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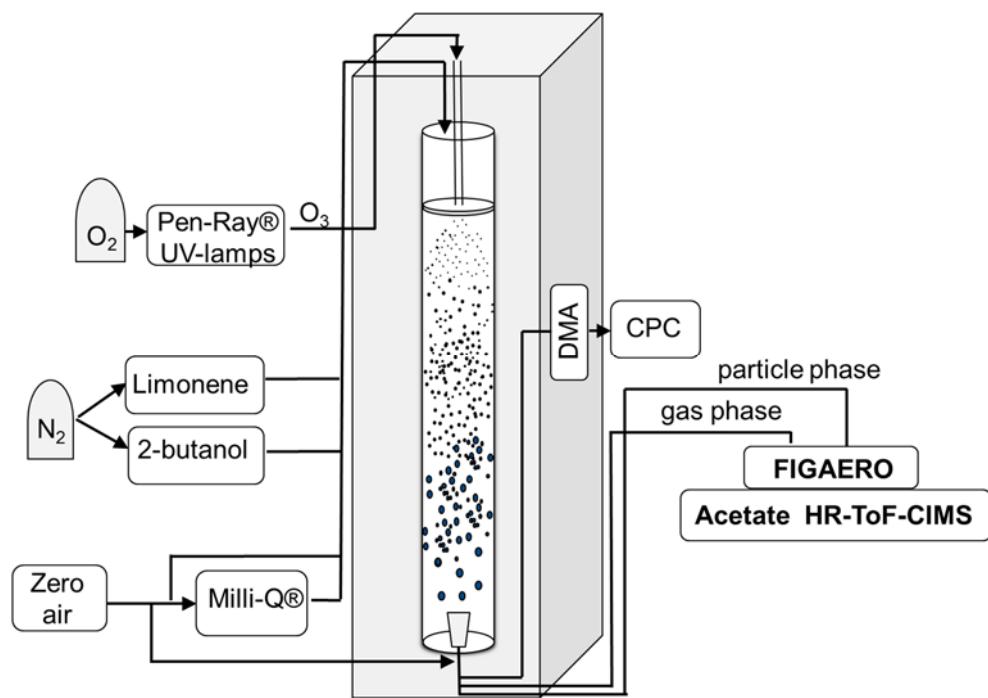

*Supplement of*

## **Carboxylic acids from limonene oxidation by ozone and hydroxyl radicals: insights into mechanisms derived using a FIGAERO-CIMS**

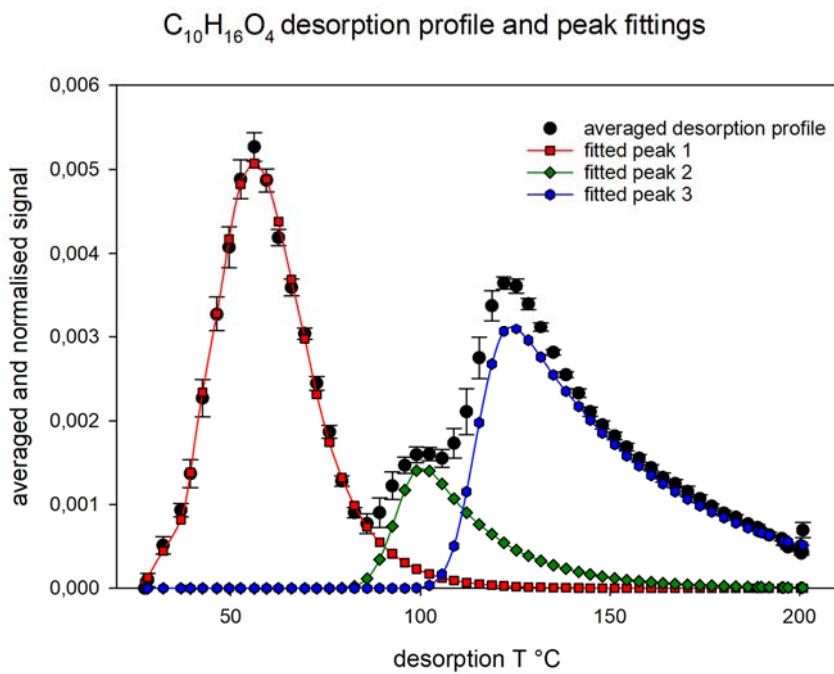
**Julia Hammes et al.**

*Correspondence to:* Mattias Hallquist (hallq@chem.gu.se)

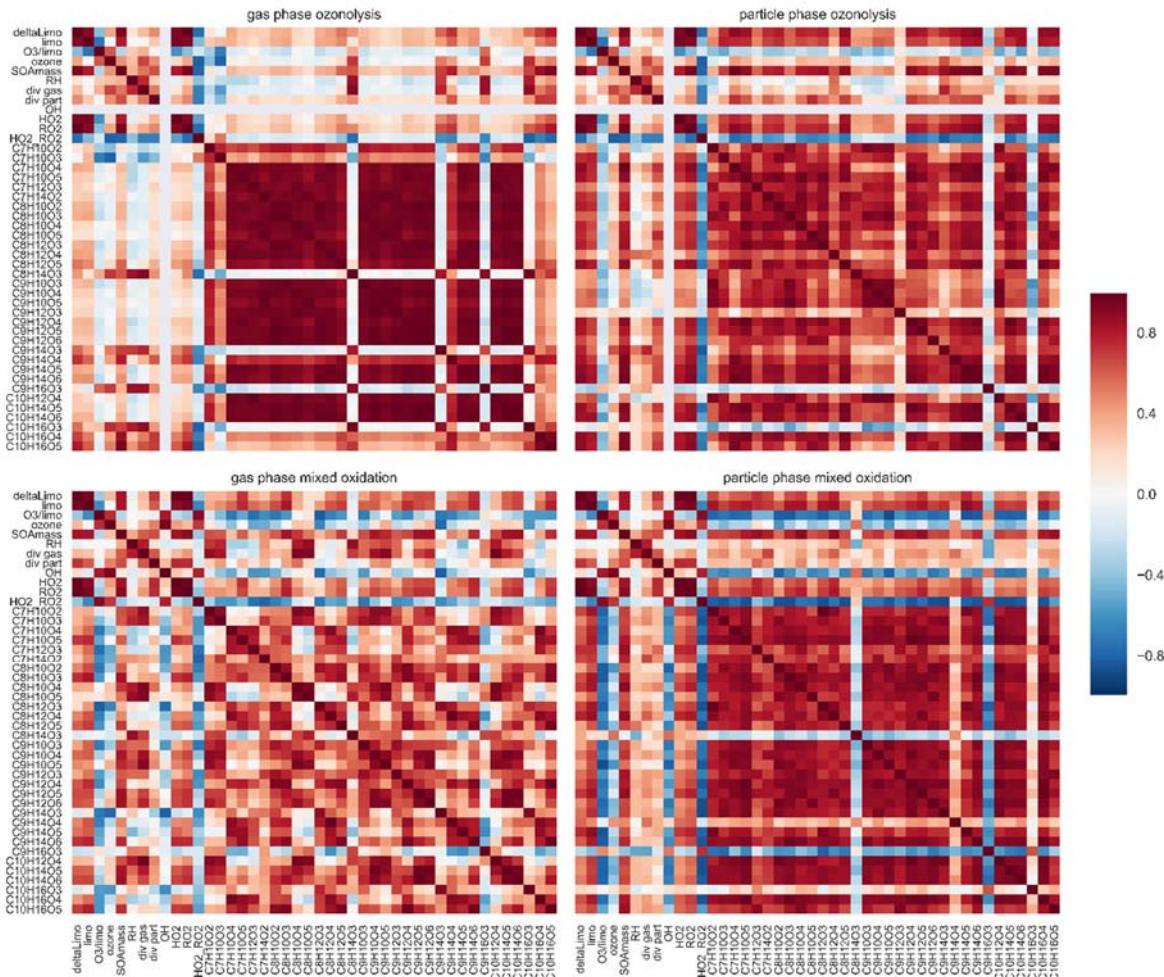
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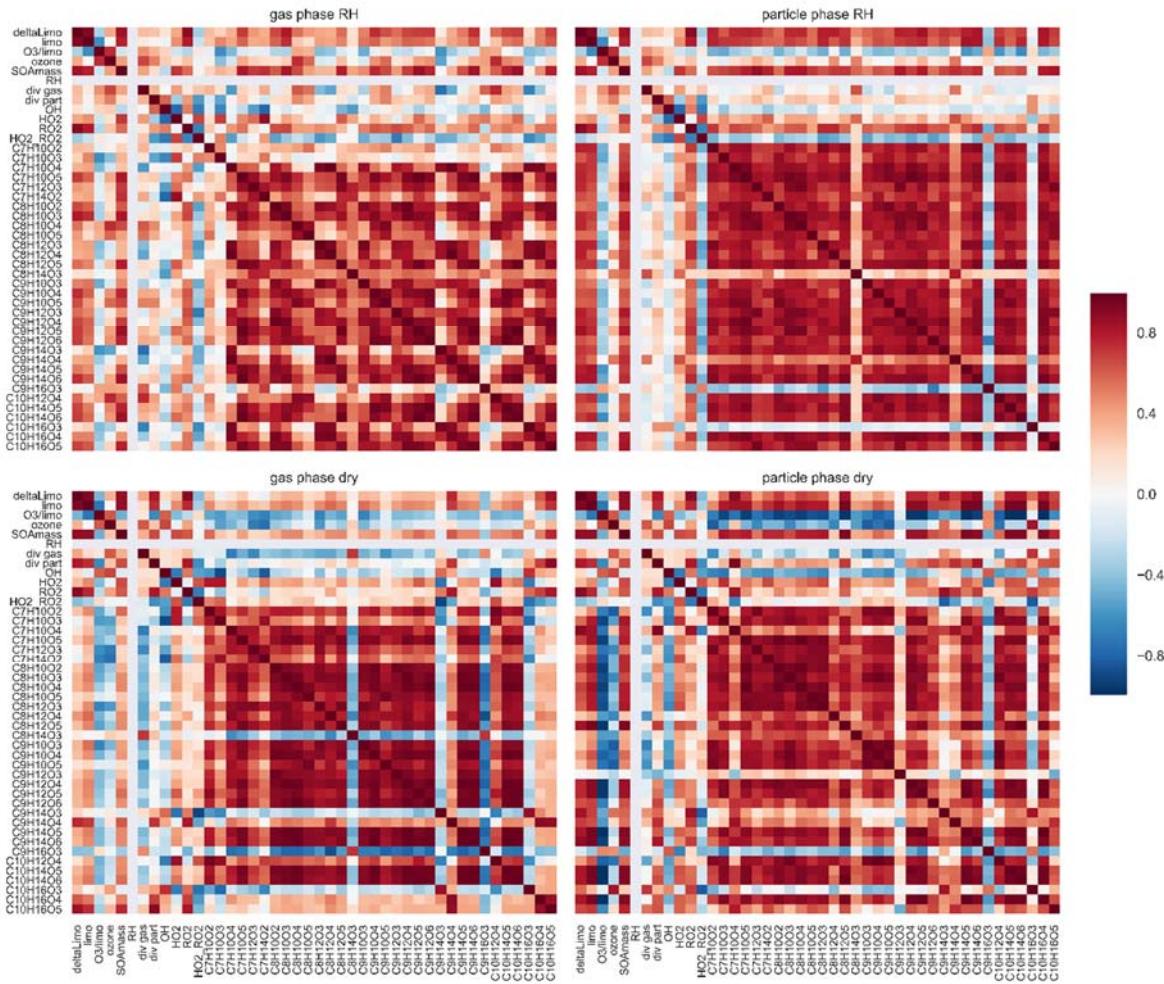
**SI Figure 1.** Schematic of the laminar flow reactor G-FROST.



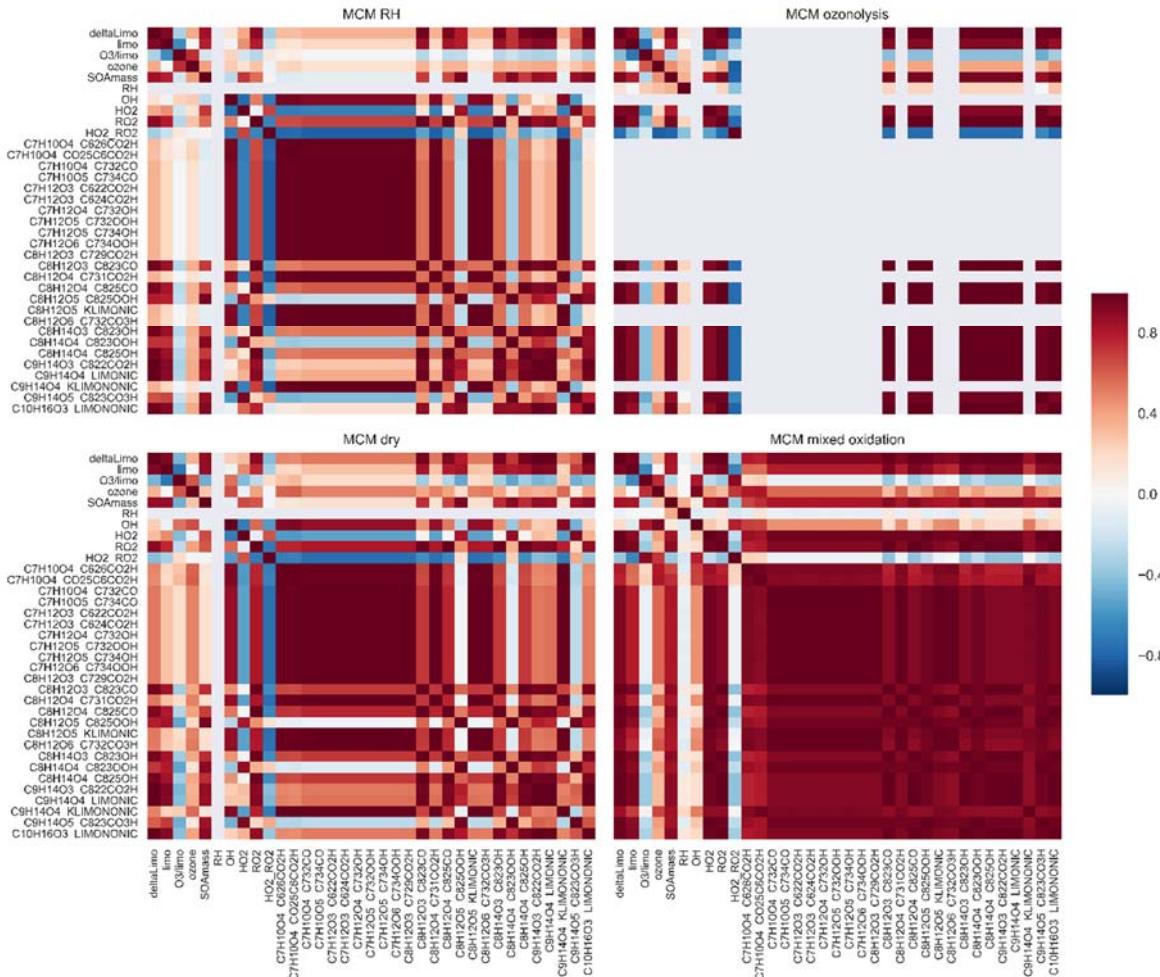
**SI Figure 2.** Example of the averaged FIGAERO desorption profile for  $\text{C}_{10}\text{H}_{16}\text{O}_4$  (four repetitions) with the standard deviation as error bars. Three distinct peaks can be identified. The first peak is attributed to  $\text{C}_{10}\text{H}_{16}\text{O}_4$  desorption from the filter and the other peaks are associated with thermal decomposition products from oligomers.



**SI Figure 3.** Rank correlation matrices corresponding to the gas- and particle-phase results for each of the 32 dominant acids obtained via pure ozonolysis and mixed oxidation. The evaluation using spearman correlation is similar to other correlations giving values (colour code used in figure in bracket) of 0 (white), -1 (dark blue) and 1 (dark red) for no correlation, perfect negative and positive correlation, respectively. The rank correlation reduces influences on outliers and non-linear effects.

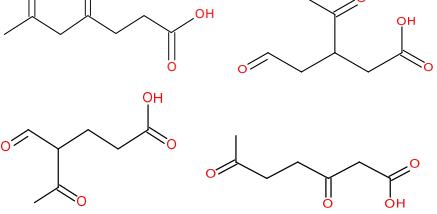
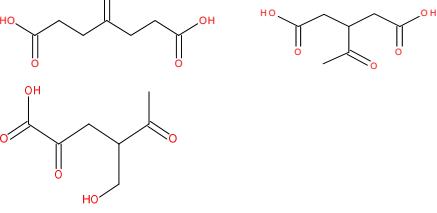
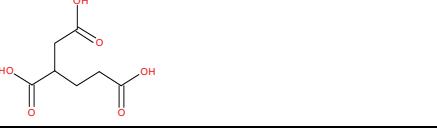
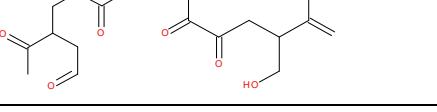
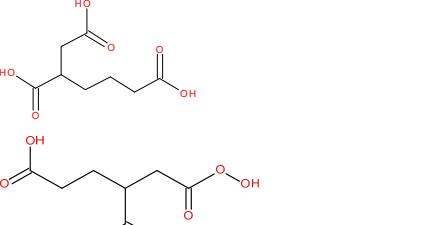
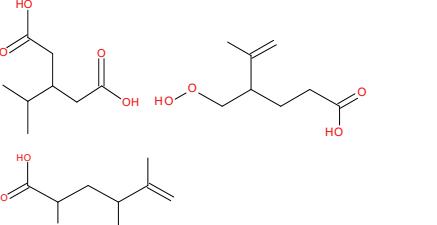


**SI Figure 4.** Rank correlation matrices for the 32 dominant acid measured in the all humid respectively dry experiments considering the gas and particle phases. The evaluation using spearman correlation is similar to other correlations giving values (colour code used in figure in bracket) of 0 (white), -1 (dark blue) and 1 (dark red) for no correlation, perfect negative and positive correlation, respectively. The rank correlation reduces influences on outliers and non-linear effects.



**SI Figure 5.** Correlation plots for MCM modelling results. The evaluation using spearman correlation is similar to other correlations giving values (colour code used in figure in bracket) of 0 (white), -1 (dark blue) and 1 (dark red) for no correlation, perfect negative and positive correlation, respectively. The rank correlation reduces influences on outliers and non-linear effects.

**SI Table 1.** Literature overview of previously reported carboxylic acids. The proposed structure is derived from the references given. Indicated is if the corresponding molecular formula was found in the top 10 of our study.

Name	Formula	MCM names	In top 10	Ref	Proposed structure
3,6-oxoheptanoic acid	C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>	C626CO2H, C732CO, CO25C6CO2H	Y	(Jaoui et al., 2005;Jaoui et al., 2006), MCM	
4-oxoheptanedioic acid, ketonorlimonic acid	C <sub>7</sub> H <sub>10</sub> O <sub>5</sub>	C734CO	Y	(Jaoui et al., 2005;Jaoui et al., 2006;Rossignol et al., 2012), MCM	
3-carboxyhexanedioic acid	C <sub>7</sub> H <sub>10</sub> O <sub>6</sub>		N	(Rossignol et al., 2012)	
ketolimonalic acid, norlimonic acid	C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	C731CO2H, C825CO	Y	(Glasius et al., 2000;Jaoui et al., 2006;Walser et al., 2008), MCM	
ketolimonic acid	C <sub>8</sub> H <sub>12</sub> O <sub>5</sub>	KLIMONIC	Y	(Glasius et al., 2000;Jaoui et al., 2005;Jaoui et al., 2006;Rossignol et al., 2012;Rossignol et al., 2013), MCM	
3-carboxyheptanedioic acid	C <sub>8</sub> H <sub>12</sub> O <sub>6</sub>	C732CO3H	N	(Jaoui et al., 2005;Jaoui et al., 2006), MCM	
3-isopropyl pentanedioic acid	C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	C823OOH, C825OH	N	(Jaoui et al., 2005;Jaoui et al., 2006), MCM	

limonic acid, norlimononic acid	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	C822CO2H	Y	(Glasius et al., 2000;Leungsakul et al., 2005a;Jaoui et al., 2006;Walser et al., 2008), MCM	
limonic acid, ketolimononic acid	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	LIMONIC, KLIMONONIC	Y	(Glasius et al., 2000;Leungsakul et al., 2005a;Jaoui et al., 2006;Walser et al., 2008;Rossignol et al., 2012), MCM	
5 or 7 hydroxyketolimononic acid	C <sub>9</sub> H <sub>14</sub> O <sub>5</sub>	C823CO3H	Y	(Glasius et al., 2000;Jaoui et al., 2005;Leungsakul et al., 2005a;Jaoui et al., 2006;Walser et al., 2008), MCM	
3-acetyl-4-methylhept- 2-enedioic acid	C <sub>10</sub> H <sub>14</sub> O <sub>5</sub>		Y	(Rossignol et al., 2012)	
limononic acid	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	LIMONONIC	Y	(Glasius et al., 2000;Leungsakul et al., 2005a;Jaoui et al., 2006;Walser et al., 2008;Rossignol et al., 2012), MCM	
5 or 7 hydroxylimononic acid	C <sub>10</sub> H <sub>16</sub> O <sub>4</sub>		Y	(Glasius et al., 2000;Leungsakul et al., 2005a;Jaoui et al., 2006;Walser et al., 2008)	

**SI Table 2.** Gas-phase measurement results for each of the 32 dominating carboxylic acids. Results reported as normalised intensity and colour coded according to their predominance with dark red representing the highest and dark green the lowest acids in the respective experiment. \*Experiment 10-12 had significant higher concentration than all other experiments. We decided to leave them in the correlation analysis but removed them from the yield calculation. A possible explanation is a non-working MFC in the FIGARO sampling unit.

#	C7H <sub>10</sub> O <sub>2</sub>	C7H <sub>10</sub> O <sub>3</sub>	C7H <sub>10</sub> O <sub>4</sub>	C7H <sub>10</sub> O <sub>5</sub>	C7H <sub>12</sub> O <sub>2</sub>	C7H <sub>14</sub> O <sub>2</sub>	C8H <sub>10</sub> O <sub>2</sub>	C8H <sub>10</sub> O <sub>3</sub>	C8H <sub>10</sub> O <sub>4</sub>	C8H <sub>10</sub> O <sub>5</sub>	C8H <sub>12</sub> O <sub>3</sub>	C8H <sub>14</sub> O <sub>3</sub>	C9H <sub>10</sub> O <sub>3</sub>	C9H <sub>10</sub> O <sub>4</sub>	C9H <sub>12</sub> O <sub>3</sub>	C9H <sub>12</sub> O <sub>4</sub>	C9H <sub>12</sub> O <sub>5</sub>	C9H <sub>12</sub> O <sub>6</sub>	C9H <sub>14</sub> O <sub>3</sub>	C9H <sub>14</sub> O <sub>4</sub>	C9H <sub>14</sub> O <sub>5</sub>	C9H <sub>14</sub> O <sub>6</sub>	C9H <sub>16</sub> O <sub>3</sub>	C10H <sub>12</sub> O <sub>4</sub>	C10H <sub>14</sub> O <sub>5</sub>	C10H <sub>14</sub> O <sub>6</sub>	C10H <sub>16</sub> O <sub>3</sub>	C10H <sub>16</sub> O <sub>4</sub>	C10H <sub>16</sub> O <sub>5</sub>			
1	0.020	0.039	0.069	0.002	0.035	0.014	0.008	0.005	0.012	0.019	0.024	0.082	0.008	0.007	0.004	0.003	0.003	0.014	0.007	0.005	0.002	0.028	0.064	0.013	0.001	0.002	0.002	0.006	0.002	0.162	0.026	0.003
2	0.024	0.050	0.100	0.004	0.045	0.017	0.011	0.008	0.015	0.024	0.030	0.148	0.012	0.009	0.006	0.005	0.003	0.019	0.013	0.008	0.002	0.033	0.120	0.022	0.002	0.001	0.003	0.010	0.003	0.181	0.038	0.006
3	0.030	0.067	0.153	0.007	0.062	0.021	0.021	0.013	0.020	0.026	0.044	0.266	0.032	0.009	0.010	0.008	0.007	0.024	0.025	0.020	0.004	0.039	0.200	0.052	0.006	0.001	0.004	0.018	0.007	0.200	0.077	0.019
4	0.009	0.025	0.097	0.004	0.052	0.015	0.006	0.005	0.006	0.009	0.018	0.095	0.011	0.000	0.002	0.003	0.003	0.007	0.007	0.005	0.001	0.021	0.076	0.023	0.002	0.000	0.001	0.005	0.002	0.076	0.039	0.003
5	0.009	0.023	0.096	0.004	0.046	0.013	0.005	0.005	0.006	0.009	0.017	0.113	0.011	0.000	0.002	0.003	0.002	0.007	0.007	0.005	0.001	0.019	0.086	0.023	0.002	0.000	0.001	0.005	0.002	0.073	0.036	0.004
6	0.014	0.035	0.112	0.006	0.050	0.014	0.010	0.008	0.009	0.010	0.033	0.174	0.014	0.000	0.005	0.004	0.003	0.011	0.012	0.007	0.002	0.021	0.125	0.030	0.003	0.000	0.002	0.008	0.003	0.082	0.053	0.008
7	0.033	0.072	0.030	0.002	0.034	0.017	0.004	0.005	0.008	0.011	0.011	0.040	0.011	0.004	0.003	0.003	0.002	0.006	0.004	0.007	0.002	0.005	0.029	0.012	0.001	0.002	0.005	0.002	0.009	0.011	0.003	
8	0.019	0.107	0.032	0.002	0.034	0.019	0.004	0.005	0.008	0.011	0.011	0.041	0.009	0.004	0.002	0.003	0.002	0.006	0.004	0.006	0.002	0.005	0.031	0.010	0.001	0.002	0.005	0.002	0.009	0.011	0.002	
9	0.021	0.157	0.047	0.004	0.040	0.025	0.008	0.007	0.009	0.014	0.016	0.065	0.018	0.005	0.004	0.004	0.003	0.008	0.008	0.012	0.002	0.008	0.049	0.018	0.003	0.001	0.003	0.009	0.004	0.013	0.021	0.007
10*	3.659	12.392	0.633	0.199	2.372	0.128	0.343	0.747	0.383	0.552	0.383	0.159	0.028	0.000	0.471	0.594	0.187	11.605	0.854	0.087	0.472	0.000	0.044	0.054	0.008	0.000	0.102	0.040	0.012	0.000	0.013	0.000
11*	14.464	10.084	0.841	0.132	2.410	0.148	0.574	2.319	0.980	1.017	0.684	0.399	0.058	0.000	1.981	2.398	0.807	24.463	2.059	0.192	0.731	0.000	0.061	0.095	0.025	0.000	0.404	0.104	0.043	0.000	0.000	0.000
12*	18.051	8.445	1.024	0.127	2.664	0.161	0.727	2.696	1.106	1.107	0.921	0.787	0.194	0.000	2.855	2.992	0.911	21.137	1.930	0.278	0.706	0.000	0.335	0.233	0.055	0.000	0.608	0.183	0.078	0.000	0.088	0.016
13	0.013	0.031	0.082	0.003	0.034	0.012	0.008	0.006	0.011	0.013	0.021	0.126	0.013	0.003	0.004	0.004	0.003	0.012	0.008	0.008	0.002	0.021	0.102	0.021	0.002	0.000	0.002	0.009	0.003	0.113	0.033	0.006
14	0.013	0.032	0.090	0.004	0.037	0.013	0.009	0.006	0.012	0.014	0.023	0.146	0.015	0.003	0.004	0.004	0.003	0.012	0.010	0.009	0.002	0.023	0.118	0.024	0.003	0.000	0.002	0.009	0.004	0.115	0.035	0.007
15	0.023	0.051	0.129	0.007	0.051	0.016	0.018	0.012	0.016	0.015	0.033	0.198	0.032	0.002	0.007	0.007	0.004	0.018	0.019	0.019	0.003	0.028	0.154	0.050	0.006	0.000	0.004	0.017	0.008	0.130	0.069	0.019
16	0.010	0.021	0.086	0.003	0.036	0.010	0.006	0.005	0.008	0.011	0.016	0.086	0.010	0.000	0.002	0.003	0.003	0.008	0.007	0.006	0.002	0.018	0.061	0.025	0.002	0.000	0.002	0.007	0.002	0.087	0.029	0.004
17	0.010	0.022	0.092	0.004	0.036	0.010	0.006	0.005	0.008	0.010	0.017	0.114	0.010	0.000	0.002	0.003	0.003	0.008	0.008	0.006	0.002	0.017	0.081	0.025	0.002	0.000	0.002	0.006	0.002	0.088	0.029	0.004
18	0.019	0.040	0.125	0.008	0.049	0.014	0.014	0.012	0.013	0.013	0.034	0.195	0.026	0.000	0.005	0.006	0.004	0.014	0.017	0.016	0.003	0.022	0.134	0.050	0.005	0.000	0.003	0.015	0.006	0.101	0.060	0.015
19	0.016	0.048	0.050	0.004	0.060	0.026	0.007	0.006	0.017	0.019	0.016	0.075	0.028	0.007	0.003	0.005	0.004	0.010	0.009	0.015	0.003	0.008	0.059</td									

**SI Table 3.** Particle-phase measurement results for each of the 32 dominant carboxylic acids. Results reported as normalised intensity and colour coded according to their predominance with dark red representing the highest and dark green the lowest acid in the respective experiment. \*Experiment 10-12 had significant higher concentration than all other experiments. We decided to leave them in the correlation analysis but removed them from the yield calculation. A possible explanation is a non-working MFC in the FIGARO sampling unit.

#	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>10</sub> O <sub>3</sub>	C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>7</sub> H <sub>10</sub> O <sub>5</sub>	C <sub>7</sub> H <sub>12</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>5</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>12</sub> O <sub>4</sub>	C <sub>9</sub> H <sub>12</sub> O <sub>5</sub>	C <sub>9</sub> H <sub>12</sub> O <sub>6</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>5</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>6</sub>	C <sub>9</sub> H <sub>16</sub> O <sub>3</sub>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	C <sub>10</sub> H <sub>14</sub> O <sub>5</sub>	C <sub>10</sub> H <sub>14</sub> O <sub>6</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>4</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>5</sub>		
1	0.019	0.035	0.001	0.007	0.010	0.003	0.042	0.009	0.007	0.008	0.026	0.007	0.059	0.001	0.006	0.006	0.006	0.012	0.014	0.029	0.008	0.003	0.000	0.008	0.022	0.001	0.003	0.030	0.016	0.000	0.047	0.013
2	0.089	0.064	0.085	0.019	0.000	0.012	0.086	0.014	0.011	0.011	0.066	0.015	0.133	0.004	0.007	0.026	0.013	0.008	0.082	0.072	0.016	0.012	0.008	0.183	0.041	0.000	0.009	0.084	0.037	0.000	0.076	0.000
3	0.480	0.241	0.362	0.098	0.180	0.044	0.470	0.244	0.100	0.120	0.269	0.288	0.963	0.000	0.064	0.142	0.080	0.095	0.437	0.387	0.104	0.092	0.000	0.688	0.325	0.000	0.061	0.468	0.085	0.008	0.382	0.309
4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
7	0.004	0.005	0.000	0.001	0.003	0.003	0.004	0.001	0.002	0.000	0.001	0.002	0.002	0.001	0.000	0.000	0.001	0.000	0.000	0.001	0.002	0.004	0.000	0.000	0.008	0.001	0.004	0.000	0.000	0.008	0.001	
8	0.004	0.035	0.001	0.002	0.001	0.008	0.008	0.006	0.004	0.006	0.000	0.021	0.006	0.002	0.001	0.007	0.017	0.000	0.000	0.019	0.004	0.006	0.001	0.010	0.008	0.000	0.008	0.005	0.008	0.005		
9	0.032	0.068	0.085	0.016	0.047	0.020	0.062	0.015	0.020	0.024	0.004	0.158	0.007	0.003	0.022	0.007	0.020	0.047	0.063	0.012	0.005	0.023	0.164	0.055	0.001	0.008	0.029	0.037	0.001	0.108	0.076	
10*	0.625	0.023	0.000	0.004	0.337	0.018	0.019	0.035	0.028	0.007	0.026	0.000	0.005	0.010	0.099	0.057	0.023	1.219	0.008	0.006	0.011	0.000	0.005	0.001	0.006	0.012	0.010	0.002	0.000	0.004	0.000	
11*	0.464	0.476	0.000	0.008	0.042	0.021	0.098	0.094	0.028	0.003	0.016	0.000	0.066	0.018	0.196	0.121	0.058	1.331	0.014	0.053	0.000	0.000	0.036	0.007	0.001	0.064	0.021	0.021	0.000	0.028	0.000	
12*	0.798	0.655	0.709	0.221	0.442	0.189	0.390	0.367	0.225	0.360	0.354	0.302	1.103	0.054	0.187	0.750	0.136	0.000	0.694	1.086	0.559	0.000	0.321	0.858	0.383	0.000	0.218	0.508	0.188	0.000	0.462	0.374
13	0.000	0.024	0.044	0.011	0.039	0.011	0.049	0.011	0.021	0.015	0.000	0.001	0.098	0.002	0.009	0.012	0.007	0.018	0.034	0.041	0.009	0.006	0.001	0.000	0.021	0.009	0.007	0.028	0.015	0.011	0.049	0.031
14	0.055	0.023	0.075	0.013	0.040	0.010	0.038	0.022	0.025	0.006	0.047	0.021	0.103	0.002	0.011	0.007	0.007	0.011	0.024	0.082	0.006	0.002	0.000	0.117	0.042	0.006	0.007	0.039	0.019	0.002	0.057	0.035
15	0.202	0.112	0.245	0.065	0.119	0.030	0.252	0.119	0.078	0.029	0.126	0.066	0.367	0.012	0.021	0.040	0.017	0.088	0.206	0.218	0.038	0.025	0.160	0.404	0.161	0.000	0.022	0.075	0.088	0.000	0.131	0.198
16	0.002	0.001	0.000	0.000	0.002	0.004	0.001	0.001	0.001	0.000	0.002	0.013	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.001	0.003	0.002	0.000	0.000		
17	0.007	0.017	0.021	0.004	0.010	0.003	0.019	0.007	0.007	0.003	0.005	0.000	0.030	0.009	0.003	0.003	0.002	0.006	0.005	0.008	0.004	0.002	0.000	0.024	0.013	0.008	0.002	0.013	0.006	0.002	0.011	0.000
18	0.129	0.101	0.297	0.025	0.187	0.043	0.198	0.055	0.034	0.045	0.088	0.156	0.090	0.008	0.020	0.084	0.019	0.093	0.096	0.222	0.033	0.012	0.205	0.376	0.229	0.003	0.022	0.148	0.087	0.003	0.350	0.115
19	0.018	0.027	0.016	0.008	0.033	0.013	0.031	0.014	0.016	0.011	0.018	0.003	0.051	0.007	0.002	0.010	0.003	0.006	0.017	0.031	0.003	0.005	0.003	0.051	0.010	0.013	0.003	0.024	0.017	0.001	0.026	0.015
20	0.031	0.031	0.025	0.014	0.047	0.039	0.041	0.024	0.029	0.019	0.019	0.000	0.170	0																		

**SI Table 4.** MCM modelling results in ppb for the dominant acids also identified as products in the experimental results. The results of MCM species with the same chemical formula were summed up. The results are colour coded from highest (red) to lowest (green) for each modelled experiment. Detailed modelling results for each species are shown in SI Table 5.

#	C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>7</sub> H <sub>10</sub> O <sub>5</sub>	C <sub>7</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>5</sub>	C <sub>8</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>5</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>
<b>1</b>	0.00	0.00	0.01	0.11	0.06	0.00	0.09	0.37	0.22	0.00	0.09
<b>2</b>	0.00	0.00	0.02	0.31	0.18	0.01	0.26	1.01	0.60	0.00	0.24
<b>3</b>	0.01	0.01	0.09	1.16	0.69	0.06	0.98	3.75	2.23	0.02	0.87
<b>4</b>	0.00	0.00	0.01	0.11	0.06	0.00	0.09	0.37	0.22	0.00	0.06
<b>5</b>	0.00	0.00	0.02	0.31	0.18	0.01	0.26	1.00	0.60	0.00	0.16
<b>6</b>	0.01	0.01	0.09	1.16	0.69	0.06	0.98	3.74	2.22	0.02	0.61
<b>7</b>	0.00	0.00	0.00	0.03	0.02	0.01	0.03	0.22	0.12	0.01	0.10
<b>8</b>	0.00	0.00	0.00	0.09	0.05	0.02	0.09	0.62	0.34	0.03	0.25
<b>9</b>	0.00	0.00	0.00	0.35	0.19	0.09	0.35	2.35	1.28	0.11	0.90
<b>10</b>	0.00	0.00	0.00	0.03	0.02	0.01	0.03	0.22	0.12	0.01	0.06
<b>11</b>	0.00	0.00	0.00	0.09	0.05	0.02	0.09	0.61	0.33	0.03	0.16
<b>12</b>	0.00	0.00	0.00	0.34	0.19	0.09	0.34	2.32	1.27	0.11	0.57
<b>13</b>	0.00	0.00	0.03	0.21	0.12	0.01	0.15	0.56	0.35	0.00	0.15
<b>14</b>	0.01	0.01	0.08	0.58	0.34	0.04	0.43	1.52	0.97	0.01	0.41
<b>15</b>	0.07	0.03	0.30	2.19	1.34	0.16	1.64	5.75	3.66	0.03	1.55
<b>16</b>	0.00	0.00	0.03	0.21	0.12	0.01	0.15	0.56	0.35	0.00	0.12
<b>17</b>	0.01	0.01	0.08	0.58	0.34	0.04	0.43	1.51	0.96	0.01	0.32
<b>18</b>	0.07	0.03	0.30	2.19	1.34	0.16	1.63	5.71	3.62	0.03	1.18
<b>19</b>	0.00	0.00	0.00	0.06	0.04	0.02	0.06	0.44	0.24	0.02	0.18
<b>20</b>	0.00	0.00	0.00	0.18	0.10	0.05	0.18	1.21	0.66	0.05	0.47
<b>21</b>	0.00	0.00	0.00	0.69	0.38	0.18	0.69	4.55	2.48	0.20	1.71
<b>22</b>	0.00	0.00	0.00	0.06	0.03	0.02	0.06	0.44	0.24	0.02	0.12
<b>23</b>	0.00	0.00	0.00	0.18	0.10	0.05	0.18	1.20	0.65	0.05	0.31
<b>24</b>	0.00	0.00	0.00	0.68	0.37	0.18	0.68	4.51	2.46	0.20	1.13
<b>25</b>	0.01	0.01	0.05	0.30	0.19	0.03	0.20	0.67	0.46	0.01	0.19
<b>26</b>	0.05	0.02	0.16	0.85	0.57	0.10	0.56	1.75	1.23	0.01	0.54
<b>27</b>	0.23	0.10	0.65	3.28	2.26	0.42	2.13	6.56	4.68	0.04	2.08
<b>28</b>	0.01	0.01	0.05	0.30	0.19	0.03	0.20	0.66	0.45	0.01	0.18
<b>29</b>	0.05	0.02	0.16	0.85	0.57	0.10	0.55	1.72	1.20	0.01	0.49
<b>30</b>	0.23	0.10	0.65	3.28	2.26	0.42	2.11	6.44	4.57	0.04	1.87
<b>31</b>	0.00	0.00	0.00	0.12	0.07	0.02	0.12	0.72	0.40	0.03	0.25
<b>32</b>	0.00	0.00	0.00	0.31	0.17	0.07	0.31	1.91	1.05	0.07	0.67
<b>33</b>	0.00	0.00	0.00	1.13	0.62	0.28	1.13	7.07	3.88	0.29	2.52

**SI Table 5.** Experimental results from CIMS gas measurements for the carboxylic acids also found in MCM. The results are colour coded from highest (dark red) to lowest (dark green) measured normalised intensity.

#	C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>7</sub> H <sub>10</sub> O <sub>5</sub>	C <sub>7</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>5</sub>	C <sub>8</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>5</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>
<b>1</b>	0.07	0.00	0.03	0.02	0.08	0.01	0.01	0.03	0.06	0.01	0.16
<b>2</b>	0.10	0.00	0.04	0.03	0.15	0.01	0.01	0.03	0.12	0.02	0.18
<b>3</b>	0.15	0.01	0.06	0.04	0.27	0.03	0.01	0.04	0.20	0.05	0.20
<b>4</b>	0.10	0.00	0.05	0.02	0.09	0.01	0.00	0.02	0.08	0.02	0.08
<b>5</b>	0.10	0.00	0.05	0.02	0.11	0.01	0.00	0.02	0.09	0.02	0.07
<b>6</b>	0.11	0.01	0.05	0.03	0.17	0.01	0.00	0.02	0.12	0.03	0.08
<b>7</b>	0.03	0.00	0.03	0.01	0.04	0.01	0.00	0.01	0.03	0.01	0.01
<b>8</b>	0.03	0.00	0.03	0.01	0.04	0.01	0.00	0.01	0.03	0.01	0.01
<b>9</b>	0.05	0.00	0.04	0.02	0.07	0.02	0.00	0.01	0.05	0.02	0.01
<b>10</b>	0.63	0.20	2.37	0.38	0.16	0.03	0.00	0.00	0.04	0.05	0.00
<b>11</b>	0.84	0.13	2.41	0.68	0.40	0.06	0.00	0.00	0.06	0.10	0.00
<b>12</b>	1.02	0.13	2.66	0.92	0.79	0.19	0.00	0.00	0.34	0.23	0.00
<b>13</b>	0.08	0.00	0.03	0.02	0.13	0.01	0.00	0.02	0.10	0.02	0.11
<b>14</b>	0.09	0.00	0.04	0.02	0.15	0.01	0.00	0.02	0.12	0.02	0.12
<b>15</b>	0.13	0.01	0.05	0.03	0.20	0.03	0.00	0.03	0.15	0.05	0.13
<b>16</b>	0.09	0.00	0.04	0.02	0.09	0.01	0.00	0.02	0.06	0.02	0.09
<b>17</b>	0.09	0.00	0.04	0.02	0.11	0.01	0.00	0.02	0.08	0.03	0.09
<b>18</b>	0.12	0.01	0.05	0.03	0.20	0.03	0.00	0.02	0.13	0.05	0.10
<b>19</b>	0.05	0.00	0.06	0.02	0.07	0.03	0.01	0.01	0.06	0.02	0.02
<b>20</b>	0.05	0.00	0.05	0.01	0.07	0.02	0.01	0.01	0.06	0.02	0.02
<b>21</b>	0.08	0.01	0.07	0.02	0.12	0.05	0.01	0.01	0.10	0.05	0.03
<b>22</b>	0.04	0.00	0.03	0.01	0.04	0.01	0.00	0.00	0.02	0.01	0.01
<b>23</b>	0.05	0.00	0.04	0.01	0.06	0.01	0.00	0.01	0.04	0.01	0.01
<b>24</b>	0.07	0.01	0.05	0.02	0.11	0.03	0.00	0.01	0.08	0.03	0.01
<b>25</b>	0.03	0.00	0.03	0.01	0.04	0.01	0.00	0.00	0.02	0.01	0.01
<b>26</b>	0.03	0.00	0.03	0.01	0.04	0.01	0.00	0.00	0.02	0.01	0.01
<b>27</b>	0.05	0.00	0.04	0.02	0.06	0.02	0.01	0.00	0.05	0.02	0.01
<b>28</b>	0.10	0.01	0.04	0.02	0.13	0.01	0.00	0.02	0.10	0.03	0.09
<b>29</b>	0.09	0.00	0.04	0.02	0.13	0.01	0.00	0.02	0.11	0.03	0.08
<b>30</b>	0.10	0.01	0.04	0.02	0.17	0.01	0.00	0.02	0.13	0.04	0.07
<b>31</b>	0.07	0.01	0.09	0.02	0.11	0.05	0.01	0.01	0.09	0.04	0.02
<b>32</b>	0.07	0.01	0.07	0.02	0.12	0.03	0.01	0.01	0.10	0.02	0.02
<b>33</b>	0.12	0.02	0.10	0.03	0.23	0.10	0.01	0.01	0.20	0.08	0.03

**SI Table 6.** Modelling results in ppb of all 25 known acid species in MCM. The table shows the chemical formula and respective MCM species. The results are colour coded from highest (dark red) to lowest (dark green) modelled concentration for each experiment. MCM species are abbreviated as follows: a = C626CO2H, b = CO25C6CO2H, c = C732CO, d = C734CO, e = C622CO2H, f = C624CO2H, g = C732OH, h = C732OOH, i = C734OH, j = C734OOH, k = C729CO2H, l = C823CO, m = C731CO2H, n = C825CO, o = C825OOH, p = KLIMONIC, q = C732CO3H, r = C823OH, s = C823OOH, t = C825OH, u = C822CO2H, v = LIMONIC, w = KLIMONONIC, x = C823CO3H, y = LIMONONIC.

	C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>				C <sub>7</sub> H <sub>10</sub> O <sub>5</sub>				C <sub>7</sub> H <sub>12</sub> O <sub>3</sub>				C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>				C <sub>7</sub> H <sub>12</sub> O <sub>5</sub>				C <sub>7</sub> H <sub>12</sub> O <sub>6</sub>				C <sub>8</sub> H <sub>12</sub> O <sub>3</sub>				C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>				C <sub>8</sub> H <sub>12</sub> O <sub>5</sub>				C <sub>8</sub> H <sub>12</sub> O <sub>6</sub>				C <sub>8</sub> H <sub>14</sub> O <sub>3</sub>				C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>				C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>				C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>				C <sub>9</sub> H <sub>14</sub> O <sub>5</sub>				C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>			
	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	w	x	y																																							
1	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.10	0.00	0.06	0.00	0.00	0.00	0.09	0.03	0.05	0.37	0.22	0.00	0.00	0.09																																							
2	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.03	0.28	0.01	0.17	0.01	0.01	0.00	0.26	0.08	0.16	1.01	0.59	0.00	0.00	0.24																																							
3	0.00	0.00	0.01	0.01	0.08	0.01	0.01	0.00	0.01	0.00	0.12	1.04	0.05	0.63	0.03	0.03	0.00	0.98	0.29	0.59	3.75	2.22	0.01	0.02	0.87																																							
4	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.10	0.00	0.06	0.00	0.00	0.00	0.09	0.03	0.05	0.37	0.22	0.00	0.00	0.06																																							
5	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.03	0.27	0.01	0.17	0.01	0.01	0.00	0.26	0.08	0.16	1.00	0.59	0.00	0.00	0.16																																							
6	0.00	0.00	0.01	0.01	0.08	0.01	0.01	0.00	0.01	0.00	0.12	1.04	0.05	0.63	0.03	0.03	0.00	0.98	0.29	0.59	3.74	2.22	0.01	0.02	0.61																																							
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.02	0.01	0.00	0.00	0.03	0.10	0.02	0.22	0.12	0.00	0.01	0.10																																							
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.05	0.02	0.00	0.00	0.09	0.30	0.05	0.62	0.34	0.00	0.03	0.25																																							
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.00	0.19	0.09	0.00	0.00	0.35	1.18	0.19	2.35	1.28	0.00	0.11	0.90																																							
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.02	0.01	0.00	0.00	0.03	0.10	0.02	0.22	0.12	0.00	0.01	0.06																																							
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.05	0.02	0.00	0.00	0.09	0.30	0.05	0.61	0.33	0.00	0.03	0.16																																							
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.34	0.00	0.19	0.09	0.00	0.00	0.34	1.18	0.19	2.32	1.27	0.00	0.11	0.57																																							
13	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.03	0.17	0.01	0.11	0.00	0.01	0.00	0.15	0.05	0.09	0.56	0.35	0.00	0.00	0.15																																							
14	0.00	0.00	0.01	0.01	0.07	0.01	0.01	0.00	0.01	0.00	0.10	0.48	0.05	0.30	0.01	0.03	0.00	0.43	0.14	0.27	1.52	0.96	0.01	0.01	0.41																																							
15	0.01	0.00	0.05	0.03	0.27	0.03	0.05	0.02	0.03	0.00	0.36	1.84	0.20	1.14	0.05	0.12	0.00	1.64	0.50	1.01	5.75	3.60	0.06	0.03	1.55																																							
16	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.03	0.17	0.01	0.11	0.00	0.01	0.00	0.15	0.05	0.09	0.56	0.35	0.00	0.00	0.12																																							
17	0.00	0.00	0.01	0.01	0.07	0.01	0.01	0.00	0.01	0.00	0.10	0.48	0.05	0.30	0.01	0.03	0.00	0.43	0.14	0.26	1.51	0.95	0.01	0.01	0.32																																							
18	0.01	0.00	0.05	0.03	0.27	0.03	0.05	0.02	0.03	0.00	0.36	1.83	0.20	1.14	0.05	0.12	0.00	1.63	0.50	1.01	5.71	3.59	0.03	0.03	1.18																																							
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.04	0.02	0.00	0.00	0.06	0.20	0.04	0.44	0.24	0.00	0.02	0.18																																							
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.00	0.10	0.05	0.00	0.00	0.18	0.59	0.10	1.21	0.66	0.00	0.05	0.47																																							
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.69	0.00	0.38	0.18	0.00	0.00	0.69	2.29	0.38	4.55	2.48	0.00	0.20	1.71																																							
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.03	0.02	0.00	0.00	0.06	0.20	0.03	0.44	0.24	0.00	0.02	0.12																																							
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.00	0.10	0.05	0.00	0.00	0.18	0.59	0.10	1.20	0.65	0.00	0.05	0.31																																							
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.68	0.00	0.37	0.18	0.00	0.00	0.68	2.29	0.37	4.51	2.46	0.00	0.20	1.13																																							

25	0.00	0.00	0.01	0.01	0.04	0.00	0.01	0.00	0.01	0.00	0.06	0.24	0.04	0.15	0.01	0.02	0.00	0.20	0.09	0.13	0.67	0.44	0.01	0.01	0.19
26	0.01	0.00	0.04	0.02	0.14	0.01	0.04	0.01	0.02	0.00	0.18	0.67	0.14	0.43	0.02	0.08	0.00	0.56	0.20	0.36	1.75	1.19	0.04	0.01	0.54
27	0.06	0.00	0.17	0.10	0.58	0.06	0.16	0.05	0.09	0.00	0.70	2.58	0.61	1.65	0.06	0.36	0.00	2.13	0.67	1.36	6.56	4.50	0.18	0.04	2.08
28	0.00	0.00	0.01	0.01	0.04	0.00	0.01	0.00	0.01	0.00	0.06	0.24	0.04	0.15	0.01	0.02	0.00	0.20	0.09	0.13	0.66	0.44	0.01	0.01	0.18
29	0.01	0.00	0.04	0.02	0.14	0.01	0.04	0.01	0.02	0.00	0.18	0.67	0.14	0.42	0.02	0.08	0.00	0.55	0.20	0.35	1.72	1.18	0.03	0.01	0.49
30	0.06	0.00	0.17	0.10	0.59	0.06	0.16	0.05	0.09	0.00	0.71	2.56	0.61	1.65	0.06	0.36	0.00	2.11	0.67	1.35	6.44	4.45	0.13	0.04	1.87
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.07	0.02	0.00	0.00	0.12	0.30	0.07	0.72	0.40	0.00	0.03	0.25
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.00	0.17	0.07	0.00	0.00	0.31	0.87	0.17	1.91	1.05	0.00	0.07	0.67
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.13	0.00	0.62	0.28	0.00	0.00	1.13	3.44	0.62	7.07	3.88	0.00	0.29	2.52

**SI Table 7.** Results from the CIMS measurements for carboxylic acids found in MCM averaged over four experiment repetitions (measurements cycles). The results correspond to the sum of gas and particle phases normalised intensities for the respective compounds (for experiments 4–6 and 28–30 only gas-phase data is available).

	C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>7</sub> H <sub>10</sub> O <sub>5</sub>	C <sub>7</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>5</sub>	C <sub>8</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>5</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>
<b>1</b>	0.07	0.01	0.02	0.05	0.09	0.07	0.01	0.03	0.06	0.02	0.16
<b>2</b>	0.19	0.02	0.03	0.10	0.16	0.14	0.01	0.05	0.13	0.21	0.18
<b>3</b>	0.51	0.10	0.06	0.31	0.55	0.99	0.01	0.13	0.20	0.74	0.21
<b>4</b>	0.10	0.00	0.01	0.02	0.09	0.01	0.00	0.02	0.08	0.02	0.08
<b>5</b>	0.10	0.00	0.01	0.02	0.11	0.01	0.00	0.02	0.09	0.02	0.07
<b>6</b>	0.11	0.01	0.01	0.03	0.17	0.01	0.00	0.02	0.12	0.03	0.08
<b>7</b>	0.03	0.00	0.02	0.01	0.04	0.01	0.01	0.01	0.03	0.02	0.01
<b>8</b>	0.03	0.00	0.03	0.02	0.04	0.03	0.01	0.01	0.03	0.03	0.01
<b>9</b>	0.13	0.02	0.04	0.05	0.07	0.18	0.01	0.01	0.07	0.18	0.01
<b>10</b>	0.63	0.20	0.15	0.41	0.16	0.03	0.01	0.00	0.04	0.06	0.00
<b>11</b>	0.84	0.14	0.17	0.70	0.40	0.12	0.02	0.00	0.06	0.13	0.00
<b>12</b>	1.73	0.35	0.35	1.28	1.09	1.30	0.05	0.00	0.66	1.09	0.00
<b>13</b>	0.13	0.01	0.02	0.02	0.13	0.11	0.00	0.03	0.10	0.02	0.12
<b>14</b>	0.17	0.02	0.02	0.07	0.17	0.12	0.01	0.02	0.12	0.14	0.12
<b>15</b>	0.37	0.07	0.05	0.16	0.26	0.40	0.01	0.05	0.31	0.45	0.13
<b>16</b>	0.09	0.00	0.01	0.02	0.09	0.01	0.01	0.02	0.06	0.03	0.09
<b>17</b>	0.11	0.01	0.01	0.02	0.11	0.04	0.01	0.02	0.08	0.05	0.09
<b>18</b>	0.42	0.03	0.06	0.12	0.35	0.12	0.01	0.03	0.34	0.43	0.10
<b>19</b>	0.07	0.01	0.04	0.03	0.08	0.08	0.01	0.01	0.06	0.08	0.02
<b>20</b>	0.08	0.02	0.06	0.03	0.07	0.19	0.02	0.02	0.08	0.14	0.02
<b>21</b>	0.33	0.05	0.08	0.10	0.44	0.37	0.02	0.04	0.38	0.28	0.03
<b>22</b>	0.04	0.00	0.01	0.01	0.04	0.02	0.00	0.00	0.02	0.02	0.01
<b>23</b>	0.05	0.01	0.02	0.02	0.06	0.04	0.01	0.01	0.04	0.04	0.01
<b>24</b>	0.22	0.04	0.08	0.12	0.11	0.28	0.03	0.03	0.32	0.38	0.02
<b>25</b>	0.04	0.01	0.02	0.03	0.04	0.06	0.01	0.00	0.02	0.03	0.01
<b>26</b>	0.06	0.01	0.03	0.03	0.05	0.03	0.01	0.00	0.03	0.03	0.01
<b>27</b>	0.09	0.02	0.03	0.06	0.15	0.13	0.01	0.01	0.14	0.12	0.02
<b>28</b>	0.10	0.01	0.01	0.02	0.13	0.01	0.00	0.02	0.10	0.03	0.09
<b>29</b>	0.09	0.00	0.01	0.02	0.13	0.01	0.00	0.02	0.11	0.03	0.08
<b>30</b>	0.10	0.01	0.01	0.02	0.17	0.01	0.00	0.02	0.13	0.04	0.07
<b>31</b>	0.14	0.03	0.06	0.06	0.16	0.15	0.02	0.01	0.10	0.13	0.02
<b>32</b>	0.18	0.03	0.06	0.05	0.19	0.24	0.02	0.02	0.12	0.09	0.02
<b>33</b>	0.40	0.18	0.07	0.15	0.58	0.30	0.02	0.04	0.66	0.76	0.03