SUPPORTING INFORMATION

Applications of high-resolution electrospray ionization mass spectrometry to measurements of average oxygen to carbon ratios in secondary organic aerosols

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Table S1. Number of ESI mass spectra collected for each sample for each ESI mode. The same number of ESI mass spectra were collected at each dilution for Mixtures A – F.

Mix A	2
Mix B	2
Mix C	2
Mix D	2
Mix E	2
Mix F	2
1 ppm Limonene SOA	2
0.5 ppm Limonene SOA	2
0.1 ppm Limonene SOA	6
0.05 ppm Limonene SOA	5
1 ppm Isoprene SOA	3

Table S2. Adjusted parameters used for the determination of O/C ratio in the Analytical Procedure for Elemental Separation (APES) from HR-AMS-ToF data.[1] The ratios of ions were obtained from single runs, rather than an average over the entire sampling time, and verified at various times throughout the reaction period. A relative ionization efficiency (R.I.E.) for the HR-AMS-ToF data of 1.0 was used for water and R.I.E. of 1.4 was used for organics.

	$[(CO^+)_{org}:(CO_2^+)_{org}]_{frag}$	$(H_2O^+)_{org}:(CO_2^+)_{org}$	$(H_2O^+)_{org}:(OH^+)_{org}:(O^+)_{org}$
Mix A	0.95	0.46	100:25:4
Mix B	1.12	0.16	100:25:4
Mix C	0.73	0.17	100:25:4
Mix D	1.32	0.38	100:25:4
Mix E	1.66	0.50	100:25:4
Mix F	1.28	0.84	100:25:4
50 ppb Limonene SOA	2.70	0.49	100:25:4
25 ppb Limonene SOA	2.38	1.00	100:25:4
1 ppm Isoprene SOA	1.24	0.467	100:25:4
Aiken et al.[2]	1.00	0.225	100:25:4

Table S3. The relative ESI sensitivity of each standard for each dilution averaged across all mixtures for each ionization mode. Each compound's ESI sensitivity has been scaled relative to (+) mode cis-pinonic acid. The ratios of (+) mode sensitivities to (-) mode sensitivities are also listed. Table S1 provides evidence for significant matrix effects. For example, in the (+) mode, succinic acid and DL-malic acid are only observed at the lowest concentration level, while citric acid only appears in the mass spectra corresponding to the highest concentration. All compounds are detectable in the (-) mode at all dilution levels.

	10^{-8} M dilution			10^{-6} M dilution			No Dilution (10^{-4} M)		
Standard Compound	(+) ESI Sens.	(-) ESI Sens.	(+)/(-) Ratio	(+) ESI Sens.	(-) ESI Sens.	(+)/(-) Ratio	(+) ESI Sens.	(-) ESI Sens.	(+)/(-) Ratio
succinic acid	0.05 ±0.05	3.0 ±5.0	0.02 ±0.04	-	0.5 ±0.6	-	-	20 ±20	-
DL-malic acid	0.03 ±0.04	10 ±20	0.003 ±0.006	-	2.0 ±1.0	-	-	100 ±100	-
6-methyl-2,4-heptanedione	0.1 ±0.4	0.02 ±0.02	9.0 ± 30.0	0.2 ±0.3	0.02 ±0.03	10 ±20	0.5 ±0.7	2.0 ±2.0	0.3 ±0.5
7-oxooctanoic acid	4.0 ± 6.0	1.0 ±2.0	4.0 ± 8.0	7.0 ± 6.0	1.0 ±1.0	5.0 ±6.0	70 ±70	40 ±40	2.0 ±3.0
cis-pinonic acid	1.0 ± 2.0	2.0 ±4.0	0.4 ±1.0	1.0 ±1.0	2.0 ±2.0	0.4 ±0.6	1.0 ±1.0	80 ±80	0.01 ±0.02
cis-pinic acid	0.05 ±0.06	0.9 ±1.0	0.05 ±0.1	0.02 ±0.02	3.0 ±2.0	0.008 ±0.01	-	100 ±200	-
azelaic acid	2.0 ±4.0	2.0 ±4.0	1.0 ±3.0	2.0 ±3.0	4.0 ±4.0	0.6 ±1.0	20 ±30	300 ±400	0.05 ±0.1
citric acid	-	5.0 ±6.0	-	-	20 ±20	-	2.0 ±1.0	3000 ±3000	0.0007 ±0.0009
camphoric acid	0.2 ±0.3	1.0 ±1.0	0.2 ±0.4	0.08 ±0.08	3.0 ±2.0	0.03 ±0.04	20 ±20	300 ±300	0.07 ±0.1
5-oxoazelaic acid	1.0 ±2.0	1.0 ±2.0	1.0 ±3.0	5.0 ±5.0	4.0 ±4.0	1.0 ±2.0	200 ±300	400 ±600	0.4 ±0.8

Table S4. Compounds used in analysis of solution O/C using ESI-MS are tabulated with corresponding structures, molecular formulas, o/c ratios, and calculated log P values, experimental log P values are listed in parentheses were available. Prediction of log P was performed using ACD/ChemSketch Freeware version 12.01 (Advanced Chemical Development Inc., Toronto, Canada). Experimentally measured values of log P where used if they were available, and they agreed well with the predicted values.

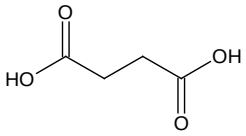
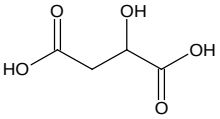
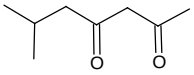
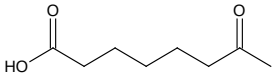
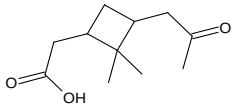
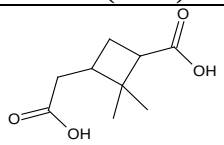
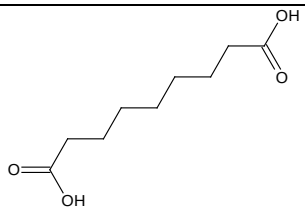
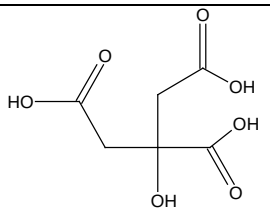
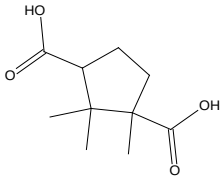
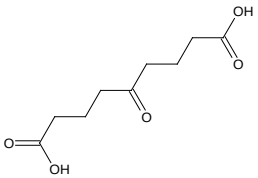
Structure				
Name	succinic acid	DL-malic acid	6-methyl-2,4-heptanedione	7-oxooctanoic acid
Formula	$C_4H_6O_4$	$C_4H_6O_5$	$C_8H_{14}O_2$	$C_8H_{14}O_3$
O/C	1.00	1.25	0.25	0.38
Log P	-0.59 (-0.59)	-1.26 (-1.26)	1.75	0.40
Structure				
Name	cis-pinonic acid	cis-pinic acid	azelaic acid	citric acid
Formula	$C_{10}H_{16}O_3$	$C_9H_{14}O_4$	$C_9H_{16}O_4$	$C_6H_8O_7$
O/C	0.30	0.44	0.44	1.17
Log P	1.26	0.94	1.33 (1.57)	-1.72
Structure				
Name	camphoric acid	5-oxoazelaic acid		
Formula	$C_{10}H_{16}O_4$	$C_9H_{14}O_5$		
O/C	0.40	0.56		
Log P	1.47	-0.11		

Table S5. Previously identified compounds in limonene SOA using GC-MS[3-4] are tabulated with corresponding structures, molecular formulas, o/c ratios, and calculated log P values. Limononaldehyde ($C_{10}H_{16}O_2$) was not detected in the negative ion mode, therefore it was not included in Figure 3. Compounds with the same elemental formulae ($C_9H_{14}O_3$, $C_{10}H_{16}O_3$, and $C_9H_{14}O_4$) could not be distinguished in the HR ESI-MS, therefore the average log P value was used in Figure 4.

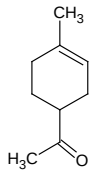
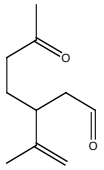
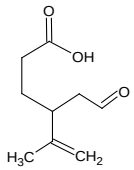
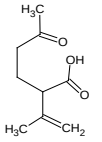
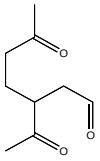
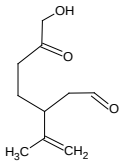
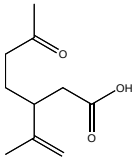
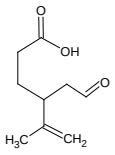
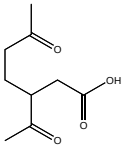
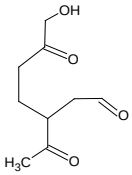
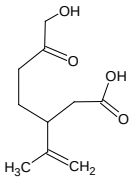
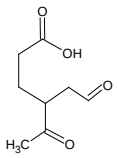
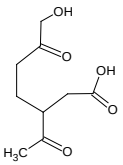
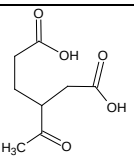
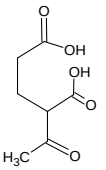
Structure					
Name	keto-limonene	limononaldehyde	limonalic acid	norlimononic acid	keto-limononaldehyde
Formula	$C_9H_{14}O$	$C_{10}H_{16}O_2$	$C_9H_{14}O_3$	$C_9H_{14}O_3$	$C_9H_{14}O_3$
O/C	0.11	0.20	0.33	0.33	0.33
Log P	2.19	1.53	1.31	1.18	0.05
Structure					
Name	7-hydroxy-limononaldehyde	limononic acid	limonic acid	keto-limononic acid	7-hydroxy-keto-limononaldehyde
Formula	$C_{10}H_{16}O_3$	$C_{10}H_{16}O_3$	$C_9H_{14}O_4$	$C_9H_{14}O_4$	$C_9H_{14}O_4$
O/C	0.30	0.30	0.44	0.44	0.44
Log P	0.91	1.40	-0.08	-0.22	-0.58
Structure					
Name	7-hydroxy-limononic acid	keto-limonalic acid	7-hydroxy-keto-limononic acid	Keto-limonic acid	norlimonic acid
Formula	$C_{10}H_{16}O_4$	$C_8H_{12}O_4$	$C_9H_{14}O_5$	$C_8H_{12}O_5$	$C_7H_{10}O_5$
O/C	0.4	0.50	0.56	0.63	0.71
Log P	0.78	-0.08	-0.84	-0.31	-0.93

Table S6. O/C values estimated for HR ESI-MS dataset obtained from the dark ozonolysis of limonene.[5] The error has been calculated based on multiple samples and ES ionization efficiencies and propagated throughout the calculation of O/C.

(+) ESI Mode	$O/C_{weighted}$	$O/C_{corrected}$
1 ppm	0.40 ± 0.01	0.45 ± 0.07
0.5 ppm	0.39 ± 0.03	0.45 ± 0.08
0.1 ppm	0.40 ± 0.02	0.49 ± 0.10
0.05 ppm	0.41 ± 0.05	0.51 ± 0.11
(-) ESI Mode	$O/C_{weighted}$	$O/C_{corrected}$
1 ppm	0.49 ± 0.01	0.47 ± 0.07
0.5 ppm	0.49 ± 0.01	0.46 ± 0.08
0.1 ppm	0.51 ± 0.04	0.47 ± 0.10
0.05 ppm	0.53 ± 0.05	0.49 ± 0.10

Table S7. O/C values estimated for HR ESI-MS dataset obtained from the dark ozonolysis of isoprene.[5] Also listed are O/C values measured from online ToF-AMS of the chamber aerosol.

	(+) ESI Mode	(-) ESI Mode	Average ESI
$O/C_{unweighted}$	0.56	0.60	0.58
$O/C_{weighted}$	0.56	0.57	0.56
$O/C_{corrected}$	0.57	0.56	0.56
O/C_{AMS}	0.58		

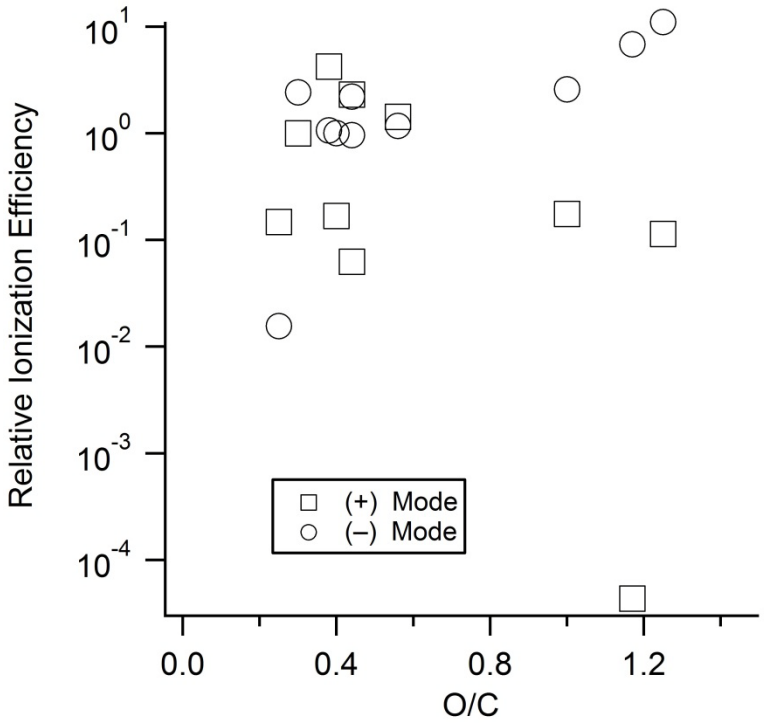


Figure S1. Average relative ionization efficiency factors scaled to (+) mode pinonic acid plotted against each compound's o/c ratio for (+) and (-) mode. As this figure demonstrates, there is no obvious correlation with the o/c ratio.

References

1. Chen, Q.; Liu, Y. J.; Donahue, N. M.; Shilling, J. E.; Martin, S. T., Particle-Phase Chemistry of Secondary Organic Material: Modeled Compared to Measured O:C and H:C Elemental Ratios Provide Constraints. *Environ. Sci. Technol.* **2011,** *45* (11), 4763-4770.
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