>7</sub> <sup>+</sup> , C <sub>6</sub> H <sub>9</sub> <sup>+</sup>	17.1 <sup>c</sup>	0.18 <sup>c</sup>	2.37	1160 $\pm$ 130	6
$\beta$ -Caryophyllene	C <sub>15</sub> H <sub>24</sub> H <sup>+</sup>	205.1951	-	-	26.4 <sup>c</sup>	0.62 <sup>c</sup>	2.89	220 $\pm$ 30	6

<sup>a</sup>(Haynes, 2014), <sup>b</sup>(Zhao and Zhang, 2004), <sup>c</sup>(Cappellin et al., 2012)

\*Fragmentation corrected for transmission

**Table S2: Summary of VOC standards calibrated before and after the field measurements, grouped by standard mixture. For each standard, the summary includes the quantitative ion, observed  $m/Q$ , fraction of the standard's total signal attributed to the quantitative ion ( $f$ ) averaged over all laboratory standard chromatograms, the ions used to calculate  $f$  in addition to the quantitative ion, molecular polarizability ( $\alpha$ ), permanent dipole moment (D), calculated proton transfer reaction rate constant ( $k_{PTR}$ ), average ( $\pm 1$  standard deviation, SD) of all field-estimated sensitivities except periods where the source malfunctioned, and the 5 s averaging limit of detection (LOD; defined as three times the standard deviation of the instrument background divided by the sensitivity) averaged across all catalyst measurements. Two standard mixtures are separated by the dashed line.**

Standard	Quantitative Ion	$m/Q$ (Th)	$f$	Ions Included in Calculating $f$	$\alpha$ ( $10^{-24}$ cm <sup>3</sup> )	D (Debye)	$k_{PTR}$ (E/N = 160 Td) ( $10^{-9}$ cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	Sensitivity $\pm 1$ SD (cps ppbv <sup>-1</sup> )	LOD (5 s) (pptv)
Acetonitrile	C <sub>2</sub> H <sub>3</sub> NH <sup>+</sup>	42.0338	0.970 $\pm$ 0.004	C <sub>2</sub> H <sub>3</sub> N(H <sub>2</sub> O)H <sup>+</sup>	4.44 <sup>a</sup>	3.93 <sup>a</sup>	3.61	1800 $\pm$ 200	14
Acetone	C <sub>3</sub> H <sub>6</sub> OH <sup>+</sup>	59.0491	0.90 $\pm$ 0.02	C <sub>3</sub> H <sub>6</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> O(H <sub>2</sub> O) <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>	6.37 <sup>a</sup>	2.88 <sup>a</sup>	2.94	5000 $\pm$ 700	14
Furan	C <sub>4</sub> H <sub>4</sub> OH <sup>+</sup>	69.0335	0.9533 $\pm$ 0.0003	C <sub>4</sub> H <sub>4</sub> O(H <sub>2</sub> O)H <sup>+</sup>	7.31 <sup>a</sup>	0.66 <sup>a</sup>	1.68	2500 $\pm$ 300	8
Benzene	C <sub>6</sub> H <sub>6</sub> H <sup>+</sup>	79.0542	0.878 $\pm$ 0.003	C <sub>6</sub> H <sub>7</sub> O <sup>+</sup>	10.4 <sup>a</sup>	0 <sup>b</sup>	1.93	4300 $\pm$ 600	9
Phenol	C <sub>6</sub> H <sub>6</sub> OH <sup>+</sup>	95.0491	-	-	11.1 <sup>a</sup>	1.24 <sup>a</sup>	2.09	360 $\pm$ 50	120
Ethylbenzene	C <sub>8</sub> H <sub>10</sub> H <sup>+</sup>	107.0855	0.388 $\pm$ 0.011	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> , C <sub>6</sub> H <sub>7</sub> <sup>+</sup>	14.2 <sup>a</sup>	0.59 <sup>a</sup>	2.21	1900 $\pm$ 200	5
t-Amyl Ethyl Ether	C <sub>7</sub> H <sub>16</sub> OH <sup>+</sup>	117.1274	-	C <sub>3</sub> H <sub>7</sub> O <sup>+</sup> , others	-	-	-	-	-
1,3,5-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub> H <sup>+</sup>	121.1012	0.84 $\pm$ 0.02	C <sub>8</sub> H <sub>9</sub> <sup>+</sup>	15.8 <sup>b</sup>	0.047 <sup>b</sup>	2.30	3700 $\pm$ 500	6
d-Limonene	C <sub>10</sub> H <sub>16</sub> H <sup>+</sup>	137.1325	0.394 $\pm$ 0.005	C <sub>7</sub> H <sub>11</sub> <sup>+</sup> , C <sub>7</sub> H <sub>9</sub> <sup>+</sup> , C <sub>7</sub> H <sub>7</sub> <sup>+</sup> , C <sub>6</sub> H <sub>9</sub> <sup>+</sup>	18.0 <sup>c</sup>	0.49 <sup>c</sup>	2.44	900 $\pm$ 100	6
Octamethyl- cyclotetrasiloxane (D4 Siloxane)	C <sub>8</sub> H <sub>24</sub> O <sub>4</sub> Si <sub>4</sub> H <sup>+</sup>	297.0825	0.256 $\pm$ 0.009	C <sub>8</sub> H <sub>24</sub> O <sub>4</sub> Si <sub>4</sub> (H <sub>2</sub> O)H <sup>+</sup> , C <sub>7</sub> H <sub>21</sub> O <sub>4</sub> Si <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> <sup>+</sup> , C <sub>7</sub> H <sub>21</sub> O <sub>4</sub> Si <sub>4</sub> (H <sub>2</sub> O) <sup>+</sup> , C <sub>7</sub> H <sub>21</sub> O <sub>4</sub> Si <sub>4</sub> <sup>+</sup> , C <sub>6</sub> H <sub>17</sub> O <sub>4</sub> Si <sub>4</sub> (H <sub>2</sub> O) <sup>+</sup>	31.3 <sup>d</sup>	0.66 <sup>d</sup>	3.11	1400 $\pm$ 200	2
Ethanol	C <sub>2</sub> H <sub>6</sub> OH <sup>+</sup>	47.0491	-	C <sub>2</sub> H <sub>6</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>2</sub> H <sub>5</sub> O <sup>+</sup>	5.26 <sup>a</sup>	1.69 <sup>a</sup>	2.01	80 $\pm$ 60	90
Acrolein	C <sub>3</sub> H <sub>4</sub> OH <sup>+</sup>	57.0335	0.915 $\pm$ 0.008	C <sub>3</sub> H <sub>4</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>3</sub> H <sub>3</sub> O <sup>+</sup>	6.38 <sup>a</sup>	2.84 <sup>a</sup>	2.93	2800 $\pm$ 400	20
Acetone	C <sub>3</sub> H <sub>6</sub> OH <sup>+</sup>	59.0491	0.893 $\pm$ 0.012	C <sub>3</sub> H <sub>6</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> O(H <sub>2</sub> O) <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>	6.37 <sup>a</sup>	2.88 <sup>a</sup>	2.94	4800 $\pm$ 700	14
Dimethyl Sulfide	C <sub>2</sub> H <sub>6</sub> SH <sup>+</sup>	63.0263	0.861 $\pm$ 0.008	CH <sub>3</sub> S <sup>+</sup>	7.42 <sup>e</sup>	1.55 <sup>e</sup>	2.02	3200 $\pm$ 400	2

**Table S2: (Continued)**

Standard	Quantitative Ion	$m/Q$ (Th)	$f$	Ions Included in Calculating $f$	$\alpha$ ( $10^{-24}$ cm <sup>3</sup> )	D (Debye)	$k_{PTR}$ (E/N = 160 Td) ( $10^{-9}$ cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	Sensitivity $\pm$ 1 SD (cps ppbv <sup>-1</sup> )	LOD (5 s) (pptv)
Methyl Vinyl Ketone	C <sub>4</sub> H <sub>6</sub> OH <sup>+</sup>	71.0491	0.805±0.008	C <sub>4</sub> H <sub>6</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>3</sub> H <sub>3</sub> O <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>	8.30 <sup>a</sup>	2.68 <sup>a</sup>	2.79	4000±500	10
Benzene	C <sub>6</sub> H <sub>6</sub> H <sup>+</sup>	79.0542	0.8785±0.0014	C <sub>6</sub> H <sub>7</sub> O <sup>+</sup>	10.4 <sup>a</sup>	0 <sup>b</sup>	1.93	3500±500	9
Cyclohexene	C <sub>6</sub> H <sub>10</sub> H <sup>+</sup>	83.0855	0.537±0.012*	C <sub>5</sub> H <sub>7</sub> <sup>+</sup> , C <sub>4</sub> H <sub>7</sub> <sup>+</sup>	10.7 <sup>a</sup>	0.33 <sup>a</sup>	1.96	1700±200	8
Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub> H <sup>+</sup>	97.0284	0.83±0.02	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub> (H <sub>2</sub> O)H <sup>+</sup> , C <sub>3</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup> , C <sub>4</sub> H <sub>5</sub> O <sup>+</sup>	10.9 <sup>b</sup>	3.87 <sup>b</sup>	3.66	5400±800	4
2-Hexanone	C <sub>6</sub> H <sub>12</sub> OH <sup>+</sup>	101.0961	0.65±0.02	C <sub>6</sub> H <sub>12</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>6</sub> H <sub>11</sub> <sup>+</sup> , C <sub>5</sub> H <sub>9</sub> O <sup>+</sup> , C <sub>4</sub> H <sub>9</sub> <sup>+</sup> , C <sub>4</sub> H <sub>7</sub> O <sup>+</sup> , C <sub>4</sub> H <sub>7</sub> <sup>+</sup> , C <sub>2</sub> H <sub>5</sub> O <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>	12.1 <sup>f</sup>	2.66 <sup>a</sup>	2.76	3300±400	1.3
Styrene	C <sub>8</sub> H <sub>8</sub> H <sup>+</sup>	105.0699	0.8931±0.0012	C <sub>6</sub> H <sub>7</sub> <sup>+</sup>	14.7 <sup>a</sup>	0.12 <sup>a</sup>	2.24	3700±500	2
Benzaldehyde	C <sub>7</sub> H <sub>6</sub> OH <sup>+</sup>	107.0491	0.639±0.011	C <sub>7</sub> H <sub>6</sub> O(H <sub>2</sub> O)H <sup>+</sup> , C <sub>7</sub> H <sub>5</sub> O <sup>+</sup> , C <sub>6</sub> H <sub>7</sub> O <sup>+</sup> C <sub>6</sub> H <sub>7</sub> <sup>+</sup>	14.1 <sup>b</sup>	3.28 <sup>b</sup>	3.25	3700±500	3
$\beta$ -Pinene	C <sub>10</sub> H <sub>16</sub> H <sup>+</sup>	137.1325	0.372±0.008	C <sub>7</sub> H <sub>11</sub> <sup>+</sup> , C <sub>7</sub> H <sub>9</sub> <sup>+</sup> , C <sub>7</sub> H <sub>7</sub> <sup>+</sup> , C <sub>6</sub> H <sub>9</sub> <sup>+</sup>	18.0 <sup>c</sup>	0.64 <sup>c</sup>	2.45	1400±200	6
Hexamethyl- cyclotrisiloxane (D3 Siloxane)	C <sub>6</sub> H <sub>18</sub> O <sub>3</sub> Si <sub>3</sub> H <sup>+</sup>	223.0637	0.346±0.011	C <sub>6</sub> H <sub>18</sub> O <sub>3</sub> Si <sub>3</sub> (H <sub>2</sub> O)H <sup>+</sup> , C <sub>5</sub> H <sub>15</sub> O <sub>3</sub> Si <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> <sup>+</sup> , C <sub>5</sub> H <sub>15</sub> O <sub>3</sub> Si <sub>3</sub> (H <sub>2</sub> O) <sup>+</sup> , C <sub>5</sub> H <sub>15</sub> O <sub>3</sub> Si <sub>3</sub> <sup>+</sup> , C <sub>4</sub> H <sub>11</sub> O <sub>3</sub> Si <sub>3</sub> (H <sub>2</sub> O) <sup>+</sup>	28.5 <sup>f</sup>	2.10 <sup>f</sup>	3.18	2000±200	2
Decamethyl- cyclopentasiloxane (D5 Siloxane)	C <sub>10</sub> H <sub>30</sub> O <sub>5</sub> Si <sub>5</sub> H <sup>+</sup>	371.1012	0.240±0.009	C <sub>10</sub> H <sub>30</sub> O <sub>5</sub> Si <sub>5</sub> (H <sub>2</sub> O)H <sup>+</sup> , C <sub>9</sub> H <sub>27</sub> O <sub>5</sub> Si <sub>5</sub> (H <sub>2</sub> O) <sub>2</sub> <sup>+</sup> , C <sub>9</sub> H <sub>27</sub> O <sub>5</sub> Si <sub>5</sub> (H <sub>2</sub> O) <sup>+</sup> , C <sub>9</sub> H <sub>27</sub> O <sub>5</sub> Si <sub>5</sub> <sup>+</sup> , C <sub>8</sub> H <sub>23</sub> O <sub>5</sub> Si <sub>5</sub> (H <sub>2</sub> O) <sup>+</sup>	39.2 <sup>d</sup>	1.35 <sup>d</sup>	3.50	1000±120	1.0

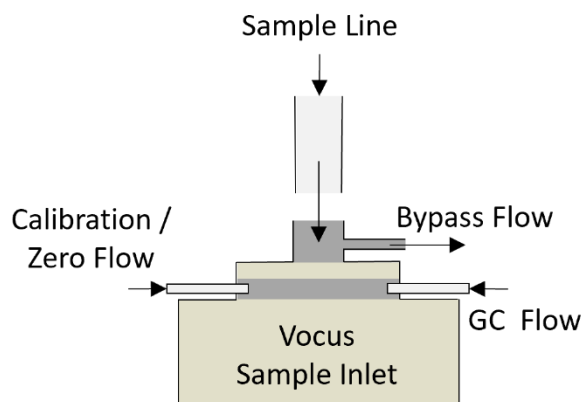
<sup>a</sup>(Haynes, 2014), <sup>b</sup>(Zhao and Zhang, 2004), <sup>c</sup>(Cappellin et al., 2012), <sup>d</sup>(Langford et al., 2013), <sup>e</sup>(Cappellin et al., 2010), <sup>f</sup>(Sekimoto et al., 2017)

\*Fragmentation corrected for transmission

**Table S3: Summary of average ( $\pm 1$  standard deviation;  $n$  is the number of measurements used in the calculations) instrument background signals from the three clean air sources used in this study for the standards presented in Tables S1 and S2 (omitting isomers). Averages were derived from the latter half of the field measurements (April 10 to the end) after the inlet capillary was replaced and all three clean air sources were used.**

Standard	Quantitative Ion	$m/Q$ (Th)	Instrument Background Signal (cps)		
			HC Trap ( $n = 9$ )	UHP Nitrogen ( $n = 9$ )	Catalyst ( $n = 194$ )
Methanol	$\text{CH}_4\text{OH}^+ + \text{CH}_4\text{O}(\text{H}_2\text{O})\text{H}^+$	33.0335	24.9 $\pm$ 1.0	190 $\pm$ 20	24.0 $\pm$ 0.9
Acetonitrile	$\text{C}_2\text{H}_3\text{NH}^+$	42.0338	720 $\pm$ 140	135 $\pm$ 6	143 $\pm$ 8
Acetaldehyde	$\text{C}_2\text{H}_4\text{OH}^+$	45.0335	10000 $\pm$ 2000	2660 $\pm$ 110	2280 $\pm$ 120
Ethanol	$\text{C}_2\text{H}_6\text{OH}^+$	47.0491	78 $\pm$ 13	12.8 $\pm$ 0.5	10.7 $\pm$ 0.6
Acrylonitrile	$\text{C}_3\text{H}_3\text{NH}^+$	54.0338	120 $\pm$ 20	15 $\pm$ 5	41 $\pm$ 8
Acrolein	$\text{C}_3\text{H}_4\text{OH}^+$	57.0335	330 $\pm$ 30	340 $\pm$ 30	175 $\pm$ 14
Acetone	$\text{C}_3\text{H}_6\text{OH}^+$	59.0491	650 $\pm$ 50	1500 $\pm$ 100	500 $\pm$ 40
Dimethyl Sulfide	$\text{C}_2\text{H}_6\text{SH}^+$	63.0263	3.0 $\pm$ 0.6	2.9 $\pm$ 0.2	2.9 $\pm$ 0.2
Furan	$\text{C}_4\text{H}_4\text{OH}^+$	69.0335	63 $\pm$ 5	71 $\pm$ 4	54 $\pm$ 3
Isoprene	$\text{C}_5\text{H}_8\text{H}^+$	69.0699	92 $\pm$ 12	140 $\pm$ 30	60 $\pm$ 8
Methyl Ethyl Ketone	$\text{C}_4\text{H}_8\text{OH}^+$	73.0648	89 $\pm$ 12	100 $\pm$ 9	89 $\pm$ 9
Methyl Vinyl Ketone	$\text{C}_4\text{H}_6\text{OH}^+$	71.0491	260 $\pm$ 20	320 $\pm$ 20	250 $\pm$ 20
Benzene	$\text{C}_6\text{H}_6\text{H}^+$	79.0542	150 $\pm$ 14	109 $\pm$ 8	90 $\pm$ 8
Cyclohexene	$\text{C}_6\text{H}_{10}\text{H}^+$	83.0855	65 $\pm$ 11	120 $\pm$ 20	35 $\pm$ 6
Toluene	$\text{C}_7\text{H}_8\text{H}^+$	93.0699	60 $\pm$ 20	32 $\pm$ 3	41 $\pm$ 8
Phenol	$\text{C}_6\text{H}_6\text{OH}^+$	95.0491	410 $\pm$ 50	420 $\pm$ 30	390 $\pm$ 30
Furfural	$\text{C}_5\text{H}_4\text{O}_2\text{H}^+$	97.0284	118 $\pm$ 9	122 $\pm$ 5	116 $\pm$ 6
2-Hexanone	$\text{C}_6\text{H}_{12}\text{OH}^+$	101.0961	3.8 $\pm$ 1.3	15 $\pm$ 4	2.8 $\pm$ 1.4
Styrene	$\text{C}_8\text{H}_8\text{H}^+$	105.0699	15 $\pm$ 4	10 $\pm$ 2	11 $\pm$ 2
Benzaldehyde	$\text{C}_7\text{H}_6\text{OH}^+$	107.0491	31 $\pm$ 5	78 $\pm$ 14	26 $\pm$ 3
m-Xylene	$\text{C}_8\text{H}_{10}\text{H}^+$	107.0855	44 $\pm$ 10	13 $\pm$ 2	37 $\pm$ 6
1,2,4-Trimethylbenzene	$\text{C}_9\text{H}_{12}\text{H}^+$	121.1012	90 $\pm$ 20	14 $\pm$ 3	58 $\pm$ 12
$\alpha$ -Pinene	$\text{C}_{10}\text{H}_{16}\text{H}^+$	137.1325	80 $\pm$ 40	22 $\pm$ 2	13 $\pm$ 4
$\beta$ -Caryophyllene	$\text{C}_{15}\text{H}_{24}\text{H}^+$	205.1951	1.7 $\pm$ 0.7	6 $\pm$ 2	1.4 $\pm$ 0.3
Hexamethylcyclotrisiloxane (D3 Siloxane)	$\text{C}_6\text{H}_{18}\text{O}_3\text{Si}_3\text{H}^+$	223.0637	2.6 $\pm$ 0.9	5 $\pm$ 2	2.5 $\pm$ 0.9
Octamethylcyclotetrasiloxane (D4 Siloxane)	$\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4\text{H}^+$	297.0825	2.1 $\pm$ 0.6	6 $\pm$ 2	2.8 $\pm$ 0.2
Decamethylpentasiloxane (D5 Siloxane)	$\text{C}_{10}\text{H}_{30}\text{O}_5\text{Si}_5\text{H}^+$	371.1012	0.36 $\pm$ 0.14	1.1 $\pm$ 0.9	0.3 $\pm$ 0.3

(a) Setup used in this study



(b) Recommended Setup

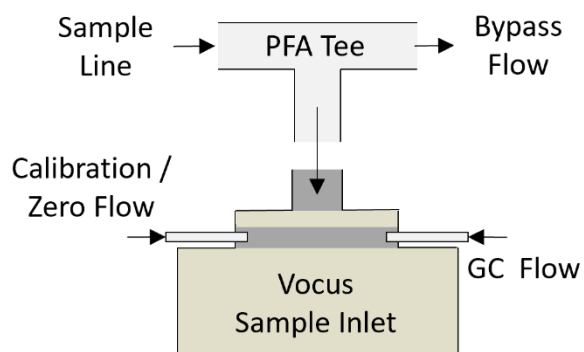
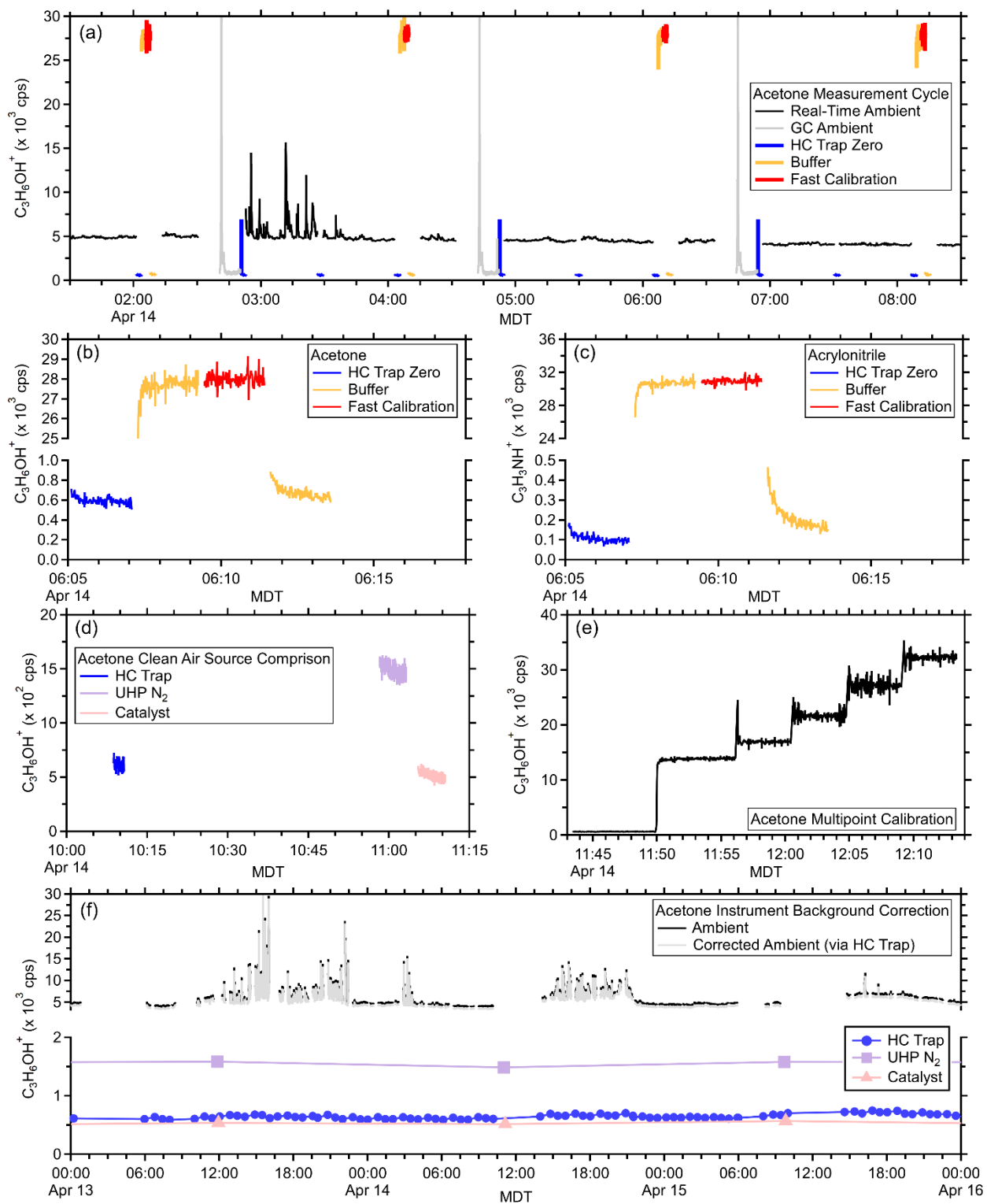
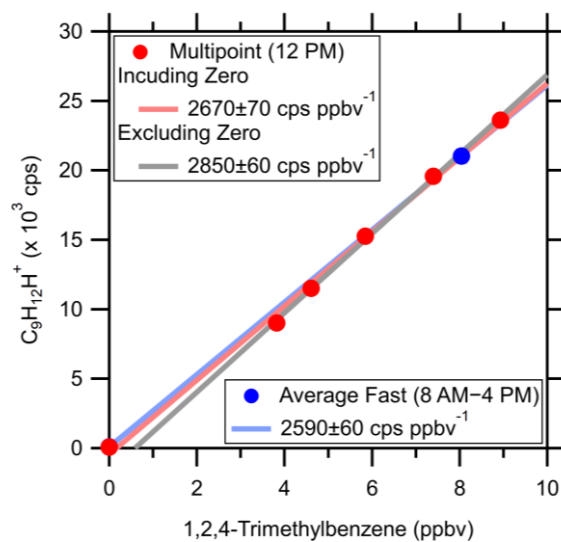


Figure S1: Schematic of the sample flow path (a) used in this study, and (b) suggested for avoiding obstructions of the inlet capillary. A PFA tee is placed on the sample inlet such that the sample line and bypass line are in sequence and the Vocus inlet is perpendicular.

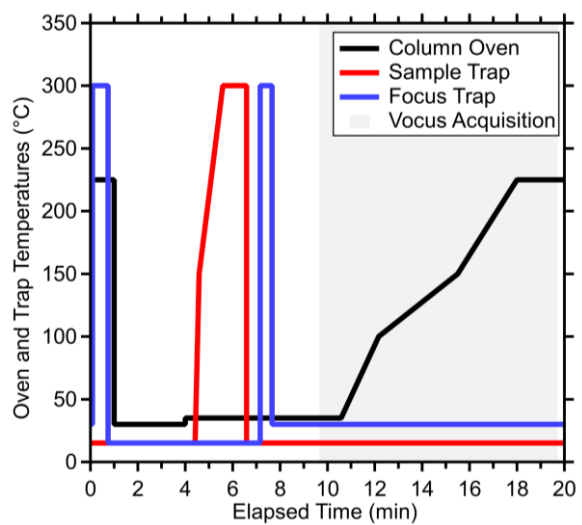


**Figure S2:** Example time series to demonstrate (a) the 2-h measurement cycle, (b) instrument background measurements and fast calibrations of acetone, (c) instrument background measurements and fast calibrations of acrylonitrile, (d) instrument background measurements for acetone with the three clean air sources, (e) a multipoint calibration of acetone (noise caused by the clean air mass flow controller), and (f) an example correction of acetone for instrument background signal by linear interpolation.



**Figure S3:** Comparison of a 1,2,4-trimethylbenzene multipoint calibration and 4 fast calibrations collected on April 14 (within  $\pm 4$  h of the multipoint calibration). The multipoint calibration was regressed twice: including the instrument background measurement (red) and excluding it (gray). Multipoint calibration sensitivity uncertainties reflect the uncertainty in the regression. The uncertainty in the fast calibration sensitivity reflects the standard deviation across the 4 calibrations.





**Figure S4: Temperature profiles of the sample trap, focus trap, and column oven during a typical GC cycle. Mass spectra were recorded during the final 10 min.**

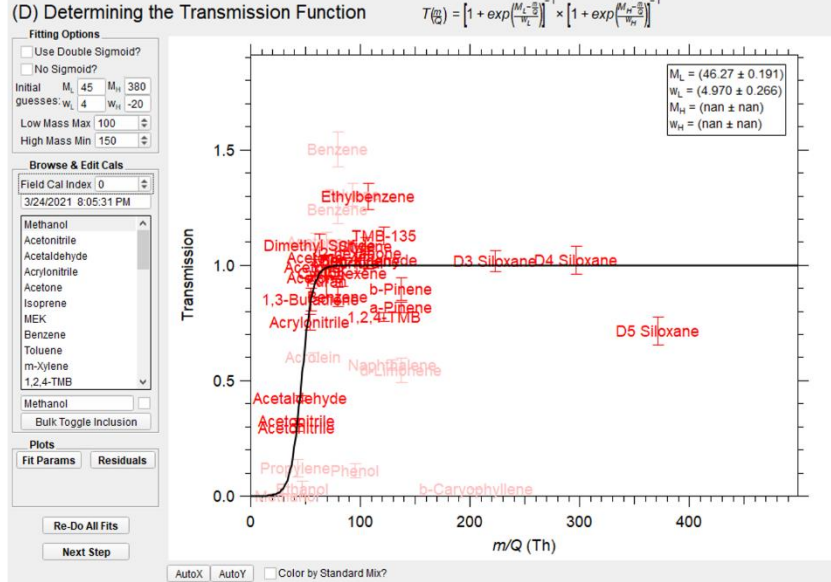
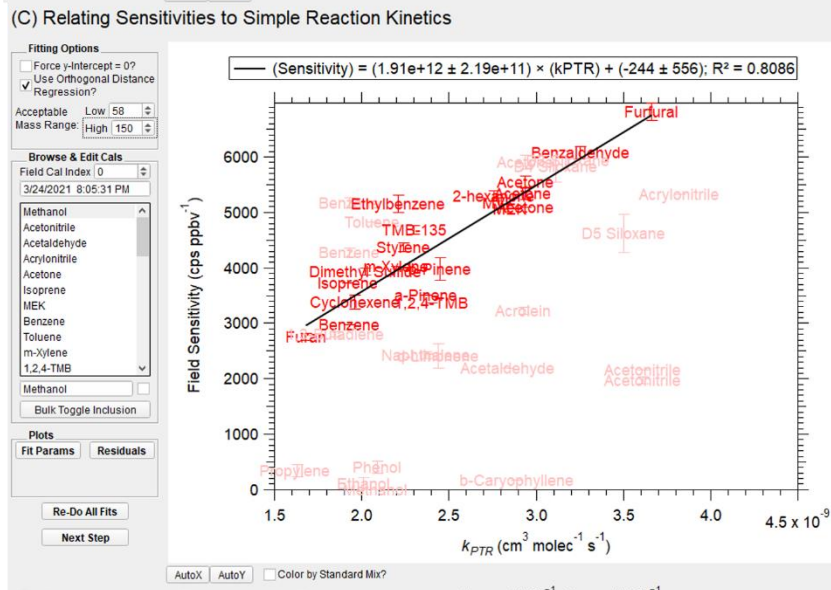
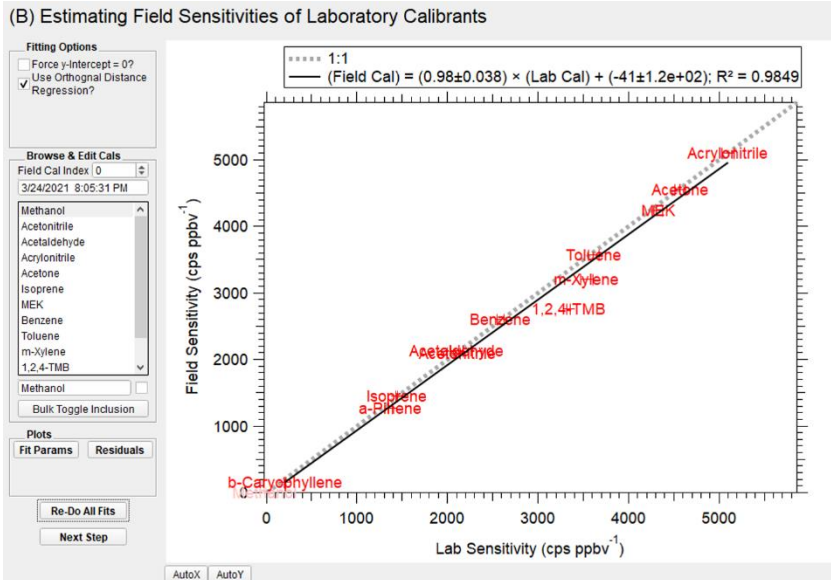
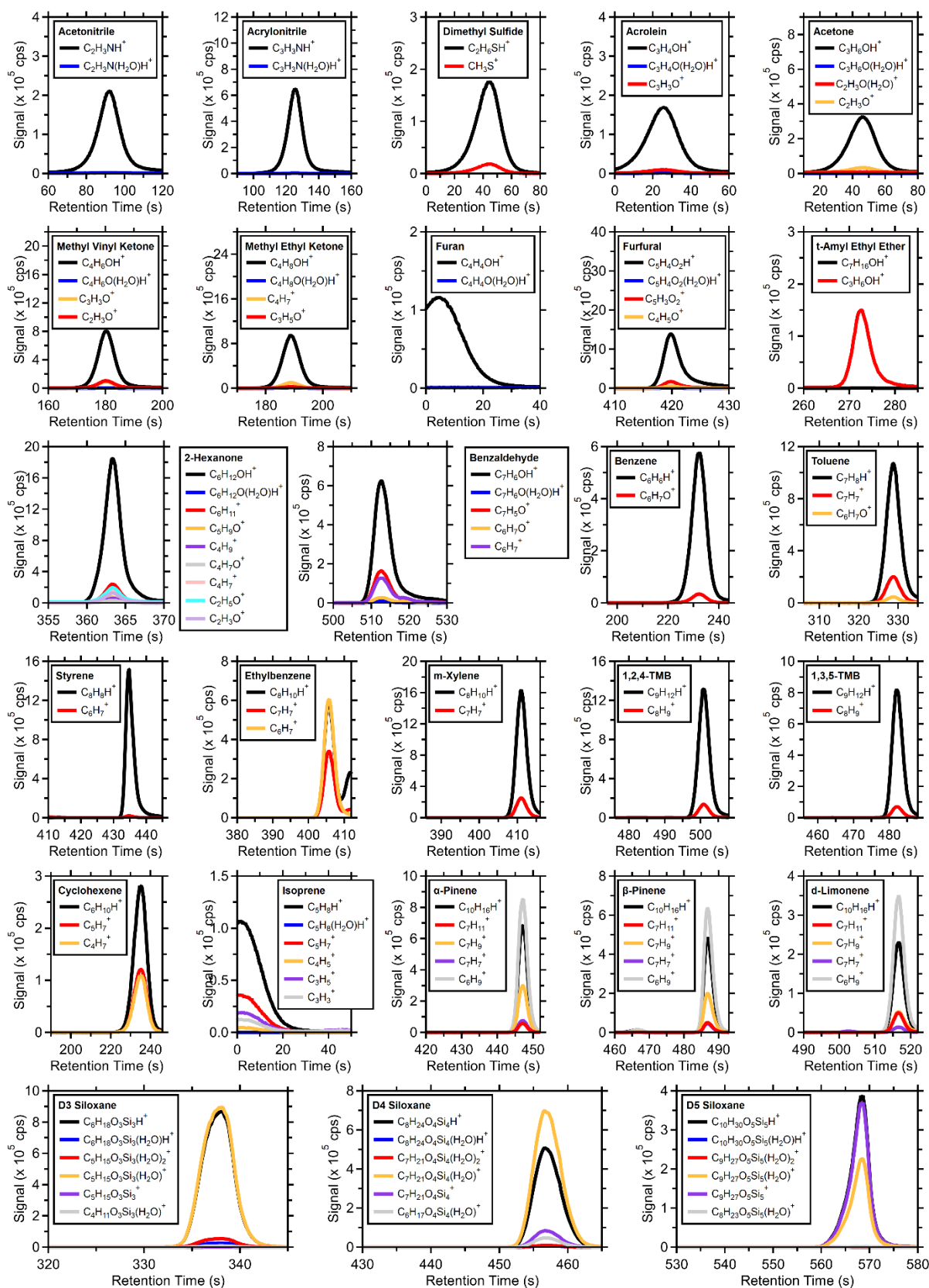


Figure S5: Screenshots of the PTR-DT interface for steps B, C, and D. The displayed data are the same shown in Fig. 1.



**Figure S6: Example chromatograms of the standards in Tables S1 and S2 (excluding duplicates) from the pre-field calibrations (~7.5 ppbv) including all fragments used to determine the quantitative ion fractions (recall that  $f$  also reflects the isotopic distribution). The black trace in all panels corresponds to the respective protonated parent ion.**

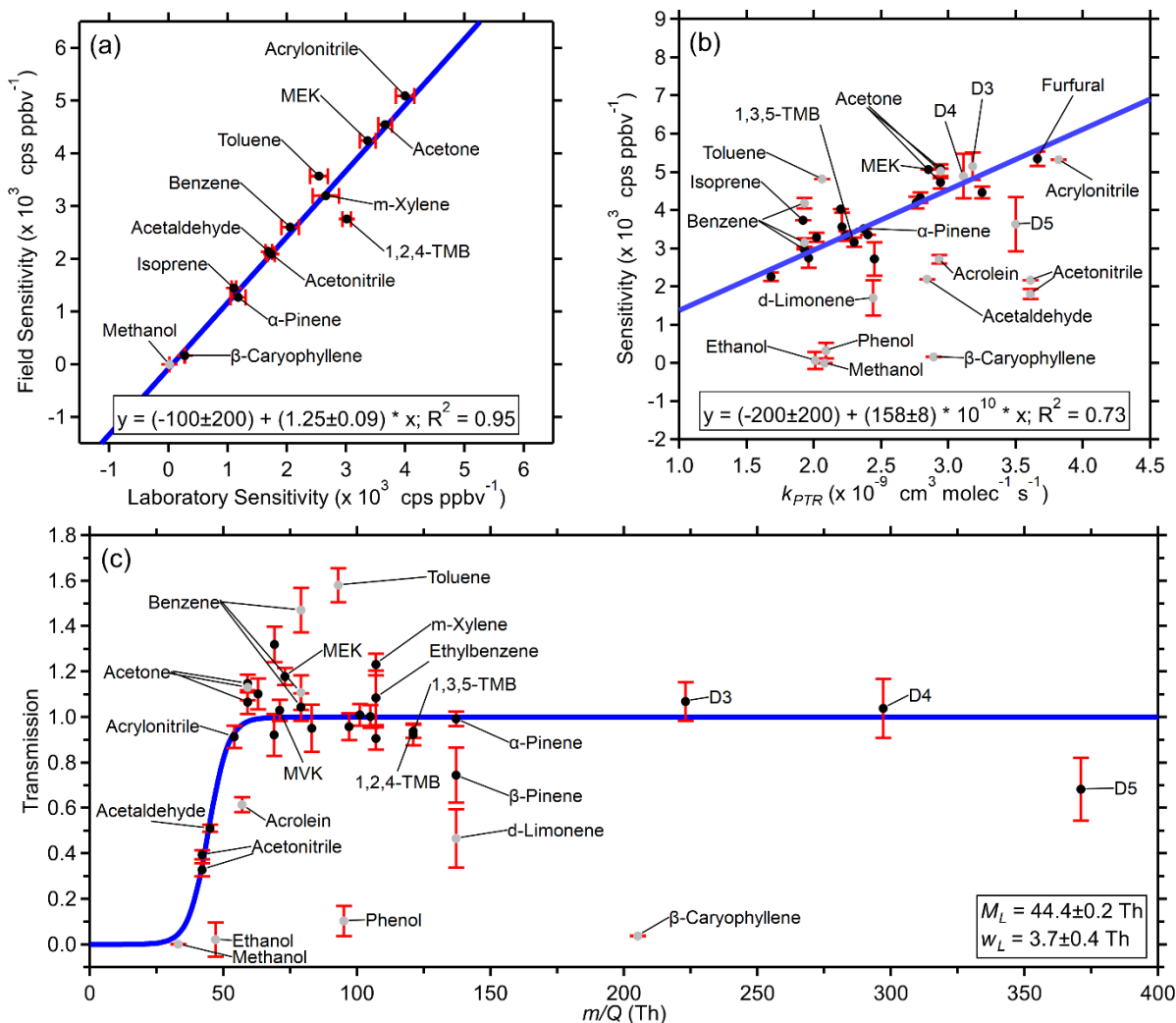
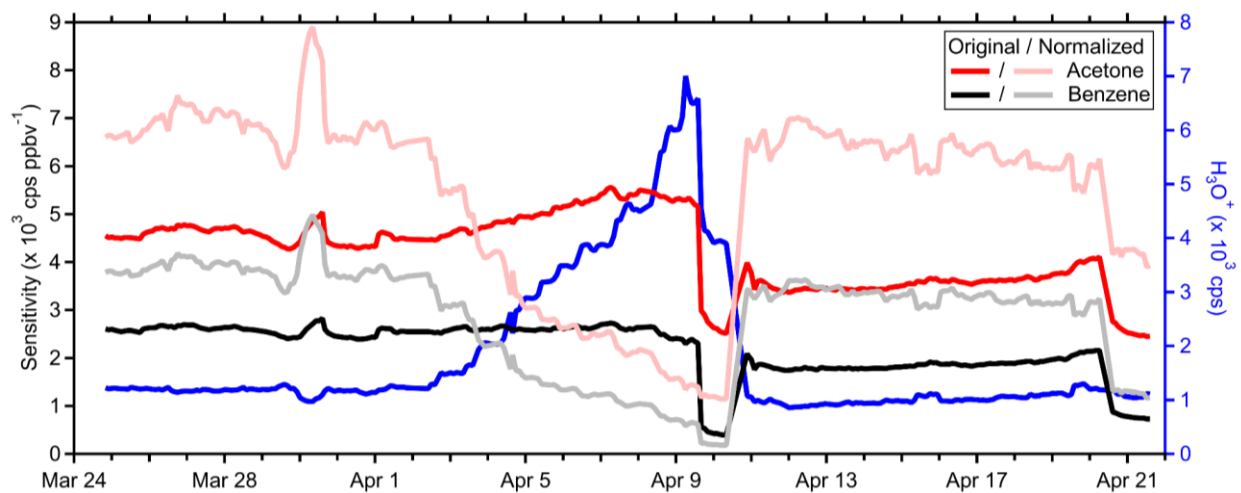
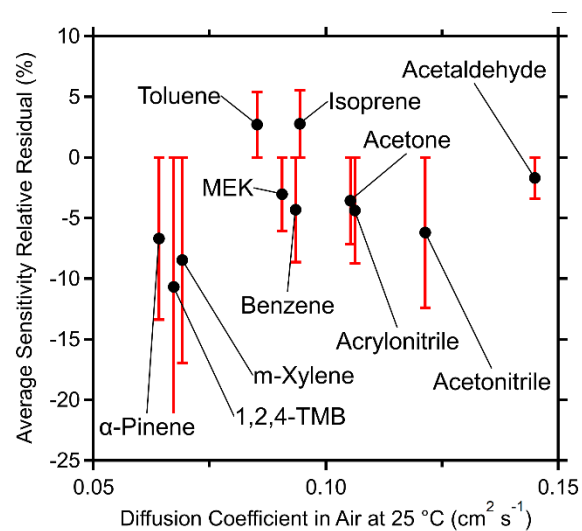


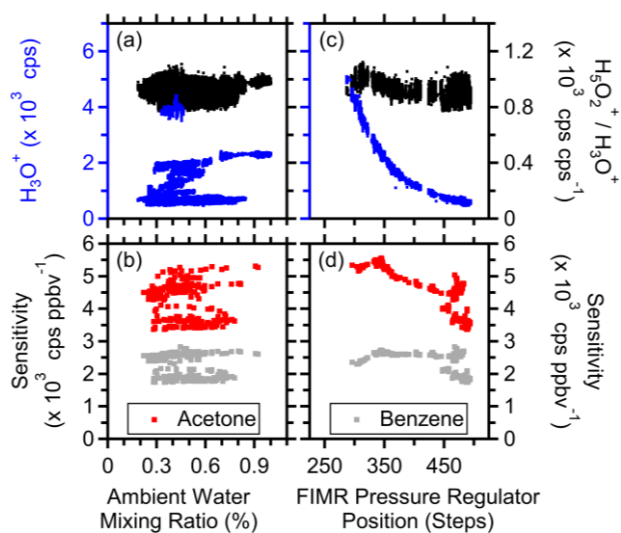
Figure S7: Example fits from the PTR-DT including (a) an orthogonal distance regression of the first field calibration sensitivities and the post-field laboratory calibration sensitivities, (b) an orthogonal distance regression of the first field calibration sensitivities and the respective PTR rate constants, and (c) an  $m/Q$ -dependent transmission curve for the first field calibration. Uncertainties in laboratory sensitivities are the standard deviation of replicate measurements. Field-estimated sensitivity uncertainties of laboratory standards were propagated with the uncertainties of the regressions in step B. Transmission uncertainties were propagated from previous steps. Grayed-out standards were excluded from the respective fits as described in Section 3. Figure 1 shows similar fits using the pre-field laboratory calibrations.



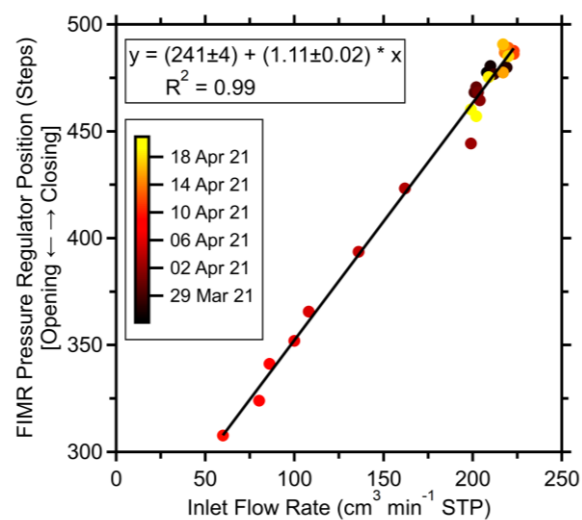
**Figure S8:** Time series of acetone and benzene sensitivities as measured and as normalized against the average signal of  $m/Q$  19 (unit mass  $\text{H}_3\text{O}^+$ ).



**Figure S9: The relationship between the observed relative residuals of the multipoint and fast calibrations and their diffusion coefficients in air at 25 °C (Yaws, 2008). Uncertainties in residuals represent one standard deviation.**



**Figure S10:** Observed relationships of the measured hydronium ion signal and selected sensitivities with ambient water mixing ratio (a–b), as well as the IMR pressure regulator position (c–d). Time periods where the ion source malfunctioned are excluded. Water mixing ratio and IMR pressure regulator position were averaged to the sensitivity measurement timescales for panels (b) and (d).



**Figure S11: Linear least-squares regression of the daily average IMR pressure regulator position against the measured inlet flow rate. The gradual obstruction of the PEEK inlet tube from April ~2-10 is coincident with reduced flow rates. To maintain a constant IMR pressure, the regulator gradually opened. Time periods where the ion source malfunctioned are excluded. The IMR pressure regulator position was averaged to a 24 h timescale.**



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