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 (α), permanent dipole moment (D), calculated proton-transfer reaction rate constant (k_{PTR}), average (±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	α (10^{-24} cm^3)	D (Debye)	k_{PTR} (E/N = 160 Td) (10^{-9} cm^3 molec^{-1} s^{-1})	Sensitivity ± 1 SD (cps ppbv^{-1})	LOD (5 s) (pptv)
Methanol	CH_4OH^+	33.0335	-	-	3.28[a]	1.70[a]	2.08	3±2	2000
Acetonitrile	$C_2H_3NH^+$	42.0338	0.967±0.002	$C_2H_3N(H_2O)H^+$	4.44[a]	3.93[a]	3.61	2000±300	14
Acetaldehyde	$C_2H_4OH^+$	45.0335	-	-	4.60[a]	2.75[a]	2.84	2000±300	60
Acrylonitrile	$C_3H_3NH^+$	54.0338	0.957±0.003	$C_3H_3N(H_2O)H^+$	8.05[a]	3.92[a]	3.82	4800±700	4
Acetone	$C_3H_6OH^+$	59.0491	0.89±0.02	$C_3H_6O(H_2O)H^+$, $C_2H_3O(H_2O)^+$, $C_2H_3O^+$	6.37[a]	2.88[a]	2.94	4300±700	14
Isoprene	$C_5H_8H^+$	69.0699	0.39±0.02*	$C_5H_8(H_2O)H^+$, $C_5H_7^+$, $C_4H_5^+$, $C_3H_5^+$, $C_3H_3^+$	9.99[a]	0.25[a]	1.92	1300±100	13
Methyl Ethyl Ketone	$C_4H_8OH^+$	73.0648	0.838±0.007	$C_4H_8O(H_2O)H^+$, $C_4H_7^+$, $C_3H_5O^+$	8.13[a]	2.78[a]	2.85	400±500	6
Benzene	$C_6H_6H^+$	79.0542	0.877±0.008	$C_6H_7O^+$	10.4[a]	0[b]	1.93	2300±400	9
Toluene	$C_7H_8H^+$	93.0699	0.74±0.02	$C_7H_7^+$, $C_6H_7O^+$	12.1[a]	0.375[a]	2.06	3200±500	4
m-Xylene	$C_8H_{10}H^+$	107.0855	0.79±0.02	$C_7H_7^+$	14.2[a]	0.27[b]	2.20	3100±400	5
1,2,4-Trimethylbenzene	$C_9H_{12}H+$	121.1012	0.82±0.02	$C_8H_9^+$	17.2[b]	0.29[b]	2.40	3100±400	6
α-Pinene	$C_{10}H_{16}H^+$	137.1325	0.36±0.02	$C_7H_{11}^+$, $C_7H_9^+$, $C_7H_7^+$, $C_6H_9^+$	17.1[c]	0.18[c]	2.37	1160±130	6
β-Caryophyllene	$C_{15}H_{24}H^+$	205.1951	-	-	26.4[c]	0.62[c]	2.89	220±30	6

[a](Haynes, 2014), [b](Zhao and Zhang, 2004), [c](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 (α), permanent dipole moment (D), calculated proton transfer reaction rate constant (k_{PTR}), average (±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	α (10^{-24} cm^3)	D (Debye)	k_{PTR} (E/N = 160 Td) (10^{-9} cm^3 molec^{-1} s^{-1})	Sensitivity $\pm$ 1 SD (cps ppbv^{-1})	LOD (5 s) (pptv)
Acetonitrile	$C_2H_3NH^+$	42.0338	0.970±0.004	$C_2H_3N(H_2O)H^+$	4.44[a]	3.93[a]	3.61	1800±200	14
Acetone	$C_3H_6OH^+$	59.0491	0.90±0.02	$C_3H_6O(H_2O)H^+$, $C_2H_3O(H_2O)^+$, $C_2H_3O^+$	6.37[a]	2.88[a]	2.94	5000±700	14
Furan	$C_4H_4OH^+$	69.0335	0.9533±0.0003	$C_4H_4O(H_2O)H^+$	7.31[a]	0.66[a]	1.68	2500±300	8
Benzene	$C_6H_6H^+$	79.0542	0.878±0.003	$C_6H_7O^+$	10.4[a]	0[b]	1.93	4300±600	9
Phenol	$C_6H_6OH^+$	95.0491	-	-	11.1[a]	1.24[a]	2.09	360±50	120
Ethylbenzene	$C_8H_{10}H^+$	107.0855	0.388±0.011	$C_7H_7^+$, $C_6H_7^+$	14.2[a]	0.59[a]	2.21	1900±200	5
t-Amyl Ethyl Ether	$C_7H_{16}OH^+$	117.1274	-	$C_3H_7O^+$, others	-	-	-	-	-
1,3,5-Trimethylbenzene	$C_9H_{12}H+$	121.1012	0.84±0.02	$C_8H_9^+$	15.8[b]	0.047[b]	2.30	3700±500	6
d-Limonene	$C_{10}H_{16}H^+$	137.1325	0.394±0.005	$C_7H_{11}^+$, $C_7H_9^+$, $C_7H_7^+$, $C_6H_9^+$	18.0[c]	0.49[c]	2.44	900±100	6
Octamethyl-cyclotetrasiloxane (D4 Siloxane)	$C_8H_{24}O_4Si_4H^+$	297.0825	0.256±0.009	$C_8H_{24}O_4Si_4(H_2O)H^+$, $C_7H_{21}O_4Si_4(H_2O)_2^+$, $C_7H_{21}O_4Si_4(H_2O)^+$, $C_7H_{21}O_4Si_4^+$, $C_6H_{17}O_4Si_4(H_2O)_2^+$	31.3[d]	0.66[d]	3.11	1400±200	2
Ethanol	$C_2H_6OH^+$	47.0491	-	$C_2H_6O(H_2O)H^+$, $C_2H_5O^+$	5.26[a]	1.69[a]	2.01	80±60	90
Acrolein	$C_3H_4OH^+$	57.0335	0.915±0.008	$C_3H_4O(H_2O)H^+$, $C_3H_3O^+$	6.38[a]	2.84[a]	2.93	2800±400	20
Acetone	$C_3H_6OH^+$	59.0491	0.893±0.012	$C_3H_6O(H_2O)H^+$, $C_2H_3O(H_2O)^+$, $C_2H_3O^+$	6.37[a]	2.88[a]	2.94	4800±700	14
Dimethyl Sulfide	$C_2H_6SH^+$	63.0263	0.861±0.008	CH_3S^+	7.42[e]	1.55[e]	2.02	3200±400	2

Standard	Quantitative Ion	m/Q (Th)	f	Ions Included in Calculating f	α $(10^{-24}\,cm^3)$	D (Debye)	k_{PTR} (E/N = 160 Td) $(10^{-9}\,cm^3\,molec^{-1}\,s^{-1})$	Sensitivity ± 1 SD (cps ppbv^{-1})	LOD (5 s) (pptv)
Methyl Vinyl Ketone	$C_4H_6OH^+$	71.0491	0.805±0.008	$C_4H_6O(H_2O)H^+$, $C_3H_3O^+$, $C_2H_3O^+$	8.30[a]	2.68[a]	2.79	4000±500	10
Benzene	$C_6H_6H^+$	79.0542	0.8785±0.0014	$C_6H_7O^+$	10.4[a]	0[b]	1.93	3500±500	9
Cyclohexene	$C_6H_{10}H^+$	83.0855	0.537±0.012*	$C_5H_7^+$, $C_4H_7^+$	10.7[a]	0.33[a]	1.96	1700±200	8
Furfural	$C_5H_4O_2H^+$	97.0284	0.83±0.02	$C_5H_4O_2(H_2O)H^+$, $C_5H_3O_2^+$, $C_4H_5O^+$	10.9[b]	3.87[b]	3.66	5400±800	4
2-Hexanone	$C_6H_{12}OH^+$	101.0961	0.65±0.02	$C_6H_{12}O(H_2O)H^+$, $C_6H_{11}^+$, $C_5H_9O^+$, $C_4H_9^+$, $C_4H_7O^+$, $C_4H_7^+$, $C_2H_5O^+$, $C_2H_3O^+$	12.1[f]	2.66[a]	2.76	3300±400	1.3
Styrene	$C_8H_8H^+$	105.0699	0.8931±0.0012	$C_6H_7^+$	14.7[a]	0.12[a]	2.24	3700±500	2
Benzaldehyde	$C_7H_6OH^+$	107.0491	0.639±0.011	$C_7H_6O(H_2O)H^+$, $C_7H_5O^+$, $C_6H_7O^+$ $C_6H_7^+$	14.1[b]	3.28[b]	3.25	3700±500	3
β-Pinene	$C_{10}H_{16}H^+$	137.1325	0.372±0.008	$C_7H_{11}^+$, $C_7H_9^+$, $C_7H_7^+$, $C_6H_9^+$	18.0[c]	0.64[c]	2.45	1400±200	6
Hexamethyl-cyclotrisiloxane (D3 Siloxane)	$C_6H_{18}O_3Si_3H^+$	223.0637	0.346±0.011	$C_8H_{24}O_4Si_4(H_2O)H^+$, $C_5H_{15}O_3Si_3(H_2O)_2^+$, $C_5H_{15}O_3Si_3(H_2O)^+$, $C_5H_{15}O_3Si_3^+$, $C_4H_{11}O_3Si_3(H_2O)_2^+$	28.5[f]	2.10[f]	3.18	2000±200	2
Decamethyl-cyclopentasiloxane (D5 Siloxane)	$C_{10}H_{30}O_5Si_5H^+$	371.1012	0.240±0.009	$C_8H_{24}O_4Si_4(H_2O)H^+$, $C_9H_{27}O_5Si_5(H_2O)_2^+$, $C_9H_{27}O_5Si_5(H_2O)^+$, $C_9H_{27}O_5Si_5^+$, $C_8H_{23}O_5Si_5(H_2O)_2^+$	39.2[d]	1.35[d]	3.50	1000±120	1.0

[a](Haynes, 2014), [b](Zhao and Zhang, 2004), [c](Cappellin et al., 2012), [d](Langford et al., 2013), [e](Cappellin et al., 2010), [f](Sekimoto et al., 2017)
*Fragmentation corrected for transmission

Supplemental Figures
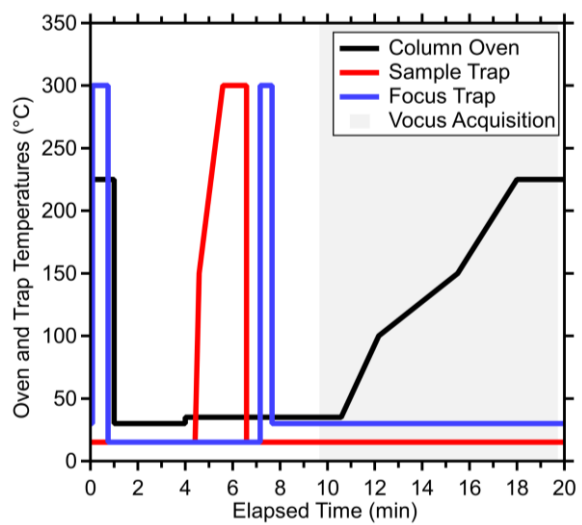
Figure S1: Temperature profiles of the sample trap, focus trap, and column oven during a typical GC cycle. Mass spectra were recorded during the final 10 min.
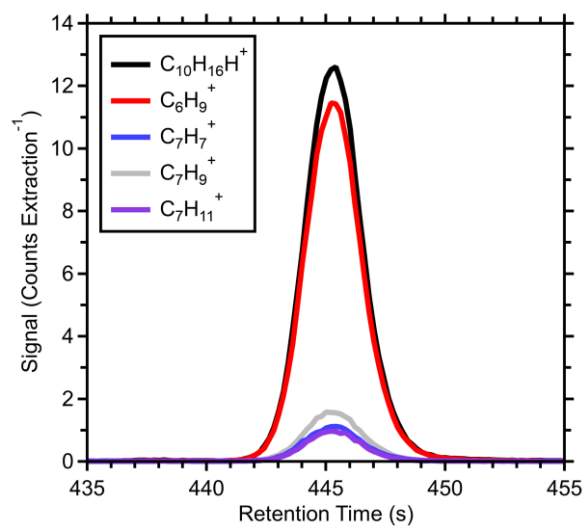
Figure S2: Example standard chromatogram of an α-pinene standard including the fragments used to determine the quantitative ion fraction.
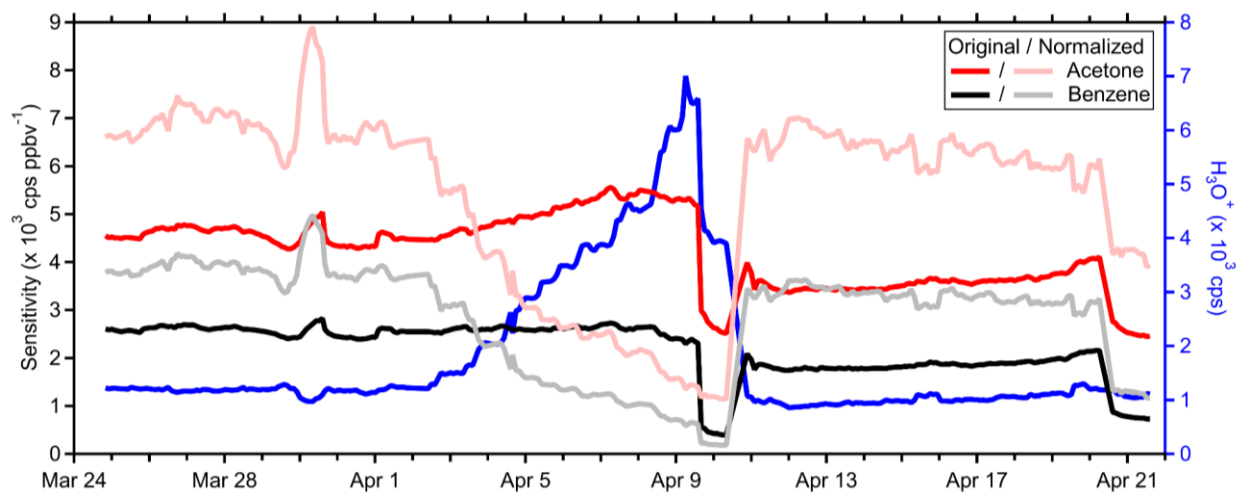
Figure S3: Time series of acetone and benzene sensitivities as measured and as normalized against the average signal of m/Q 19 (H_3O^+).
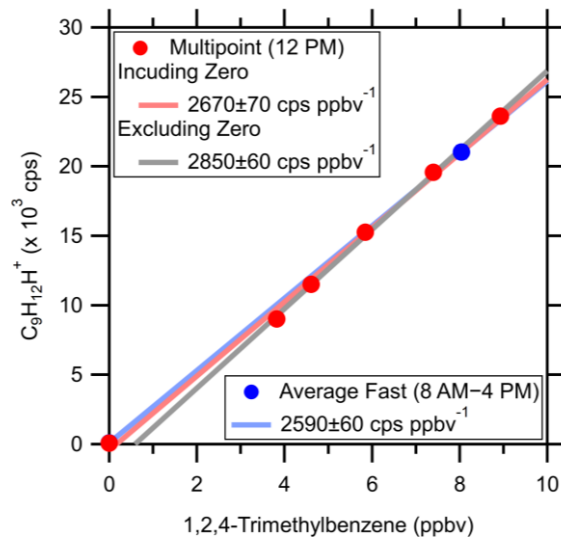
Figure S4: Comparison of a 1, 2, 4-trimethylbenzene multipoint calibration and 4 fast calibrations collected on April 14. The multipoint calibration was regressed twice: including the instrument background measurement (red) and excluding it (gray). Multipoint calibration sensitivity uncertainties reflect the uncertainty in the regression. The uncertainty in the fast calibration sensitivity reflects the standard deviation across the 4 calibrations.
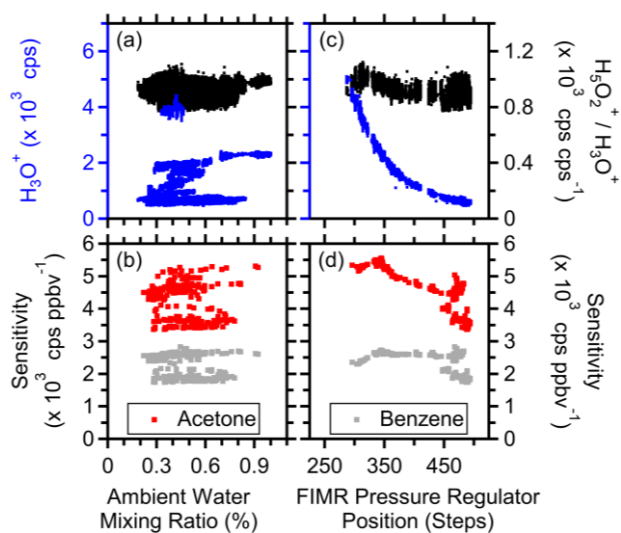
Figure S5: Observed relationships of the measured hydronium ion signal and selected sensitivities with ambient water mixing ratio (a–b), as well as the IMR pressure regulator position (c–d). Time periods where the ion source malfunctioned are excluded. Water mixing ratio and IMR pressure regulator position were averaged to the sensitivity measurement timescales for panels (b) and (d).
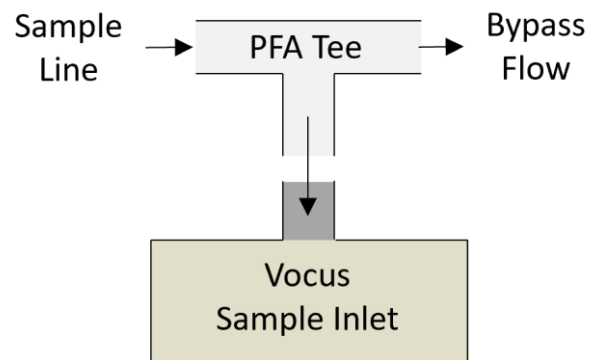
Figure S6: Schematic of the suggested sample flow path to avoid obstruction of the inlet capillary. A PFA tee is placed on the sample inlet such that the sample line and bypass line are in sequence and the Vocus inlet is perpendicular.
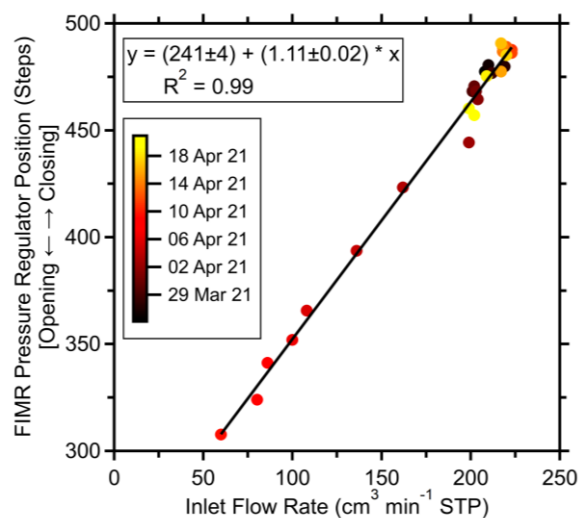
Figure S7: Linear least-squares regression of the daily average IMR pressure regulator position against the measured inlet flow rate. The gradual obstruction of the PEEK inlet tube from April ~2-10 is coincident with reduced flow rates. To maintain a constant IMR pressure, the regulator gradually opened. Time periods where the ion source malfunctioned are excluded. The IMR pressure regulator position was averaged to a 24 h timescale.

References

Cappellin, L., Probst, M., Limtrakul, J., Biasioli, F., Schuhfried, E., Soukoulis, C., Märk, T. D., and Gasperi, F.: Proton transfer reaction rate coefficients between H3O+ and some sulphur compounds, Int. J. Mass Spectrom., 295, 43–48, https://doi.org/10.1016/j.ijms.2010.06.023, 2010.

Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P. M., Soukoulis, C., Aprea, E., Märk, T. D., Gasperi, F., and Biasioli, F.: On Quantitative Determination of Volatile Organic Compound Concentrations Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry, Environ. Sci. Technol., 46, 2283–2290, https://doi.org/10.1021/es203985t, 2012.

Haynes, W. M. (Ed.): CRC Handbook of Chemistry and Physics, 95th Edition., CRC Press, New York, 2014.

Langford, V. S., Gray, J. D. C., and McEwan, M. J.: Selected ion flow tube studies of several siloxanes, Rapid Commun. Mass Spectrom., 27, 700–706, https://doi.org/10.1002/rcm.6496, 2013.

Sekimoto, K., Li, S.-M., Yuan, B., Koss, A., Coggon, M., Warneke, C., and de Gouw, J.: Calculation of the sensitivity of proton-transfer-reaction mass spectrometry (PTR-MS) for organic trace gases using molecular properties, Int. J. Mass Spectrom., 421, 71–94, https://doi.org/10.1016/j.ijms.2017.04.006, 2017.

Zhao, J. and Zhang, R.: Proton transfer reaction rate constants between hydronium ion (H3O+) and volatile organic compounds, Atmos. Environ., 38, 2177–2185, https://doi.org/10.1016/j.atmosenv.2004.01.019, 2004.