

1 Supplementary Information for

2 **Response of protonated, adduct, and fragmented ions in Vocus proton-**
3 **transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS)**

4

5 Fangbing Li¹, Dan Dan Huang², Linhui Tian¹, Bin Yuan³, Wen Tan⁴, Liang Zhu⁴,
6 Penglin Ye⁵, Douglas Worsnop⁵, Ka In Hoi¹, Kai Meng Mok¹, Yong Jie Li¹

7 ¹Department of Civil and Environmental Engineering, Department of Ocean Science
8 and Technology, and Centre for Regional Oceans, Faculty of Science and
9 Technology, University of Macau, Macau, China

10 ²State Environmental Protection Key Laboratory of Cause and Prevention of Urban
11 Air Pollution Complex, Shanghai Academy of Environmental Sciences, Shanghai,
12 China

13 ³Institute for Environment and Climate Research, Jinan University, Guangzhou
14 510632, China

15 ⁴Tofwerk AG, Nanjing, China

16 ⁵Aerodyne Research, Inc., Billerica, Massachusetts 01821, United States

17 *Correspondence to:* Yong Jie Li (yongjieli@um.edu.mo)

18

List of the supporting information:

19

20 Tables.

21 **Table S1.** The details of instrument setting experiments.4
 22 Table S2. Details of the tested volatile organic compounds (VOCs). Also shown are their proton
 23 affinity (PA) values.5
 24 Table S3. Proton-transfer reaction rate constants (k_{ptr} , $\times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) from literature. 6
 25 Table S4. The RH dependence, sensitivity, intercept of protonated adducts, and fragmented
 26 ions.7

27 Figures.

28 Figure S1. The diagram of the RH experimental setup. MFC: mass flow controller.8
 29 Figure S2. The mass spectra of aromatic hydrocarbons (benzene, toluene, m-xylene, and 1,2,4-
 30 trimethylbenzene), and terpenoids (isoprene, α -pinene, and β -caryophyllene) in Vocus at a
 31 mixing ratio of ~ 12 ppbv (β -caryophyllene 1.2 ppbv).9
 32 Figure S3. The mass spectra of small aldehydes (formaldehyde and acetaldehyde), long-chain
 33 aldehydes (n-butanal, pentanal, and hexaldehyde), and ketones (acetone, and methyl ethyl
 34 ketone) in Vocus at a mixing ratio of ~ 12 ppbv. 10
 35 Figure S4. The mass spectra of unsaturated aldehydes (acrolein and methacrolein), aromatic
 36 aldehydes (benzaldehyde and m-tolualdehyde), nitriles (acetonitrile and acrylonitrile),
 37 and methanol in Vocus at a mixing ratio of ~ 12 ppbv. 11
 38 Figure S5. Time series of the protonated ion (MH^+) signals for selected (A) VOCs and (B)
 39 OVOCs as concentration varied from 0 to ~ 22 ppbv (~ 2 ppbv for β caryophyllene) under
 40 dry ($\text{MH} \sim 5\%$) conditions. Note the signals were magnified by 10 times for β -
 41 caryophyllene and 3 times for n-butanal, pentanal, and hexaldehyde. 12
 42 Figure S6. Time series of the protonated ion (MH^+), adduct ions ($[\text{MH} + \text{H}_2\text{O}]^+$), and
 43 fragmented ions ($[\text{MH} - \text{H}_2\text{O}]^+$) and/or ($[\text{MH} - \text{C}_x\text{H}_y]^+$) signals for n-butanal, pentanal,
 44 and hexaldehyde. Note that the time in x axis is not continuous, with some periods with
 45 noisy signals cut off. 13
 46 Figure S7. The signal intensities (panels a, b, and c, and panels g, h, and i) and fractions (panels
 47 d, e, and f, and panels j, k, and l) of protonated ion (MH^+), adduct ions ($[\text{MH} + \text{H}_2\text{O}]^+$),
 48 and fragmented ions ($[\text{MH} - \text{H}_2\text{O}]^+$ and $[\text{MH} - \text{C}_x\text{H}_y]^+$) for α -pinene as functions of E/N
 49 ratio (a, d, g, and j), RF amplitude (b, e, h, and k), and BSQ amplitude (c, f, i, and l). The
 50 difference between a/d and g/j is that the former fixed N ($p = 2.0$ mbar) and varied axial
 51 voltage (V) to change E/N ratio, while the latter fixed V (= 466 volts) and varied p (i.e.,
 52 N) to change E/N ratio. The difference between b/e and h/k and between c/f and i/l is that
 53 the former was at $p = 2.0$ mbar while the latter $p = 3.5$ mbar. If not varied, RF amplitude
 54 was set at 500 volts and BSQ amplitude at 300 volts. 14
 55 Figure S8. The signal intensities (panels a, b, and c, and panels g, h, and i) and fractions (panels
 56 d, e, and f, and panels j, k, and l) of protonated ion (MH^+), adduct ions ($[\text{MH} + \text{H}_2\text{O}]^+$),
 57 and fragmented ions ($[\text{MH} - \text{H}_2\text{O}]^+$ and $[\text{MH} - \text{C}_x\text{H}_y]^+$) for 1,2,4-trimethylbenzene as
 58 functions of E/N ratio (a, d, g, and j), RF amplitude (b, e, h, and k), and BSQ amplitude
 59 (c, f, i, and l). The difference between a/d and g/j is that the former fixed N ($p = 2.0$ mbar)
 60 and varied axial voltage (V) to change E/N ratio, while the latter fixed V (= 466 volts) and
 61 varied p (i.e., N) to change E/N ratio. The difference between b/e and h/k and between c/f
 62 and i/l is that the former was at $p = 2.0$ mbar while the latter $p = 3.5$ mbar. If not varied,
 63 RF amplitude was set at 500 volts and BSQ amplitude at 300 volts. 15
 64 Figure S9. The signal intensities (panels a, b, and c, and panels g, h, and i) and fractions (panels
 65 d, e, and f, and panels j, k, and l) of protonated ion (MH^+), adduct ions ($[\text{MH} + \text{H}_2\text{O}]^+$),
 66 and fragmented ions ($[\text{MH} - \text{H}_2\text{O}]^+$ and $[\text{MH} - \text{C}_x\text{H}_y]^+$) for acetone as functions of E/N
 67 ratio (a, d, g, and j), RF amplitude (b, e, h, and k), and BSQ amplitude (c, f, i, and l). The
 68 difference between a/d and g/j is that the former fixed N ($p = 2.0$ mbar) and varied axial
 69 voltage (V) to change E/N ratio, while the latter fixed V (= 466 volts) and varied p (i.e.,
 70 N) to change E/N ratio. The difference between b/e and h/k and between c/f and i/l is that
 71 the former was at $p = 2.0$ mbar while the latter $p = 3.5$ mbar. If not varied, RF amplitude

72	was set at 500 volts and BSQ amplitude at 300 volts.	16
73	Figure S10. The signal intensities (panels a, b, and c, and panels g, h, and i) and fractions	
74	(panels d, e, and f, and panels j, k, and l) of protonated ion (MH^+), adduct ions ($[MH +$	
75	$H_2O]^+$), and fragmented ions ($[MH - H_2O]^+$ and $[MH - C_xH_y]^+$) for hexaldehyde as	
76	functions of E/N ratio (a, d, g, and j), RF amplitude (b, e, h, and k), and BSQ amplitude	
77	(c, f, i, and l). The difference between a/d and g/j is that the former fixed N ($p = 2.0$ mbar)	
78	and varied axial voltage (V) to change E/N ratio, while the latter fixed V (= 466 volts) and	
79	varied p (i.e., N) to change E/N ratio. The difference between b/e and h/k and between c/f	
80	and i/l is that the former was at $p = 2.0$ mbar while the latter $p = 3.5$ mbar. If not varied,	
81	RF amplitude was set at 500 volts and BSQ amplitude at 300 volts.	17
82	Figure S11. The ratio of α -pinene signals (MH^+ : 137 Th; $[MH - C_xH_y]^+$: 81 Th) to all ion	
83	signals. This was used to estimate the E/N ratio.	18
84	Figure S12. The sensitivity of acetone. An intercept above zero indicates a high background	
85	value.	18
86	Figure S13. The signal intensities of H_3O^+ , $H_3OH_2O^+$, and $H_3O(H_2O)_2^+$ as conditions varied as	
87	in Figures 3 in the main text and S14 below.	19
88	Figure S14. The ratio of the logarithm of intensity (panels a, b, and c) and the difference of	
89	fractional signal of the protonated ion (MH^+) among all ions (panels d, e, and f), when	
90	changing axial voltage (V) or FIMR pressure (p) (panels a and d), RF amplitude (panels	
91	b and e), and BSQ amplitude (panels c and f). The ratios were taken after taking the	
92	logarithm of the signal intensities of MH^+ at the right-hand side of the instrument setting	
93	(after the arrow) to that at the left-hand side of the instrument setting stated in the panel	
94	label; likewise, the fractional differences are the fractions of the MH^+ signal among the	
95	protonated, fragmented, and adduct signals under these two instrumental settings.	20
96	Figure S15. The dependence of the $[MH+H_2O]^+$ signals on RH for the VOCs studied. Panels	
97	a-f: the relative sensitivity was calculated as the slope (sensitivity) under high-RH	
98	conditions to that at the dry ($RH < 5\%$) condition. Panel g: the percent change of relative	
99	sensitivity per 10% RH increase.	21
100	Figure S16. The dependence of the $[MH-H_2O]^+$ signals on RH for the VOCs and OVOCs.	
101	Panels a-d: the relative sensitivity was calculated as the slope (sensitivity) under high-RH	
102	conditions to that at the dry ($RH < 5\%$) condition. Panel e: the percent change of relative	
103	sensitivity per 10% RH increase.	22
104	Figure S17. The dependence of the $[MH-C_xH_y]^+$ signals on RH for the VOCs and OVOCs	
105	tested at a concentration of ~ 12 ppbv. Panels a-e: the relative sensitivity was calculated as	
106	the slope (sensitivity) under high-RH conditions to that at the dry ($RH < 5\%$) condition.	
107	Panel f: the percent change of relative sensitivity per 10% RH increase.	23
108		
109		

110 **Tables.**

111 **Table S1.** The details of instrument setting experiments.

Varying setting	Vocus front (volt)	Vocus back (volt)	pressure (mbar)	E/N (Td)	BSQ (volt)	RF (volt)
E	300 to 700	34	2	48 to 142	260	500
N	500	34	1.5 to 3.5	57 to 133	260	500
RF	700	34	2	171	260	500 to 13
BSQ	700	34	2	171	300 to 50	500
RF	700	34	3.5	98	260	500 to 13
BSQ	700	34	3.5	98	300 to 50	500

112

113 **Table S2.** Details of the tested volatile organic compounds (VOCs). Also shown are their
 114 proton affinity (PA) values.

Group ^a	Name	CAS#	m/Q (Th) ^b		PA (kJ mol ⁻¹) ^c
			Exact	Measured	
A1	Benzene	71-43-2	79.0542	79.0548	750.4
	Toluene	108-88-3	93.0699	93.0699	784
	m-Xylene	108-38-3	107.0855	107.0859	812.1
	1,2,4-Trimethylbenzene	95-63-6	121.1012	121.1007	798.3
A2	Isoprene	78-79-5	69.0699	69.0709	826.4
	α -Pinene	80-56-8	137.1325	137.1321	878.6 ^d
	β -Caryophyllene	87-44-5	205.1951	205.198	859.2 ^e
B1	Formaldehyde	50-00-0	31.0178	31.0171	712.5
	Acetaldehyde	75-07-0	45.0335	45.0329	768.5
B2	n-Butanal	123-72-8	73.0648	73.0656	792.7
	Pentanal	110-62-3	87.0804	87.0802	796.6
	Hexaldehyde	66-25-1	101.0961	101.0957	794.4~797 ^f
B3	Acetone	67-64-1	59.0491	59.0491	812
	Methyl ethyl Ketone	78-93-3	73.0648	73.0656	827.3
B4	Acrolein	107-02-8	57.0335	57.0332	797
	Methacrolein	78-85-3	71.0491	71.0495	808.7
B5	Benzaldehyde	100-52-1	107.0491	107.0504	834
	m-Tolualdehyde	620-23-5	121.0648	121.0651	840
C1	Acetonitrile	75-05-8	42.0338	42.0329	779.2
	Acrylonitrile	107-13-1	54.0338	54.0334	784.7
C2	Methanol	67-56-1	33.0335	33.0323	754.3

115 Notes:
 116 a, A1: aromatic hydrocarbons, A2: terpenoids, B1: small aldehydes; B2: long-chain aldehydes, B3: ketones, B4:
 117 unsaturated aldehydes, B5: aromatic aldehydes, C1: nitriles, C2: methanol;
 118 b, mass-to-charge ratio of protonated ion MH⁺;
 119 c, taken from NIST Chemistry WebBook William E. Acree and Chickos (2023), unless stated otherwise;
 120 d, from Solouki and Szulejko (2007); e, from Jenkin et al. (2012); f, from Blake et al. (2008).
 121

122 **Table S3.** Proton-transfer reaction rate constants ($k_{\text{ptr}}, \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) from literature.

Group	Name	$k_{\text{model}}^{\text{a}}$		$k_{\text{experiment}}^{\text{b}}$			N^{c}	$k_{\text{avg}}^{\text{d}}$	$k_{\text{std}}^{\text{e}}$	
A1	Benzene	1.97	1.8	1.9	2.1	1.85	—	5	1.92	0.13
	Toluene	2.12	2.05	1.9	2.2	2.3	—	5	2.11	0.14
	m-Xylene	2.26	2.3	—	—	—	—	2	2.28	0.24
	1,2,4-Trimethylbenzene	2.4	2.4	—	—	—	—	2	2.4	0.25
A2	Isoprene	1.94	1.3	2	2	1.7	2.1	6	1.84	0.12
	α -Pinene	2.44	2.2	2.6	—	—	—	3	2.41	0.22
	β -Caryophyllene	3.1	—	—	—	—	—	1	3.1	0.47
B1	Formaldehyde	3	3.4	—	—	—	—	2	3.2	0.35
	Acetaldehyde	3.36	3.5	3.6	3.7	—	—	4	3.54	0.27
B2	n-Butanal	3.49	3.8	—	—	—	—	2	3.65	0.39
	Pentanal	3.34	3.6	—	—	—	—	2	3.47	0.37
	Hexaldehyde	3.74	3.7	—	—	—	—	2	3.72	0.39
B3	Acetone	3	2.4	3.59	3.9	4.1	—	5	3.4	0.26
	Methyl ethyl Ketone	3.83	3.03	3.9	—	—	—	3	3.59	0.34
B4	Acrolein	3.35	4.2	—	—	—	—	2	3.78	0.45
	Methacrolein	3.55	—	—	—	—	—	1	3.55	0.53
B5	Benzaldehyde	4.12	3.7	—	—	—	—	2	3.91	0.43
	m-Tolualdehyde	4.9	4.1	—	—	—	—	2	4.5	0.52
C1	Acetonitrile	4.74	2.7	4.7	5.1	3.92	—	5	4.23	0.33
	Acrylonitrile	5.1	—	—	—	—	—	1	5.1	0.77
C2	Methanol	2.33	2.1	2.2	2.7	—	—	4	2.33	0.18

123 Notes:
 124 a, From Zhao and Zhang (2004);
 125 b, From Pagonis et al. (2019) and reference therein, as well as Zhao and Zhang (2004), Michel et al. (2005),
 126 Milligan et al. (2002), Lindinger et al. (1998), Cappellin et al. (2012), Sekimoto et al. (2017);
 127 c, number of values for averaging;
 128 d, averaged $k_{\text{proton-transfer}}$;
 129 e, the uncertainty of $k_{\text{proton-transfer}}$ by assuming 15% uncertainty for modeled values Zhao and Zhang (2004) as well
 130 as experiment values, weighted by the number of values.
 131

132 **Table S4.** The RH dependence, sensitivity, intercept of protonated adducts, and fragmented ions.

Group	Name	[MH+H ₂ O] ⁺			[MH-H ₂ O] ⁺			[MH-C _x H _y] ⁺			Signal percentage (%) ^b			
		Sensitivity (cps/ppbv)	Intercept (cps)	RH-dependence (%)	Sensitivity (cps/ppbv)	Intercept (cps)	RH-dependence (%)	Sensitivity (cps/ppbv)	Intercept (cps)	RH-dependence (%)	MH ⁺	[MH+H ₂ O] ⁺	[MH-H ₂ O] ⁺	[MH-C _x H _y] ⁺
A1	Benzene	— ^a	—	—	—	—	—	—	—	—	100	—	—	—
	Toluene	—	—	—	—	—	—	153.7	52.7	-1.5	98	—	—	2
	m-Xylene	—	—	—	—	—	—	2903.7	-168.1	-0.8	76	—	—	24
	1,2,4-Trimethylbenzene	—	—	—	—	—	—	1219.8	-185.5	-0.4	88	—	—	12
A2	Isoprene	—	—	—	—	—	—	154.4	211.9	-1.1	93	—	—	7
	α-Pinene	—	—	—	—	—	—	4171.2	1437.7	0.2	46	—	—	54
	β-Caryophyllene	1.4	1.7	3.5	—	—	—	—	—	—	100	—	—	<<1 ^d
B1	Formaldehyde	—	—	—	—	—	—	—	—	—	100	—	—	—
	Acetaldehyde I ^c	—	—	—	0.1	0.6	-0.79	—	—	—	100	—	<<1 ^d	—
	Acetaldehyde II ^c	—	—	—	0.2	0.6	0.67	—	—	—	100	—	<<1 ^d	—
B2	n-Butanal	201.4	327.5	5.1	5589.1	13531	0.02	—	—	—	23	3	75	? ^e
	Pentanal	1300.1	1617.1	1.4	4116.6	816.3	0.29	—	—	—	24	7	69	?
	Hexaldehyde	367	399.3	8.2	367	399.3	0.30	84	1203.6	0.6	20	6	72	2
B3	Acetone I ^c	58	433	5.4	288.1	635	0.37	131	5939.7	-3.0	91	1	3	5
	Acetone II ^c	64.5	444.3	5.3	603.5	556.6	0.38	170.9	5674.8	-2.1	91	1	3	5
	Methyl ethyl Ketone	273.4	178.3	2.8	1084.3	13728.2	-0.92	208.2	2614.9	0.2	77	2	17	2
B4	Acrolein	49.7	4057	2.3	268.7	339.2	0.47	—	—	—	91	5	4	—
	Methacrolein	385.5	746.5	2.3	217.5	176.6	-0.19	—	—	—	90	7	3	—
B5	Benzaldehyde	774.9	-457.7	2.7	—	—	—	—	—	—	95	5	—	—
	m-Tolualdehyde	985	-956.1	2.4	—	—	—	1261	742.5	-2.4	87	8	—	6
C1	Acetonitrile	46.2	1199.8	8.5	—	—	—	—	—	—	93	7	—	—
	Acrylonitrile	118.2	111	5.2	—	—	—	—	—	—	99	1	—	—
C2	Methanol	40.7	0.69	1.9	—	—	—	—	—	—	3	97	—	—

133 Notes:

134 a, not available;

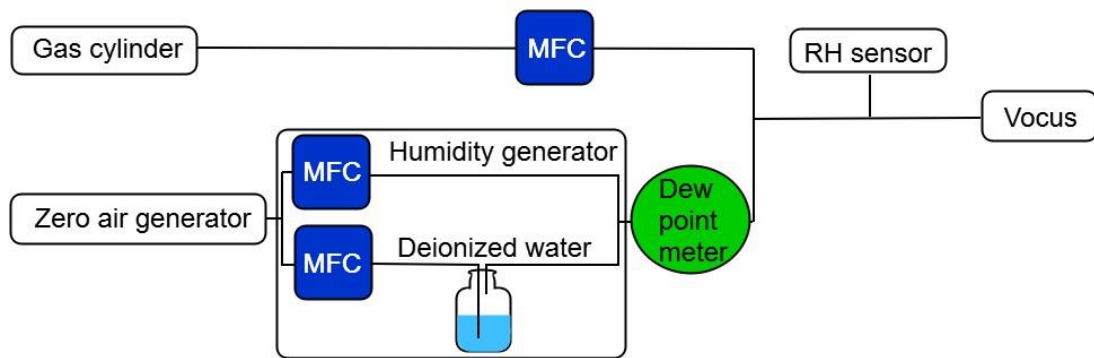
135 b, the specific percentage of fragment or adducted ion signals on all ion signals;

136 c, from gas standard cylinders I and II.

137 d, far less than 1 and closer to zero;

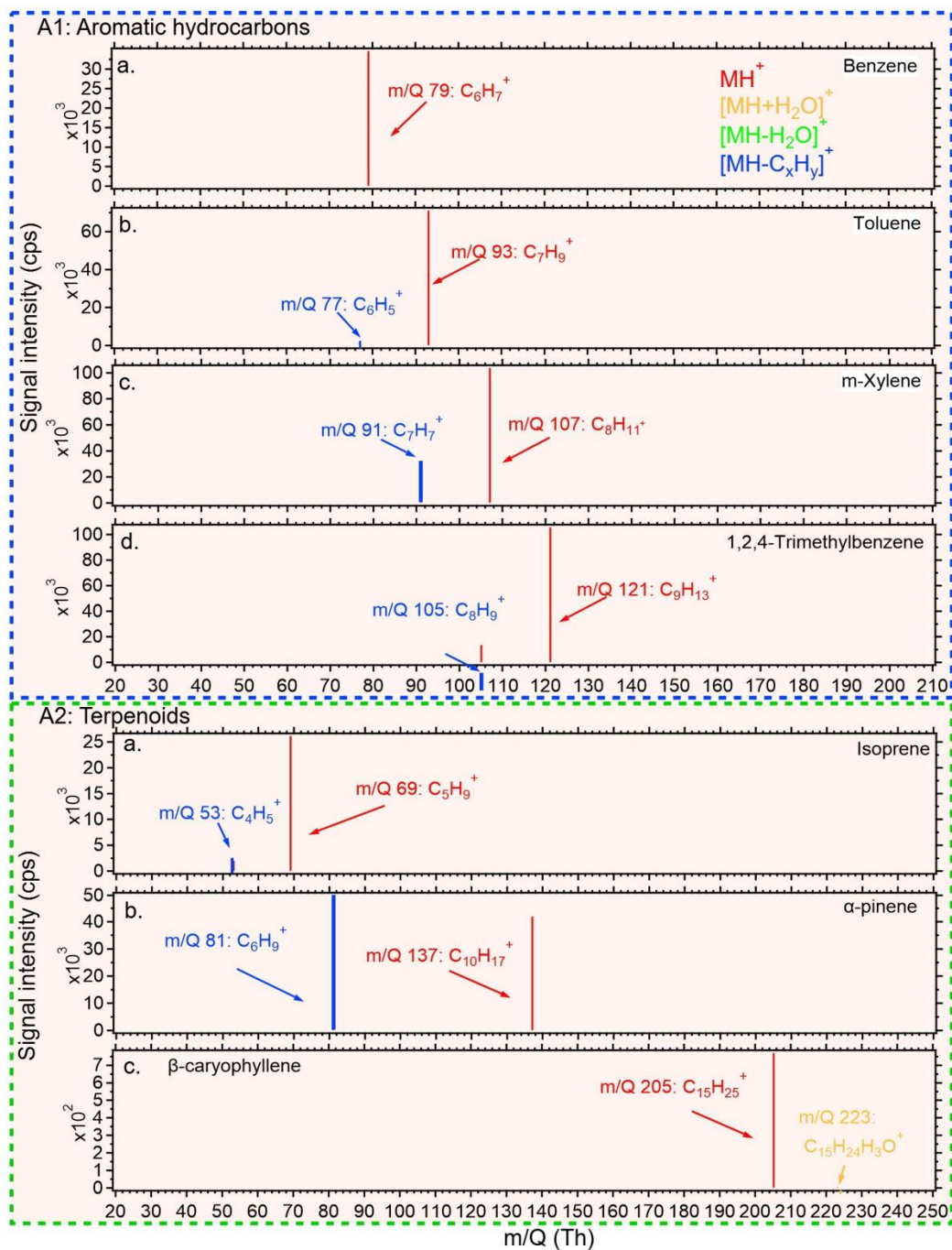
138 e, not determined due to overlapping signals.

139 **Figures.**



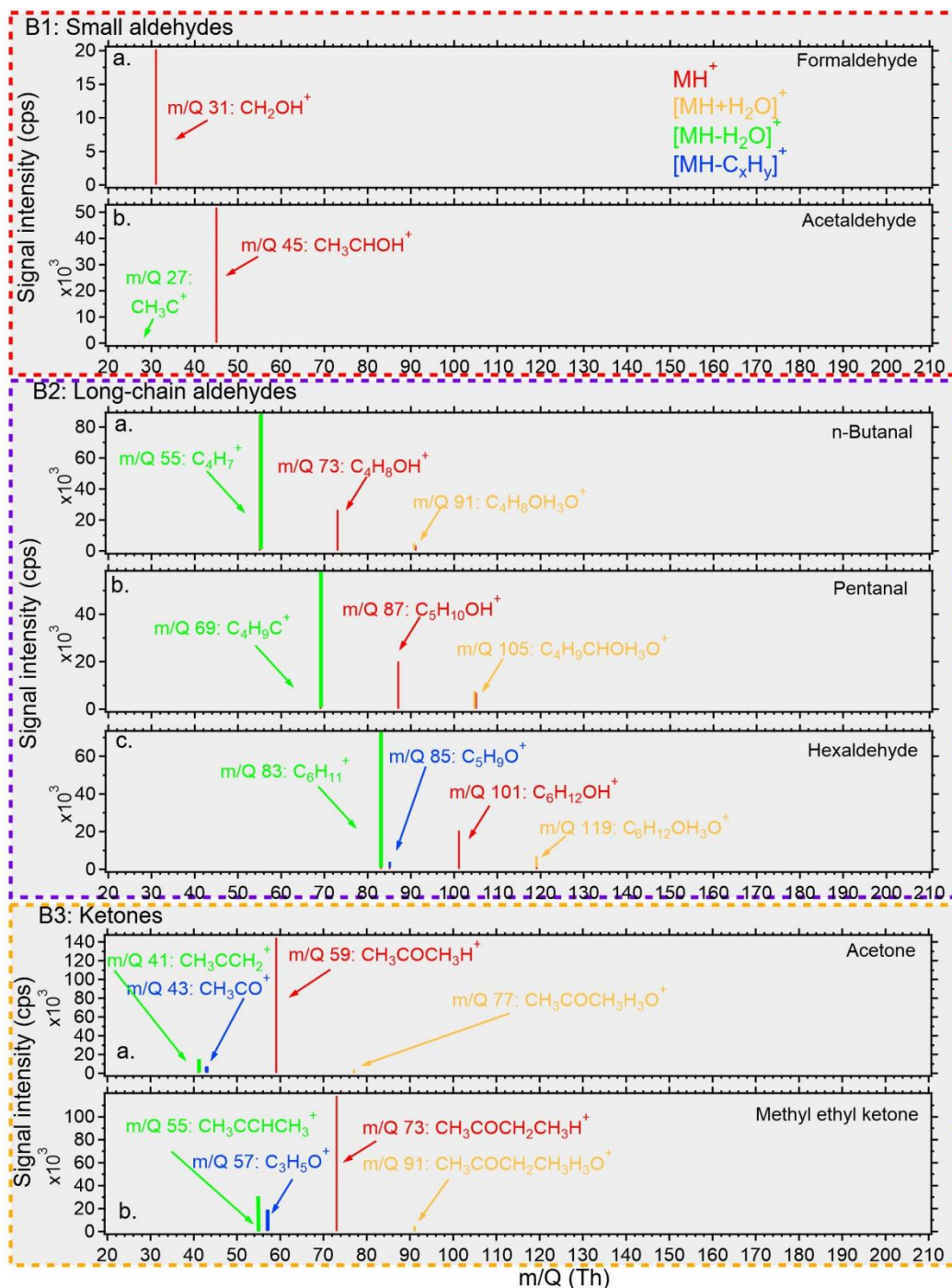
140

141 **Figure S1.** The diagram of the RH experimental setup. MFC: mass flow controller.
142



143

144 **Figure S2.** The mass spectra of aromatic hydrocarbons (benzene, toluene, m-xylene,
 145 and 1,2,4-trimethylbenene), and terpenoids (isoprene, α -pinene, and β -caryophyllene)
 146 in Vocus at a mixing ratio of ~ 12 ppbv (β -caryophyllene 1.2 ppbv).
 147



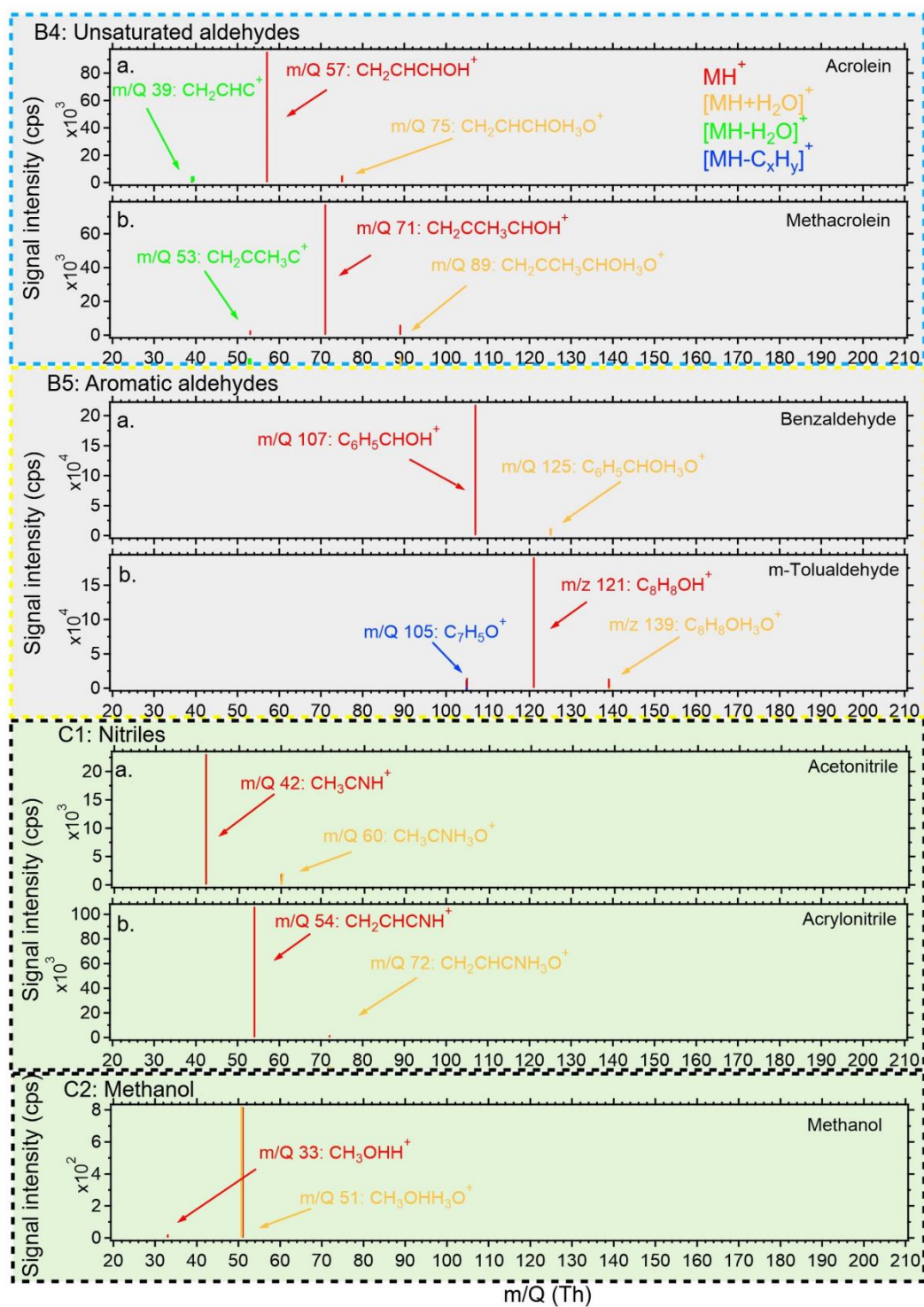
148

149 **Figure S3.** The mass spectra of small aldehydes (formaldehyde and acetaldehyde),

150 long-chain aldehydes (n-butanal, pentanal, and hexaldehyde), and ketones (acetone,

151 and methyl ethyl ketone) in Vocus at a mixing ratio of ~ 12 ppbv.

152



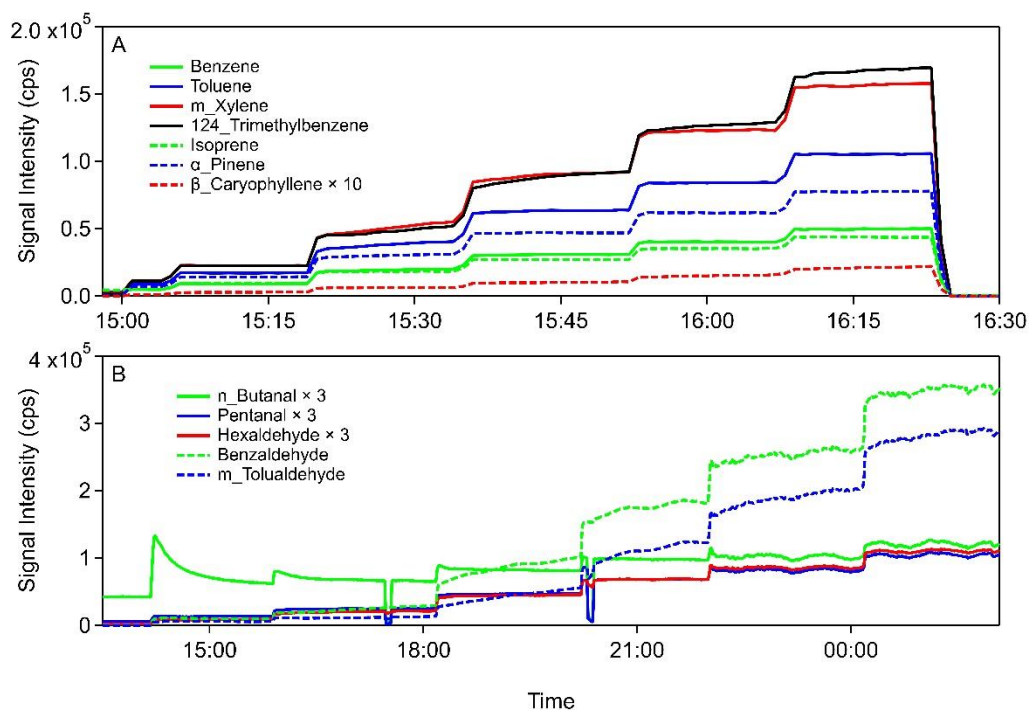
153

154 **Figure S4.** The mass spectra of unsaturated aldehydes (acrolein and methacrolein),

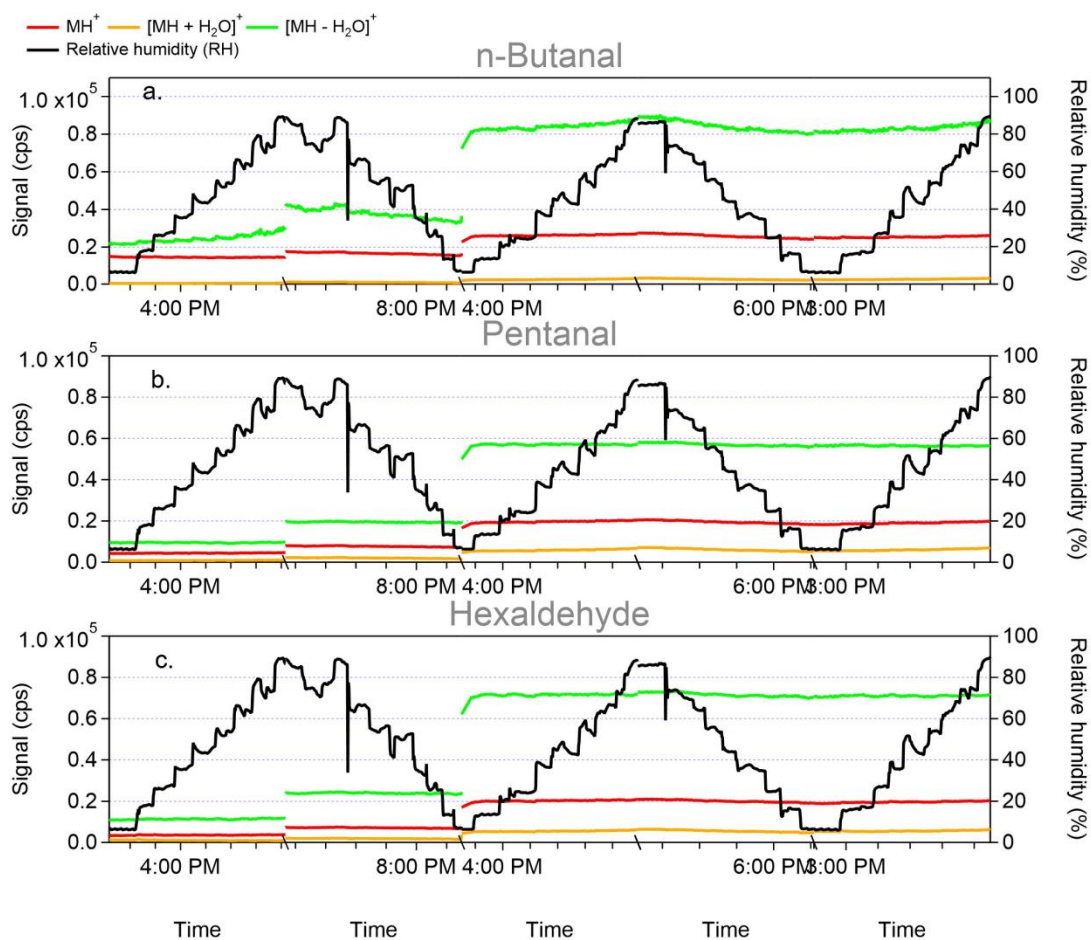
155 aromatic aldehydes (benzaldehyde and m-tolualdehyde), nitriles (acetonitrile and

156 acrylonitrile), and methanol in Vocus at a mixing ratio of ~ 12 ppbv.

157



158
 159 **Figure S5.** Time series of the protonated ion (MH^+) signals for selected (A) VOCs and
 160 (B) OVOCs as concentration varied from 0 to ~ 22 ppbv (~ 2 ppbv for β caryophyllene)
 161 under dry ($MH \sim 5\%$) conditions. Note the signals were magnified by 10 times for β -
 162 caryophyllene and 3 times for n-butanal, pentanal, and hexaldehyde.
 163

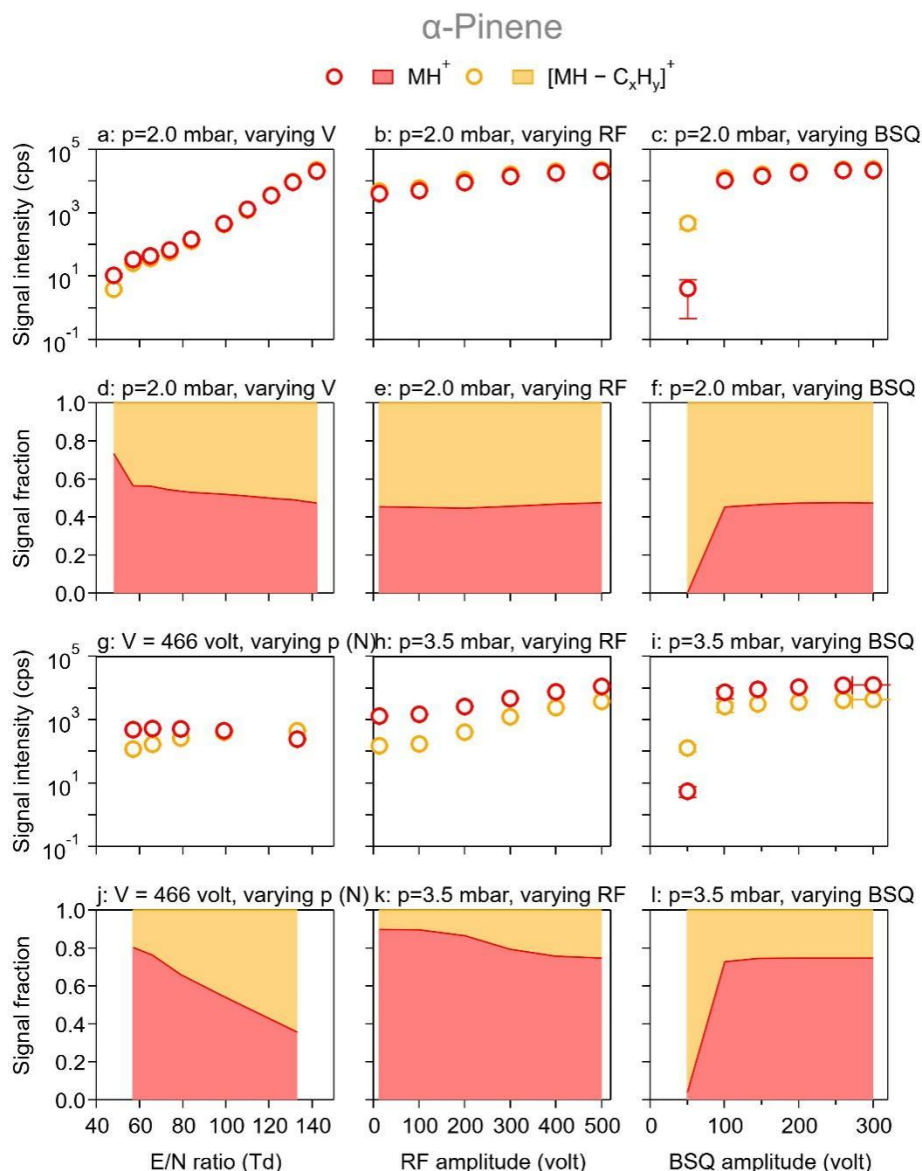


164

165

166 **Figure S6.** Time series of the protonated ion (MH^+), adduct ions ($[MH + H_2O]^+$), and
 167 fragmented ions ($[MH - H_2O]^+$) and/or ($[MH - C_xH_y]^+$) signals for n-butanal, pentanal,
 168 and hexaldehyde. Note that the time in x axis is not continuous, with some periods with
 169 noisy signals cut off.

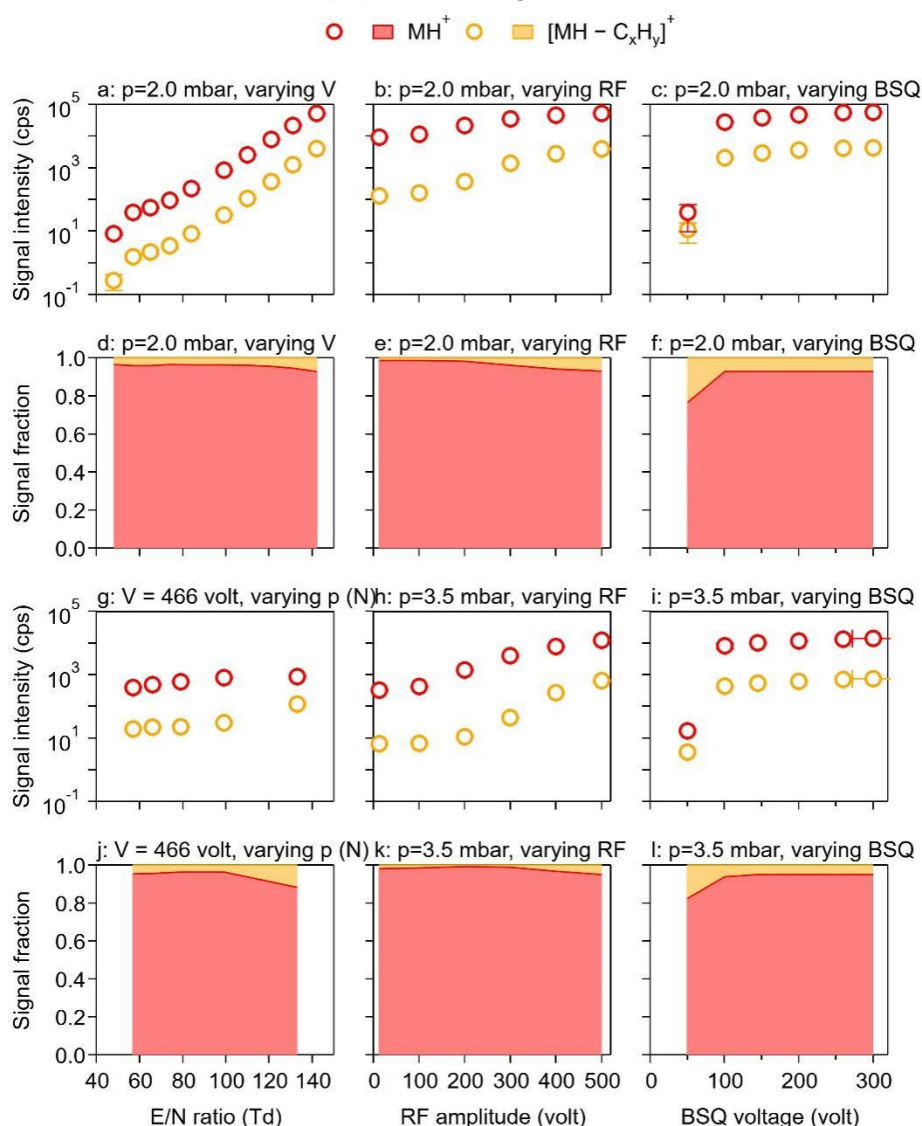
169



170
 171 **Figure S7.** The signal intensities (panels a, b, and c, and panels g, h, and i) and fractions
 172 (panels d, e, and f, and panels j, k, and l) of protonated ion (MH^+), adduct ions ($[\text{MH} +$
 173 $\text{H}_2\text{O}]^+$), and fragmented ions ($[\text{MH} - \text{H}_2\text{O}]^+$ and $[\text{MH} - \text{C}_x\text{H}_y]^+$) for α -pinene as
 174 functions of E/N ratio (a, d, g, and j), RF amplitude (b, e, h, and k), and BSQ amplitude
 175 (c, f, i, and l). The difference between a/d and g/j is that the former fixed N ($p = 2.0$
 176 mbar) and varied axial voltage (V) to change E/N ratio, while the latter fixed V (= 466
 177 volts) and varied p (i.e., N) to change E/N ratio. The difference between b/e and h/k and
 178 between c/f and i/l is that the former was at $p = 2.0$ mbar while the latter $p = 3.5$ mbar.
 179 If not varied, RF amplitude was set at 500 volts and BSQ amplitude at 300 volts.

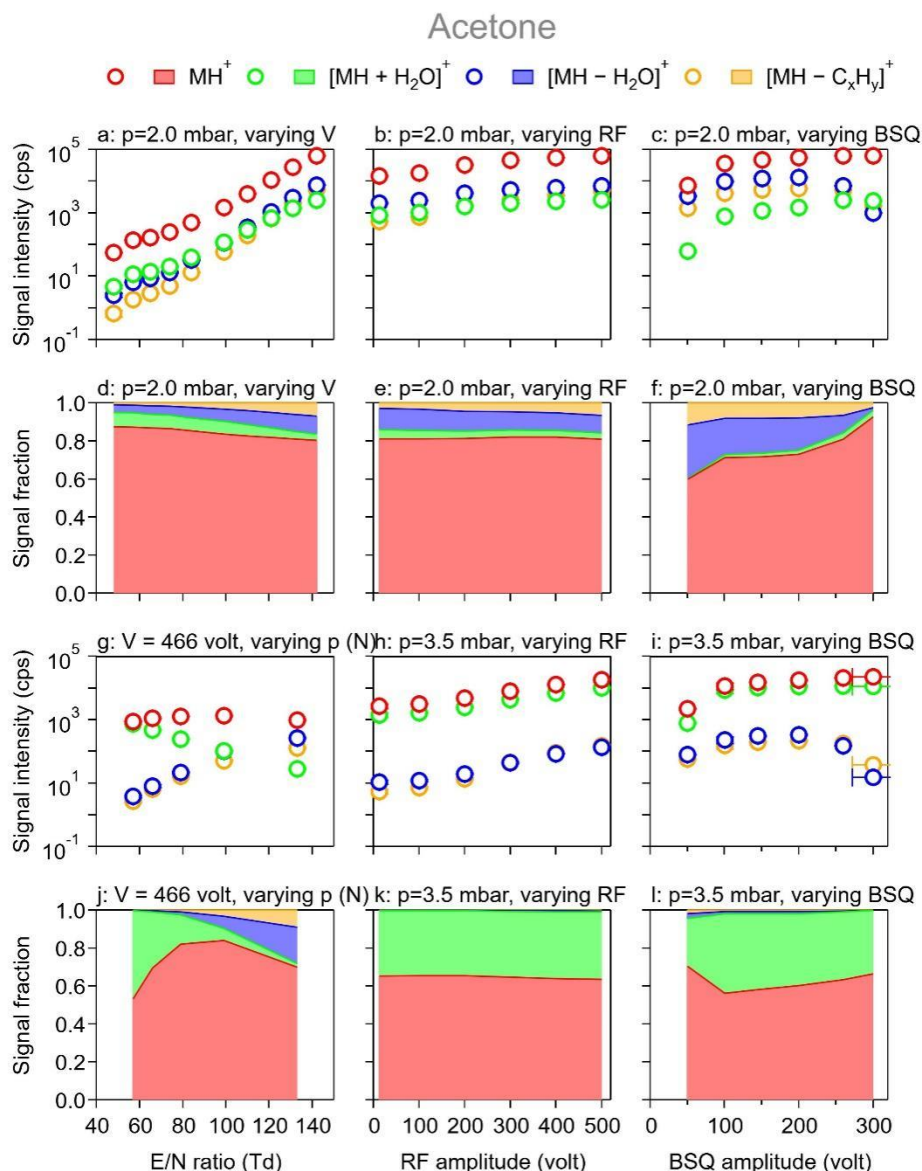
180

1,2,4-Trimethylbenzene



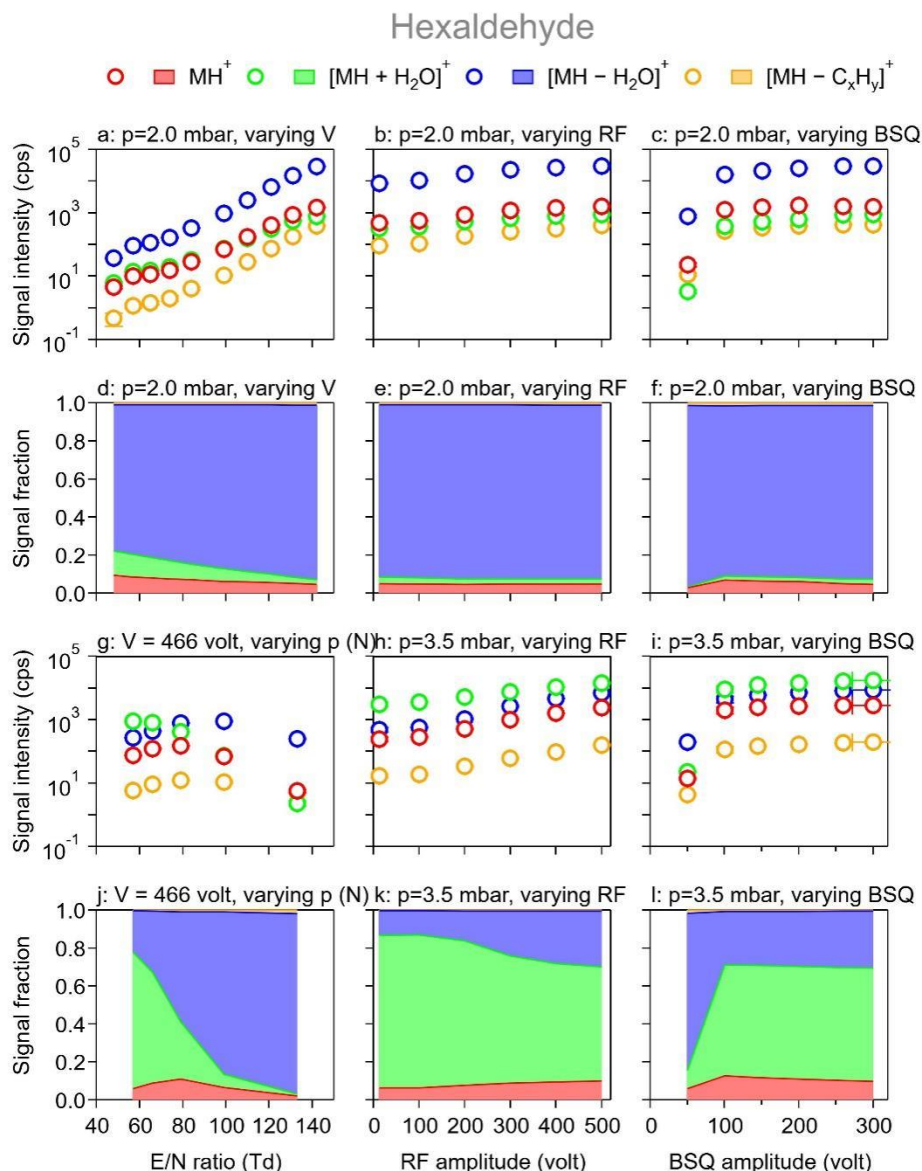
181
 182 **Figure S8.** The signal intensities (panels a, b, and c, and panels g, h, and i) and fractions
 183 (panels d, e, and f, and panels j, k, and l) of protonated ion (MH^+), adduct ions ($[\text{MH} +$
 184 $\text{H}_2\text{O}]^+$), and fragmented ions ($[\text{MH} - \text{H}_2\text{O}]^+$ and $[\text{MH} - \text{C}_x\text{H}_y]^+$) for 1,2,4-
 185 trimethylbenzene as functions of E/N ratio (a, d, g, and j), RF amplitude (b, e, h, and k),
 186 and BSQ amplitude (c, f, i, and l). The difference between a/d and g/j is that the former
 187 fixed N ($p = 2.0$ mbar) and varied axial voltage (V) to change E/N ratio, while the latter
 188 fixed V (= 466 volts) and varied p (i.e., N) to change E/N ratio. The difference between
 189 b/e and h/k and between c/f and i/l is that the former was at $p = 2.0$ mbar while the latter
 190 $p = 3.5$ mbar. If not varied, RF amplitude was set at 500 volts and BSQ amplitude at
 191 300 volts.

192

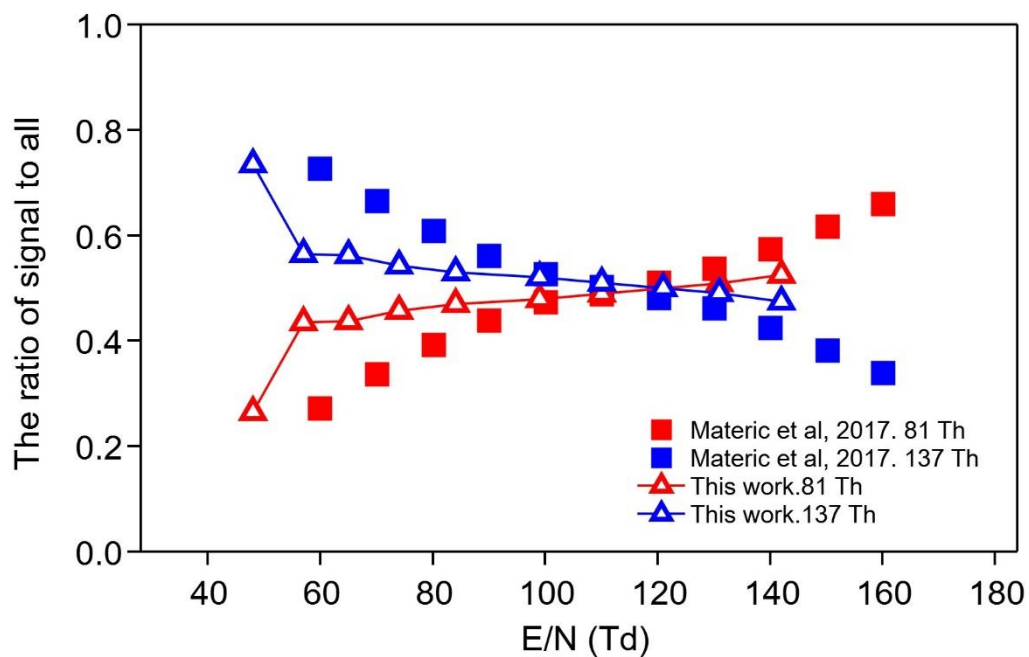


193
 194 **Figure S9.** The signal intensities (panels a, b, and c, and panels g, h, and i) and fractions
 195 (panels d, e, and f, and panels j, k, and l) of protonated ion (MH^+), adduct ions ($[\text{MH} +$
 196 $\text{H}_2\text{O}]^+$), and fragmented ions ($[\text{MH} - \text{H}_2\text{O}]^+$ and $[\text{MH} - \text{C}_x\text{H}_y]^+$) for acetone as functions
 197 of E/N ratio (a, d, g, and j), RF amplitude (b, e, h, and k), and BSQ amplitude (c, f, i,
 198 and l). The difference between a/d and g/j is that the former fixed N ($p = 2.0$ mbar) and
 199 varied axial voltage (V) to change E/N ratio, while the latter fixed V (= 466 volts) and
 200 varied p (i.e., N) to change E/N ratio. The difference between b/e and h/k and between
 201 c/f and i/l is that the former was at $p = 2.0$ mbar while the latter $p = 3.5$ mbar. If not
 202 varied, RF amplitude was set at 500 volts and BSQ amplitude at 300 volts.

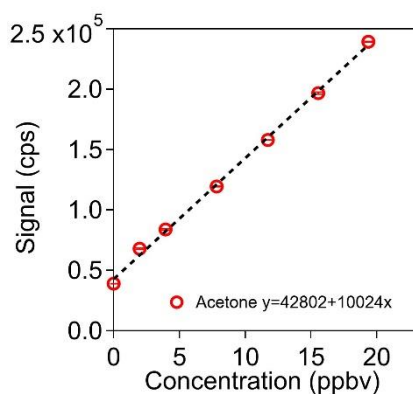
203



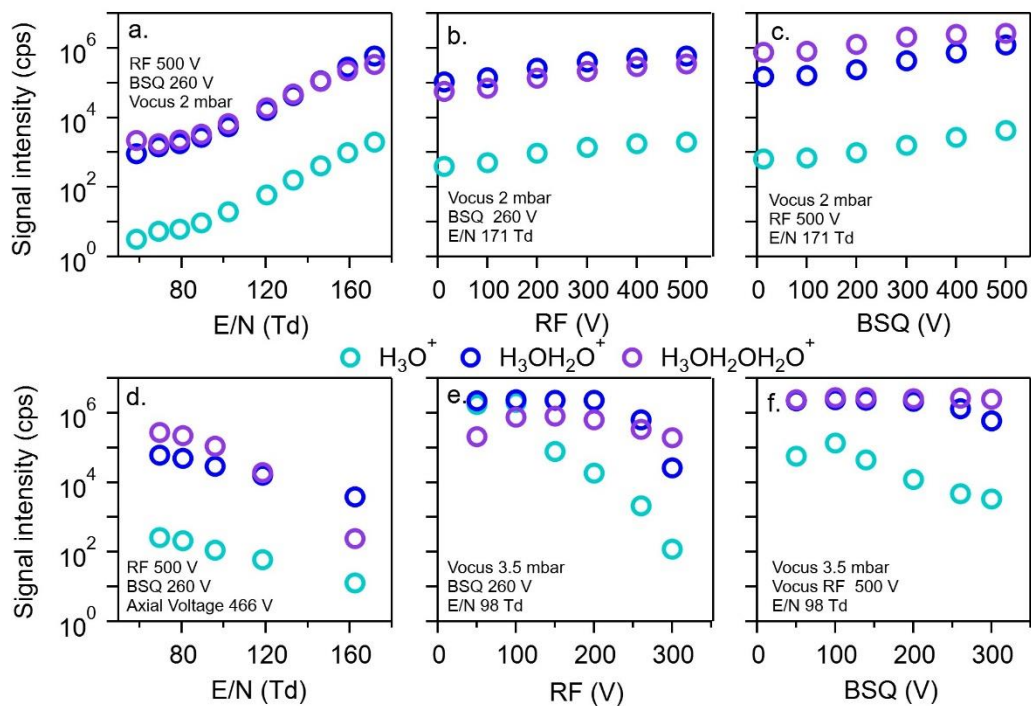
204
 205 **Figure S10.** The signal intensities (panels a, b, and c, and panels g, h, and i) and
 206 fractions (panels d, e, and f, and panels j, k, and l) of protonated ion (MH^+), adduct ions
 207 ($[\text{MH} + \text{H}_2\text{O}]^+$), and fragmented ions ($[\text{MH} - \text{H}_2\text{O}]^+$ and $[\text{MH} - \text{C}_x\text{H}_y]^+$) for
 208 hexaldehyde as functions of E/N ratio (a, d, g, and j), RF amplitude (b, e, h, and k), and
 209 BSQ amplitude (c, f, i, and l). The difference between a/d and g/j is that the former
 210 fixed N ($p = 2.0$ mbar) and varied axial voltage (V) to change E/N ratio, while the latter
 211 fixed V (= 466 volts) and varied p (i.e., N) to change E/N ratio. The difference between
 212 b/e and h/k and between c/f and i/l is that the former was at $p = 2.0$ mbar while the latter
 213 $p = 3.5$ mbar. If not varied, RF amplitude was set at 500 volts and BSQ amplitude at
 214 300 volts.
 215



216
 217 **Figure S11.** The ratio of α -pinene signals (MH^+ : 137 Th; $[MH - C_xH_y]^+$: 81 Th) to all
 218 ion signals. This was used to estimate the E/N ratio.



219
 220 **Figure S12.** The sensitivity of acetone. An intercept above zero indicates a high
 221 background value.



222

223

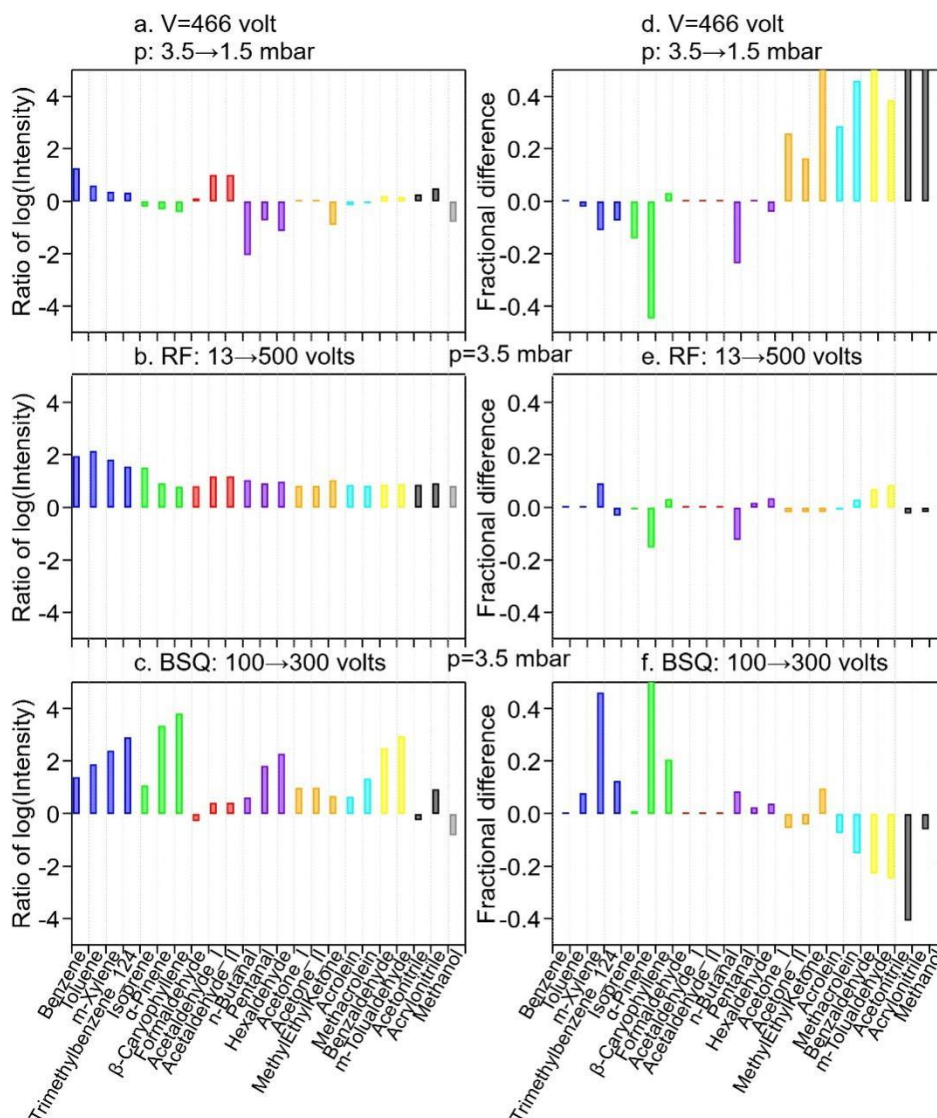
Figure S13. The signal intensities of H_3O^+ , $\text{H}_3\text{OH}_2\text{O}^+$, and $\text{H}_3\text{O}(\text{H}_2\text{O})_2^+$ as conditions

224

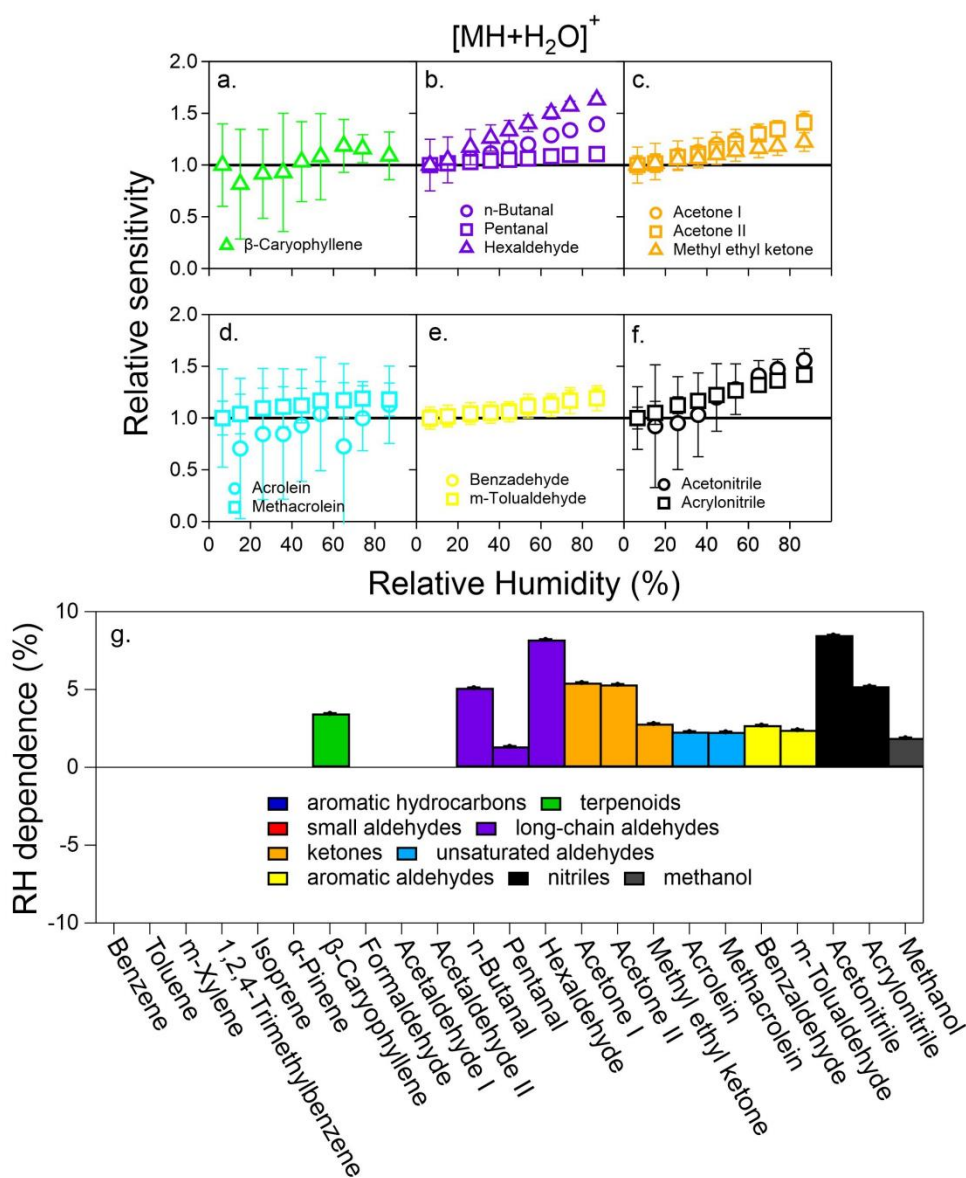
varied as in Figures 3 in the main text and S14 below.

225

■ Aromatic hydrocarbons ■ Terpenoids ■ Small aldehydes ■ Long-chain aldehydes
■ Ketones ■ Unsaturated aldehydes ■ Aromatic aldehydes ■ Nitriles ■ Methanol



226
 227 **Figure S14.** The ratio of the logarithm of intensity (panels a, b, and c) and the difference
 228 of fractional signal of the protonated ion (MH^+) among all ions (panels d, e, and f),
 229 when changing axial voltage (V) or FIMR pressure (p) (panels a and d), RF amplitude
 230 (panels b and e), and BSQ amplitude (panels c and f). The ratios were taken after taking
 231 the logarithm of the signal intensities of MH^+ at the right-hand side of the instrument
 232 setting (after the arrow) to that at the left-hand side of the instrument setting stated in
 233 the panel label; likewise, the fractional differences are the fractions of the MH^+ signal
 234 among the protonated, fragmented, and adduct signals under these two instrumental
 235 settings.
 236
 237



238

239 **Figure S15.** The dependence of the $[MH+H_2O]^+$ signals on RH for the VOCs studied.

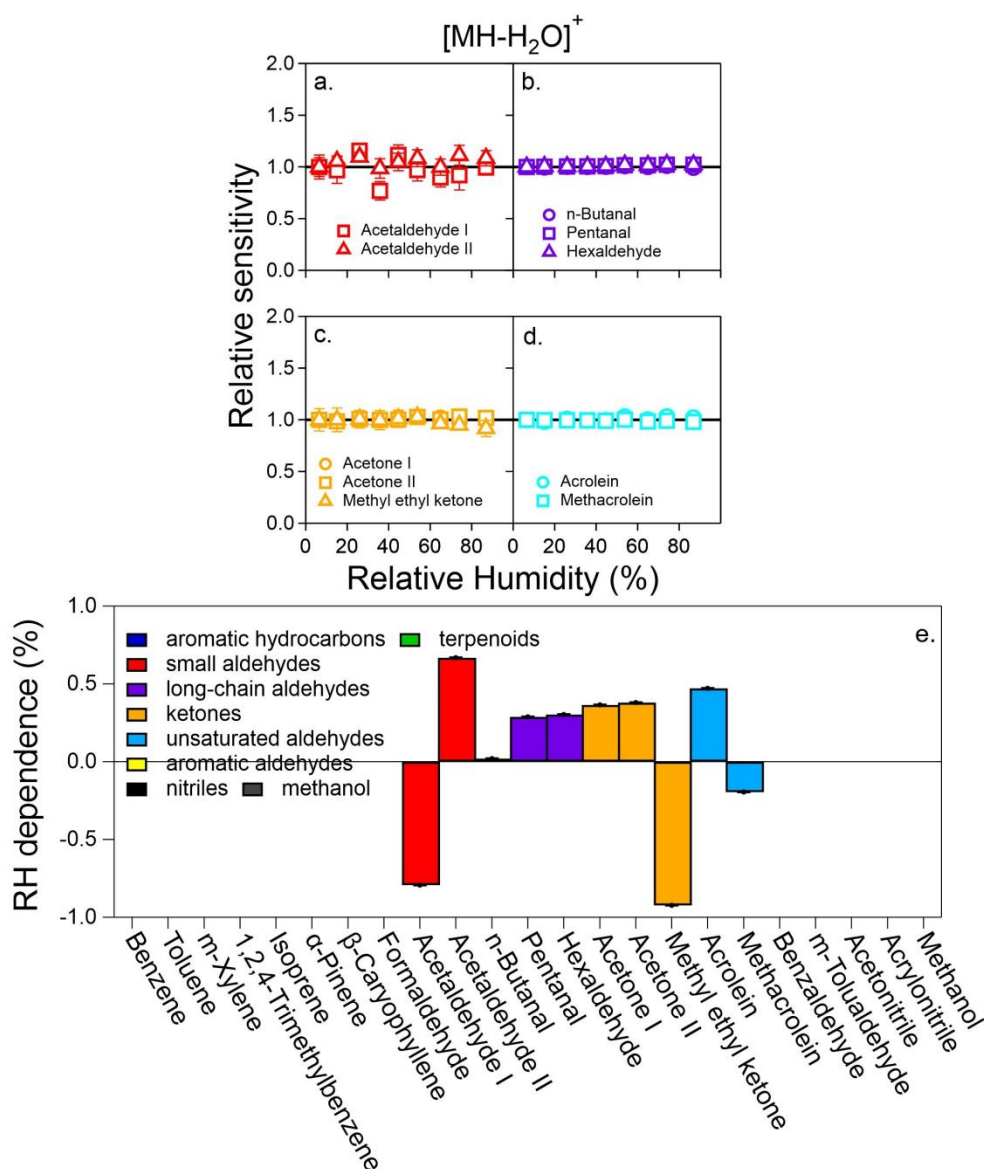
240 Panels a-f: the relative sensitivity was calculated as the slope (sensitivity) under high-

241 RH conditions to that at the dry (RH<5%) condition. Panel g: the percent change of

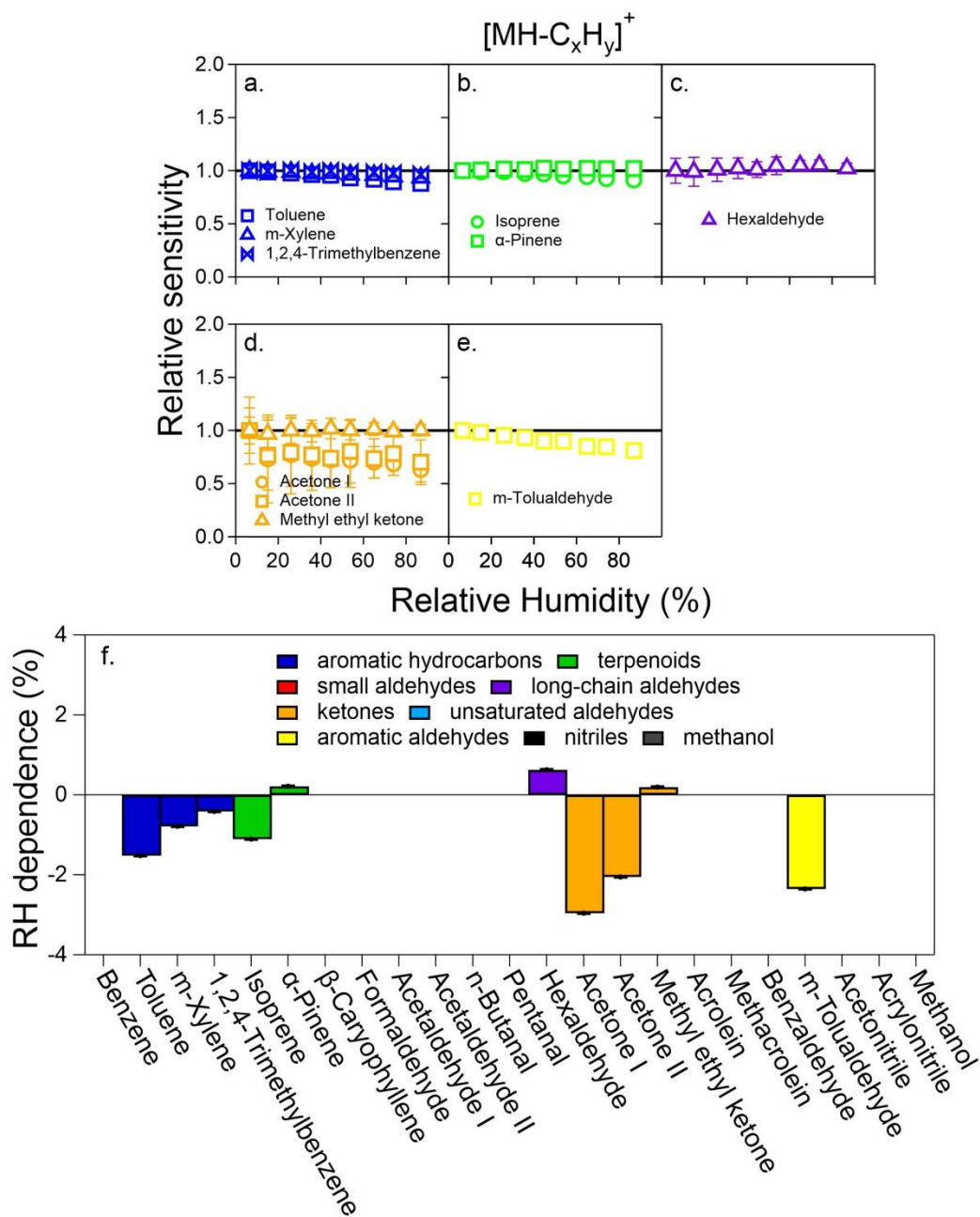
242 relative sensitivity per 10% RH increase.

243

244



245
 246 **Figure S16.** The dependence of the $[MH-H_2O]^+$ signals on RH for the VOCs and
 247 OVOCs. Panels a-d: the relative sensitivity was calculated as the slope (sensitivity)
 248 under high-RH conditions to that at the dry (RH<5%) condition. Panel e: the percent
 249 change of relative sensitivity per 10% RH increase.



250
 251 **Figure S17.** The dependence of the $[MH-C_xH_y]^+$ signals on RH for the VOCs and
 252 OVOCs tested at a concentration of ~12 ppbv. Panels a-e: the relative sensitivity was
 253 calculated as the slope (sensitivity) under high-RH conditions to that at the dry (RH<5%)
 254 condition. Panel f: the percent change of relative sensitivity per 10% RH increase.

255 **References**

- 256 Blake, R. S., Patel, M., Monks, P. S., Ellis, A. M., Inomata, S., and Tanimoto, H.: Aldehyde and ketone
257 discrimination and quantification using two-stage proton transfer reaction mass spectrometry,
258 International Journal of Mass Spectrometry, 278, 15-19, <https://doi.org/10.1016/j.ijms.2008.07.010>,
259 2008.
- 260 Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P. M., Soukoulis, C., Aprea, E., Märk, T. D.,
261 Gasperi, F., and Biasioli, F.: On Quantitative Determination of Volatile Organic Compound
262 Concentrations Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry, Environmental
263 Science & Technology, 46, 2283-2290, <https://doi.org/10.1021/es203985t>, 2012.
- 264 Jenkin, M. E., Wyche, K. P., Evans, C. J., Carr, T., Monks, P. S., Alfarra, M. R., Barley, M. H., McFiggans,
265 G. B., Young, J. C., and Rickard, A. R.: Development and chamber evaluation of the MCM v3.2
266 degradation scheme for β -caryophyllene, Atmos. Chem. Phys., 12, 5275-5308,
267 <https://doi.org/10.5194/acp-12-5275-2012>, 2012.
- 268 Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at
269 pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical
270 applications, food control and environmental research, Int J Mass Spectrom, 173, 191-241,
271 [https://doi.org/10.1016/S0168-1176\(97\)00281-4](https://doi.org/10.1016/S0168-1176(97)00281-4), 1998.
- 272 Michel, E., Schoon, N., Amelynck, C., Guimbaud, C., Catoire, V., and Arijs, E.: A selected ion flow
273 tube study of the reactions of H_3O^+ , NO^+ and O_2^+ with methyl vinyl ketone and some
274 atmospherically important aldehydes, International Journal of Mass Spectrometry, 244, 50-59,
275 <https://doi.org/10.1016/j.ijms.2005.04.005>, 2005.
- 276 Milligan, D. B., Wilson, P. F., Freeman, C. G., Meot-Ner, M., and McEwan, M. J.: Dissociative proton
277 transfer reactions of H_3^+ , N_2H^+ , and H_3O^+ with acyclic, cyclic, and aromatic hydrocarbons and
278 nitrogen compounds, and astrochemical implications, The Journal of Physical Chemistry A, 106,
279 9745-9755, <https://org.doi/10.1021/jp014659j>, 2002.
- 280 Pagonis, D., Sekimoto, K., and de Gouw, J.: A Library of Proton-Transfer Reactions of H_3O^+ Ions
281 Used for Trace Gas Detection, J Am Soc Mass Spectr, 30, 1330-1335, 2019.
- 282 Sekimoto, K., Li, S. M., Yuan, B., Koss, A., Coggon, M., Warneke, C., and de Gouw, J.: Calculation of
283 the sensitivity of proton-transfer-reaction mass spectrometry (PTR-MS) for organic trace gases
284 using molecular properties, International Journal of Mass Spectrometry, 421, 71-94, 2017.
- 285 Solouki, T. and Szulejko, J. E.: Bimolecular and unimolecular contributions to the disparate self-
286 chemical ionizations of α -Pinene and camphene isomers, J Am Soc Mass Spectr, 18, 2026-2039,
287 <https://doi.org/10.1016/j.jasms.2007.08.016>, 2007.
- 288 "Phase Transition Enthalpy Measurements of Organic and Organometallic Compounds" in NIST
289 Chemistry WebBook, NIST Standard Reference Database Number 69, last
- 290 Zhao, J. and Zhang, R.: Proton transfer reaction rate constants between hydronium ion (H_3O^+)
291 and volatile organic compounds, Atmospheric Environment, 38, 2177-2185,
292 <https://doi.org/10.1016/j.atmosenv.2004.01.019>, 2004.
- 293