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Atmospheric Chemistry and Physics Discussions

Supplement of

In situ measurements and modeling of reactive trace gases in a small biomass burning plume

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1 Slow instrument response for “sticky” analytes

The PTR-ToF-MS instrument has a response time of ~ 0.1 s. Signal rise and fall times may, however, increase to seconds or even tens of seconds for “sticky” analytes such as acetic acid (Figure S1).

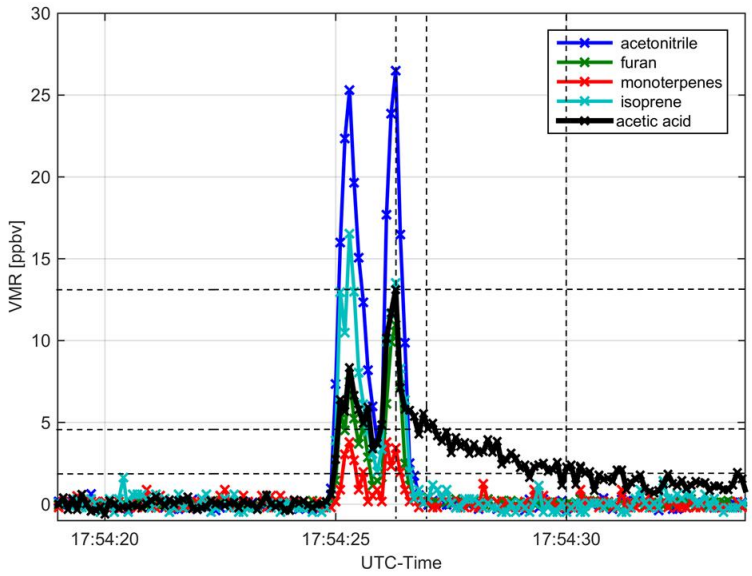

Figure S1. 10 Hz time-series of (a) acetonitrile, furan, the sum of monoterpene isomers, isoprene and acetic acid as measured during the fourth fire overflight at 17:54:25 UTC.

During the plume encounter, acetic acid molecules are partly adsorbed onto instrumental surfaces which results in an underestimation of in-plume concentrations. After the plume encounter, surface-bound molecules desorb from instrumental surfaces causing the associated signal to slowly decrease to atmospheric background values. Our experience from laboratory experiments indicates that the fraction of adsorbed analyte molecules is quantitatively recovered during desorption. A cumulative signal analysis which includes the period after the plume encounter will thus correctly quantify the amount of analyte in the plume. Figure S2 shows the cumulative mixing ratios of acetonitrile, formic acid and acetic acid as observed during the second fire overflight. The instrument response to acetonitrile is instantaneous whereas significant delays are observed for the two acids. All other signals reached 90% of their cumulative mixing ratios within the initial 10 s after the plume encounter. Only in the case of formic acid and acetic acid we thus used a cumulative signal analysis for emission quantification. In the case of formic acid we only report upper limit values due to a poor detection limit.

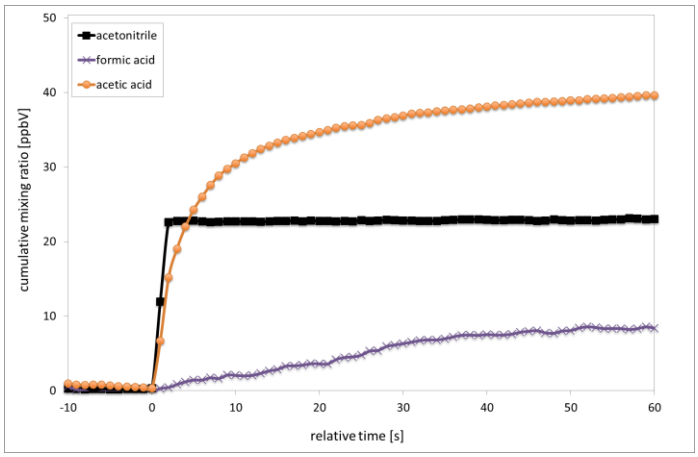

Figure S2. Cumulative mixing ratios of acetonitrile, formic acid and acetic acid as observed during the second fire overflight

2 Complete list of all detected signals

Table S2. List of all ion signals detected in the plume, their elemental composition, associated emission factors (EF) and their standard deviation (SD), emission ratios (ER) and SD, and R^2 of the least-square regression analysis. For signal quantification see Section 2.2.

m/z	elemental composition	EF	SD	ER	SD	R^2
		g/kg		ppbV/ppmV		
30.00	**NO**	**0.15**	**0.05**	**2.00**	**0.69**	**0.74**
31.02	**CH3O**	**2.31**	**0.57**	**22.70**	**1.28**	**0.99**
33.03	**CH5O**	**2.25**	**1.06**	**19.57**	**1.98**	**0.97**
41.04	C3H5	0.13	0.03	0.95	0.05	0.99
42.03	**C2H4N**	**0.19**	**0.06**	**1.55**	**0.17**	**0.96**
43.02	**C2H3O**	**0.24**	**0.08**	**1.85**	**0.10**	**0.99**
43.05	**C3H7**	**0.64**	**0.25**	**4.51**	**0.22**	**0.99**
44.01	CH2NO	0.07	0.02	0.62	0.20	0.77
44.04	C2H6N	0.02	0.00	0.11	0.01	0.95
45.03	**C2H5O**	**1.52**	**0.50**	**10.44**	**0.30**	**1.00**
45.99	NO2	0.03	0.02	0.15	0.03	0.92
47.02	**CH3O2**	**<0.13**	**0.38**	**<1.38**	**0.63**	**0.67**
54.03	C3H4N	0.05	0.01	0.32	0.07	0.88
57.04	C3H5O	0.17	0.04	0.94	0.05	0.99
57.07	C4H9	0.12	0.05	0.64	0.05	0.99
59.05	**C3H7O**	**0.83**	**0.31**	**4.15**	**0.11**	**1.00**
61.03	**C2H5O2**	**0.47**	**0.18**	**2.73**	**0.26**	**0.97**
69.03	**C4H5O**	**0.25**	**0.12**	**1.02**	**0.11**	**0.97**
69.07	**C5H9**	**0.23**	**0.14**	**1.13**	**0.10**	**0.98**
71.05	**C4H7O**	**0.33**	**0.12**	**1.44**	**0.05**	**1.00**
73.02	**C3H5O2**	**0.27**	**0.07**	**1.23**	**0.11**	**0.98**
73.07	C4H9O	0.21	0.08	0.87	0.04	0.99
75.04	**C3H7O2**	**0.28**	**0.15**	**1.10**	**0.13**	**0.96**
79.05	**C6H7**	**0.40**	**0.15**	**1.42**	**0.04**	**1.00**
81.01	C5H5O	0.11	0.05	0.40	0.04	0.98
83.05	C5H7O	0.18	0.09	0.66	0.07	0.97
83.10	C6H11	0.04	0.01	0.14	0.01	0.99
84.07	n.a.	0.03	0.01	0.11	0.01	0.99
84.99	n.a.	0.03	0.02	0.13	0.02	0.97
85.04	**C4H5O2**	**0.39**	**0.12**	**1.48**	**0.09**	**0.99**
85.08	C5H9O	0.11	0.04	0.42	0.04	0.98
87.04	**C4H7O2**	**0.44**	**0.18**	**1.62**	**0.09**	**0.99**
87.09	C5H11O	0.07	0.03	0.21	0.00	1.00
89.04	C3H5O3	0.03	0.01	0.08	0.00	0.99
93.04	C6H5O	0.04	0.01	0.13	0.01	0.98
93.07	C7H9	0.20	0.09	0.66	0.04	0.99
95.05	C6H7O	0.26	0.11	0.95	0.06	0.99
97.00	n.a.	0.18	0.09	0.60	0.04	0.99
97.03	**C5H5O2**	**2.31**	**1.07**	**7.65**	**0.64**	**0.98**
99.02	C4H3O3	0.14	0.04	0.51	0.10	0.90
99.04	C5H7O2	0.19	0.07	0.65	0.04	0.99
101.03	C4H5O3	0.03	0.03	0.16	0.00	0.98
101.05	C5H9O2	0.11	0.04	0.30	0.01	0.99
103.05	C8H7	0.13	0.06	0.44	0.03	0.98
105.07	C8H9	0.04	0.02	0.13	0.01	0.98
107.09	C8H11	0.19	0.07	0.51	0.02	1.00
109.07	C7H9O	0.21	0.09	0.59	0.03	0.99
111.05	**C6H7O2**	**0.39**	**0.21**	**1.25**	**0.14**	**0.96**
113.04	C5H5O3	0.08	0.03	0.23	0.01	0.98
117.05	C5H9O3	0.07	0.02	0.13	0.02	0.94
119.07	C9H11	0.06	0.02	0.16	0.00	1.00
121.10	C9H13	0.10	0.03	0.25	0.01	0.99
125.06	C7H9O2	0.08	0.04	0.21	0.01	0.98
127.05	C6H7O3	0.08	0.04	0.21	0.02	0.99
129.06	C10H9	0.06	0.03	0.14	0.01	0.99
133.07	C9H9O	0.05	0.02	0.12	0.01	0.99
137.13	C10H17	0.19	0.12	0.44	0.06	0.94