

Supporting Information Section

Stability of α -Pinene and d-Limonene Ozonolysis Secondary Organic Aerosol Compounds Towards Hydrolysis and Hydration

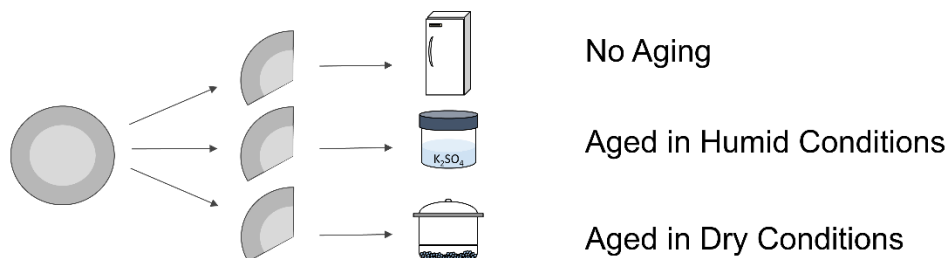
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Table S1. Aging Experiments Summary. APIN/O₃ and LIM/O₃ refer to SOA made by ozonolysis of α -pinene and d-limonene, respectively. “Humid Air” refers to samples that were aged in a relative humidity (RH ~97%) aging chamber, while “Dry Air” refers to samples that were aged in a desiccator (RH ~<2%). “Liquid Water” and “Acetonitrile” correspond to samples that were extracted using the respective solvent and then aged. Dashes indicate that the corresponding control samples were frozen until analysis was performed. In the initial experiments, a low-resolution mass spectrometer was used; it was replaced by a high-resolution mass spectrometer for the rest of the study. The Solvent System column describes the solution composition adjusted for the ESI-MS analysis (e.g., by adding equal volume of acetonitrile of to an aqueous solution of SOA).

SOA Type	Aging Conditions	Duration of Aging	ESI-MS Resolution	Solvent System
APIN/O ₃	-	-	Low	1:1 H ₂ O:ACN
APIN/O ₃	Humid Air	1 Week	Low	1:1 H ₂ O:ACN
APIN/O ₃	-	-	Low	1:1 H ₂ O:ACN
APIN/O ₃	Humid Air	2 Weeks	Low	1:1 H ₂ O:ACN
APIN/O ₃	-	-	High	H ₂ O
APIN/O ₃	Liquid Water	1 Day	High	H ₂ O
APIN/O ₃	Liquid Water	2 Days	High	H ₂ O
LIM/O ₃	-	-	High	H ₂ O
LIM/O ₃	Liquid Water	1 Day	High	H ₂ O
LIM/O ₃	Liquid Water	2 Days	High	H ₂ O
APIN/O ₃	-	-	High	1:1 H ₂ O:ACN
APIN/O ₃	Humid Air	1 Week	High	1:1 H ₂ O:ACN
APIN/O ₃	Humid Air	2 Weeks	High	1:1 H ₂ O:ACN
APIN/O ₃	Dry Air	1 Week	High	1:1 H ₂ O:ACN
APIN/O ₃	Dry Air	2 Weeks	High	1:1 H ₂ O:ACN
APIN/O ₃	-	-	High	1:1 H ₂ O:ACN
APIN/O ₃	Humid Air	1 Week	High	1:1 H ₂ O:ACN
APIN/O ₃	Humid Air	2 Weeks	High	1:1 H ₂ O:ACN
APIN/O ₃	Dry Air	1 Week	High	1:1 H ₂ O:ACN
APIN/O ₃	Dry Air	2 Weeks	High	1:1 H ₂ O:ACN
APIN/O ₃	-	-	High	1:1 H ₂ O:ACN
APIN/O ₃	Liquid Water	1 Day	High	1:1 H ₂ O:ACN
APIN/O ₃	Liquid Water	2 Days	High	1:1 H ₂ O:ACN
APIN/O ₃	Acetonitrile	1 Day	High	1:1 H ₂ O:ACN
APIN/O ₃	Acetonitrile	2 Days	High	1:1 H ₂ O:ACN
APIN/O ₃	-	-	High	1:1 H ₂ O:ACN
APIN/O ₃	Liquid Water	1 Day	High	1:1 H ₂ O:ACN
APIN/O ₃	Liquid Water	2 Days	High	1:1 H ₂ O:ACN
APIN/O ₃	Acetonitrile	1 Day	High	1:1 H ₂ O:ACN
APIN/O ₃	Acetonitrile	2 Days	High	1:1 H ₂ O:ACN

Aging by exposure to water vapor



Aging in liquid water

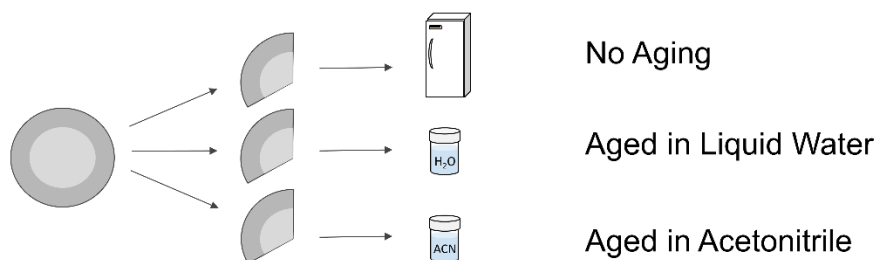


Figure S1. Aging Experiments Summary. SOA were first generated in a flow tube reactor and collected on a foil substrate. Foil substrates were the cut into segments to age the SOA in humid conditions, dry conditions (control) or sealed and frozen (control) to understand the long-term aging of SOA by exposure to water vapor. Alternatively, the foil substrates were the cut into segments to age the SOA in liquid water, acetonitrile (control) or sealed and frozen (control) to understand the long-term aging of SOA by liquid water.

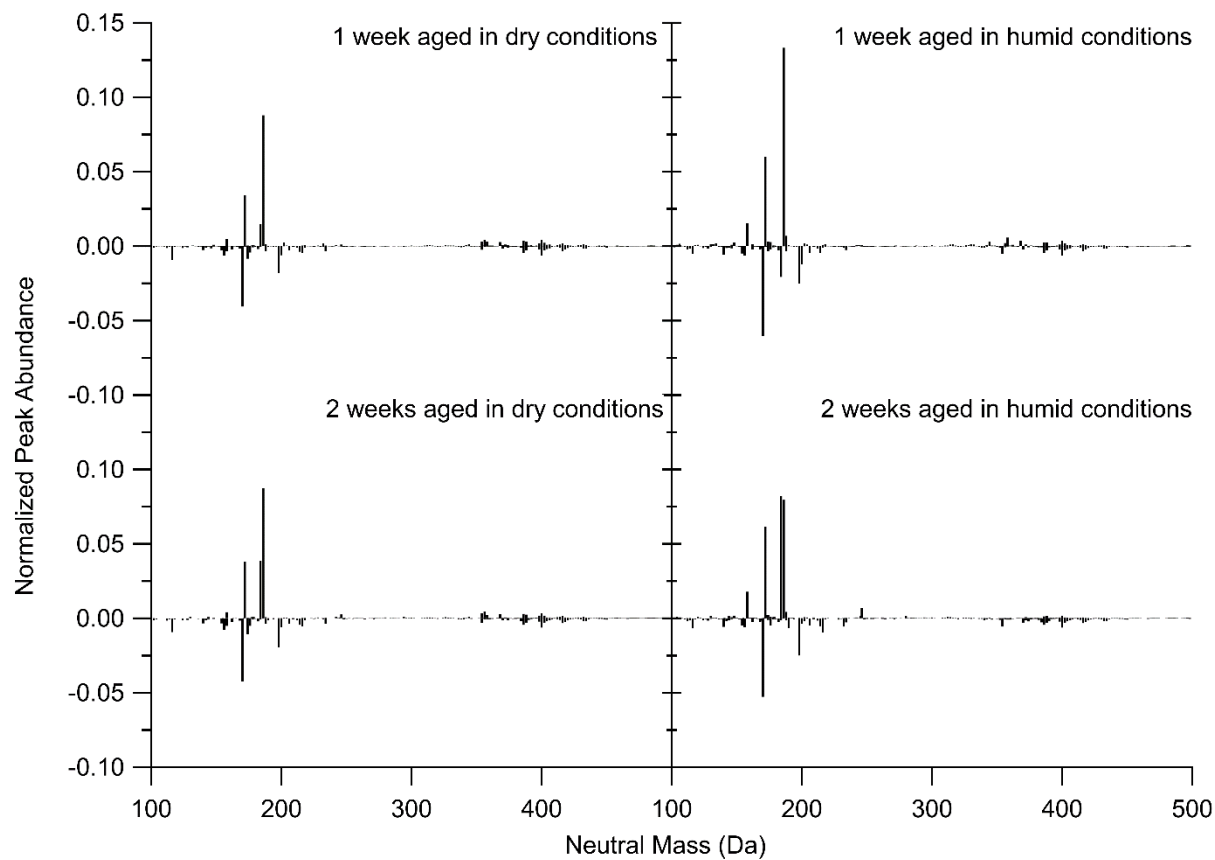
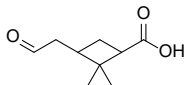
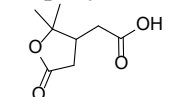
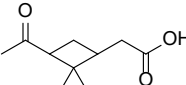
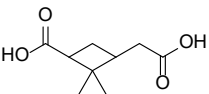
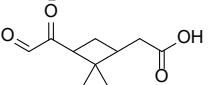


Figure S2. Difference high-resolution mass spectra of α -pinene SOA aged for 1 and 2 weeks in dry and humid conditions. Positive and negative peaks represent compounds that increased and decreased after aging by exposure to water vapor, respectively. (Trial 2)

Table S2. Major compounds in α -pinene SOA that changed after aging by exposure to water vapor (humid conditions) or desiccant (dry conditions). Ratios > 1 indicate that the correspond peak increased with aging while ratios < 1 suggest that the peak decreased after aging. (Trial 2)

Observed MW (Da)	Molecular Formula	Suggested Structure	Aged:Fresh Ratios			
			1 week aged in dry conditions	2 weeks aged in dry conditions	1 week aged in humid conditions	2 weeks aged in humid conditions
170.094	C ₉ H ₁₄ O ₃	<p>Pinalic Acid</p> 	0.46	0.44	0.20	0.30
172.074	C ₈ H ₁₂ O ₄	<p>Terpenylic acid</p> 	2.12	2.25	2.97	3.02
184.109	C ₁₀ H ₁₆ O ₃	<p>Pinonic Acid</p> 	1.11	1.28	0.85	1.59
186.089	C ₉ H ₁₄ O ₄	<p>Pinic Acid</p> 	1.66	1.65	2.00	1.59
198.089	C ₁₀ H ₁₄ O ₄	<p>Oxopinonic acid</p> 	0.35	0.30	0.09	0.09

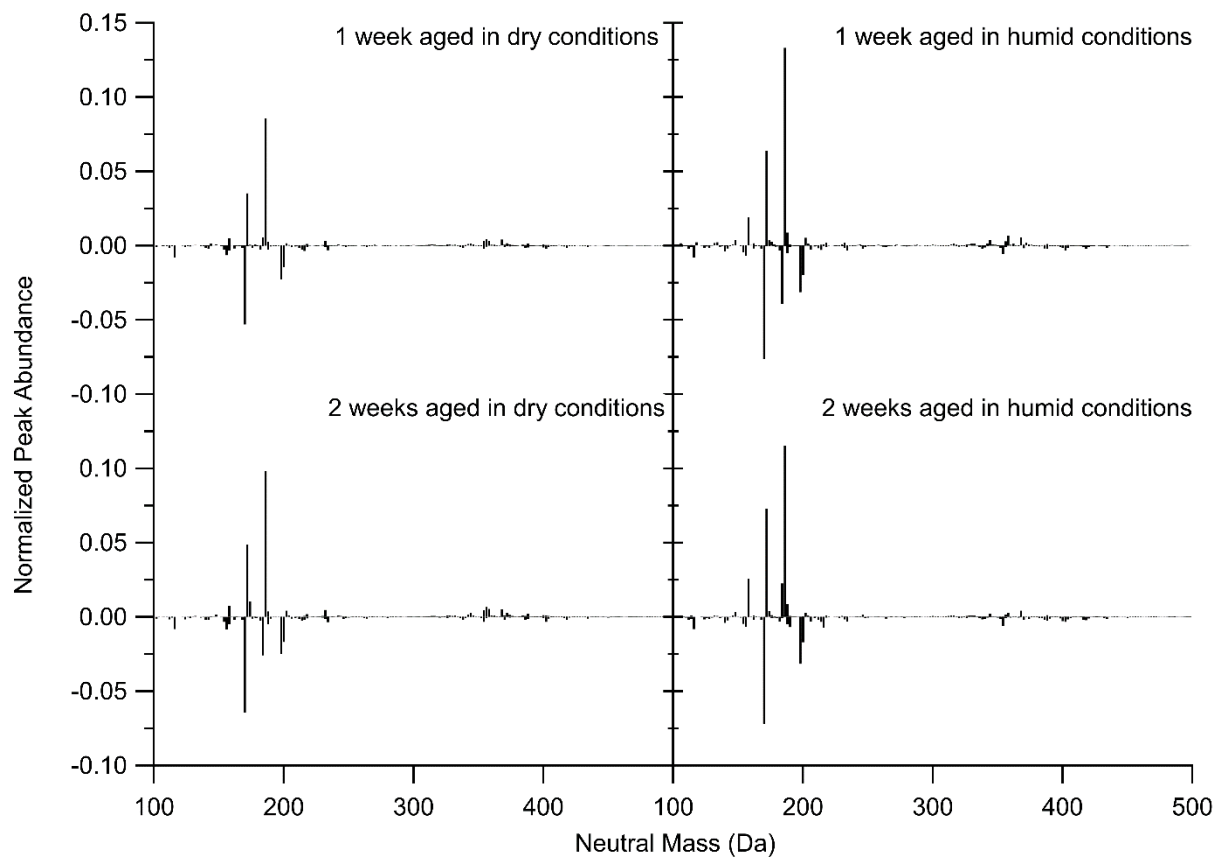
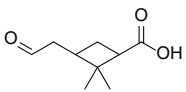
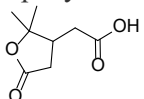
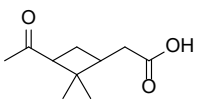
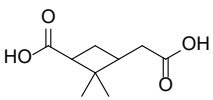
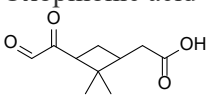


Figure S3. Difference high-resolution mass spectra of α -pinene SOA aged for 1 and 2 weeks in dry and humid conditions. Positive and negative peaks represent compounds that increased and decreased after aging by exposure to water vapor, respectively. (Trial 3)

Table S3. Major compounds in α -pinene SOA that changed after aging by exposure to water vapor (humid conditions) or desiccant (dry conditions). Ratios > 1 indicate that the correspond peak increased with aging while ratios < 1 suggest that the peak decreased after aging. (Trial 3)

Observed MW (Da)	Molecular Formula	Suggested Structure	Aged:Fresh Ratios			
			1 week aged in dry conditions	2 weeks aged in dry conditions	1 week aged in humid conditions	2 weeks aged in humid conditions
170.094	C ₉ H ₁₄ O ₃	<p>Pinalic Acid</p> 	0.42	0.29	0.16	0.21
172.074	C ₈ H ₁₂ O ₄	<p>Terpenylic acid</p> 	2.29	2.79	3.34	3.67
184.109	C ₁₀ H ₁₆ O ₃	<p>Pinonic Acid</p> 	1.03	0.84	0.76	1.14
186.089	C ₉ H ₁₄ O ₄	<p>Pinic Acid</p> 	1.68	1.78	2.05	1.92
198.089	C ₁₀ H ₁₄ O ₄	<p>Oxopinonic acid</p> 	0.33	0.27	0.08	0.07

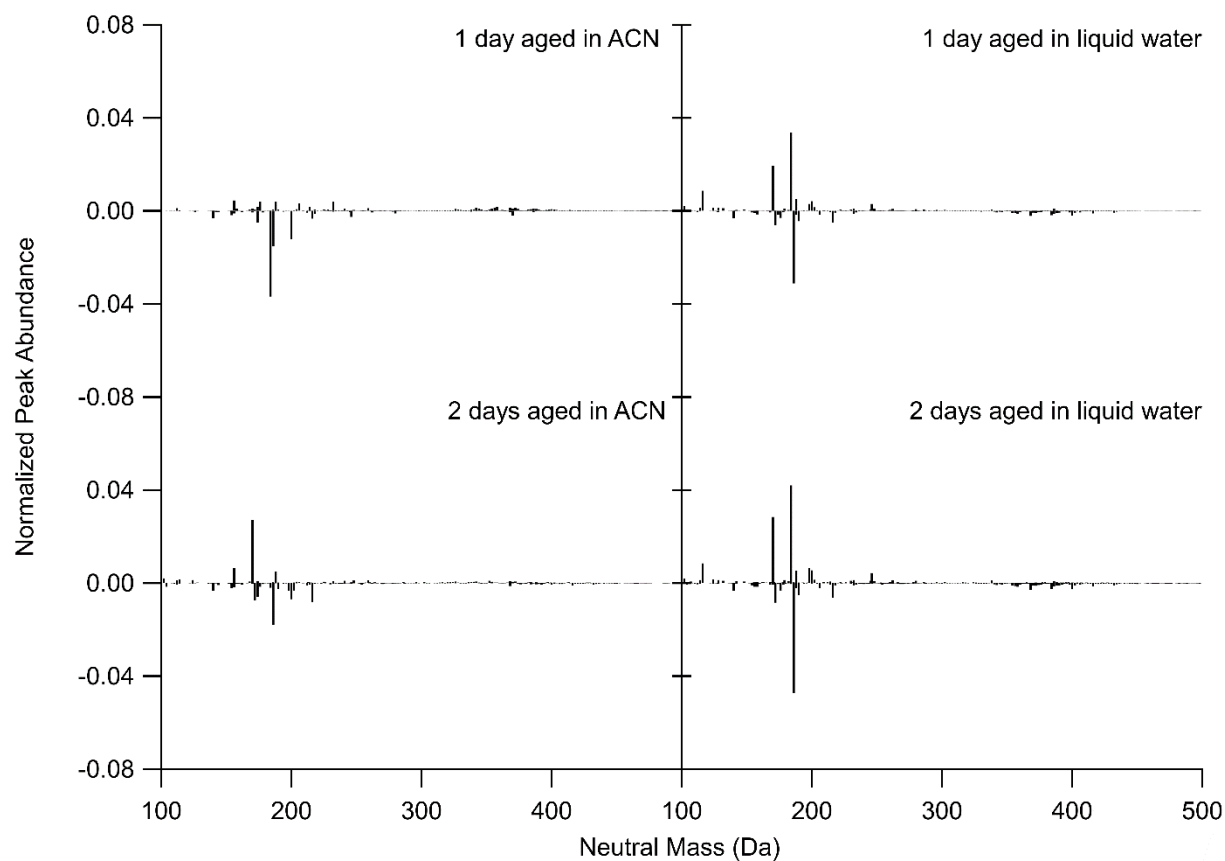
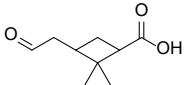
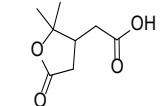
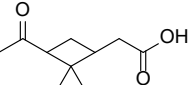
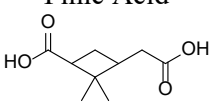
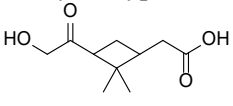


Figure S4. Difference high-resolution mass spectra of α -pinene SOA aged in acetonitrile and liquid water for 1 and 2 days. Positive peaks represent compounds that increased after aging in water and negative peaks presents compounds that decreased after aging in water. (Trial 2)

Table S4. Major compounds in α -pinene that changed after aging in acetonitrile and liquid water. Ratios > 1 indicate that the correspond peak increased with aging while ratios < 1 suggest that the peak decreased after aging. (Trial 2)

Observed MW (Da)	Molecular Formula	Suggested Structure	Aged:Fresh Ratio			
			1 day aged in ACN	2 days aged in ACN	1 day aged in liquid water	2 days aged in liquid water
170.094	C ₉ H ₁₄ O ₃	<p>Pinalic Acid</p> 	1.01	1.39	1.26	1.39
172.074	C ₈ H ₁₂ O ₄	<p>Terpenylic acid</p> 	1.02	0.80	0.83	0.77
184.109	C ₁₀ H ₁₆ O ₃	<p>Pinonic Acid</p> 	0.76	0.99	1.22	1.28
186.089	C ₉ H ₁₄ O ₄	<p>Pinic Acid</p> 	0.91	0.90	0.82	0.73
200.105	C ₁₀ H ₁₆ O ₄	<p>10-hydroxypinonic</p> 	0.79	0.88	1.07	1.10

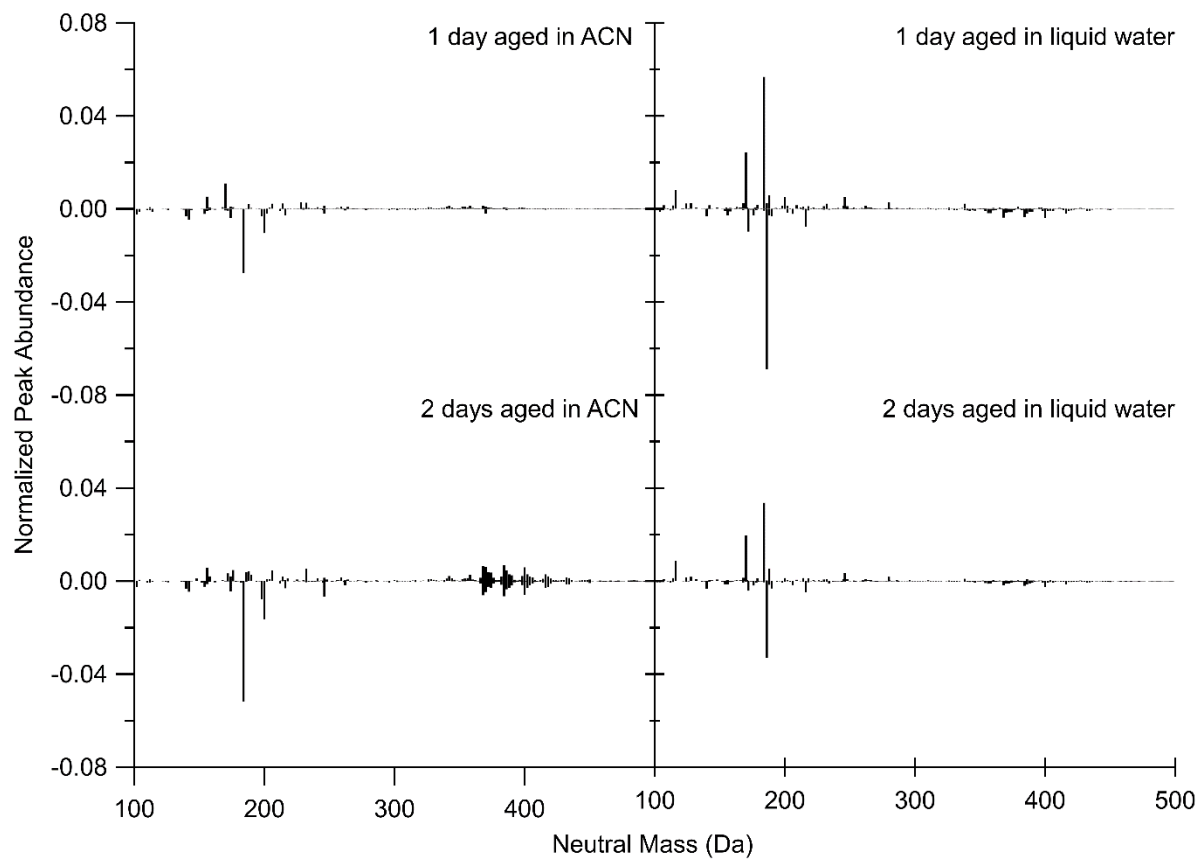
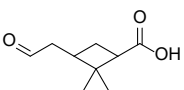
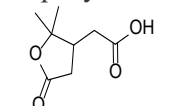
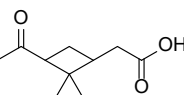
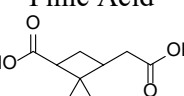
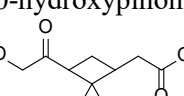


Figure S5. Difference high-resolution mass spectra of α -pinene SOA aged in acetonitrile and liquid water for 1 and 2 days. Positive peaks represent compounds that increased after aging in water and negative peaks presents compounds that decreased after aging in water. (Trial 3)

Table S5. Major compounds in α -pinene that changed after aging in acetonitrile and liquid water. Ratios > 1 indicate that the correspond peak increased with aging while ratios < 1 suggest that the peak decreased after aging. (Trial 3)

Observed MW (Da)	Molecular Formula	Suggested Structure	Aged:Fresh Ratio			
			1 day aged in ACN	2 days aged in ACN	1 day aged in liquid water	2 days aged in liquid water
170.094	C ₉ H ₁₄ O ₃	<p>Pinalic Acid</p> 	1.14	0.99	1.30	1.24
172.074	C ₈ H ₁₂ O ₄	<p>Terpenylic acid</p> 	0.98	1.09	0.72	0.88
184.109	C ₁₀ H ₁₆ O ₃	<p>Pinonic Acid</p> 	0.84	0.70	1.33	1.19
186.089	C ₉ H ₁₄ O ₄	<p>Pinic Acid</p> 	0.99	1.02	0.58	0.80
200.105	C ₁₀ H ₁₆ O ₄	<p>10-hydroxypinonic</p> 	0.83	0.73	1.08	1.02

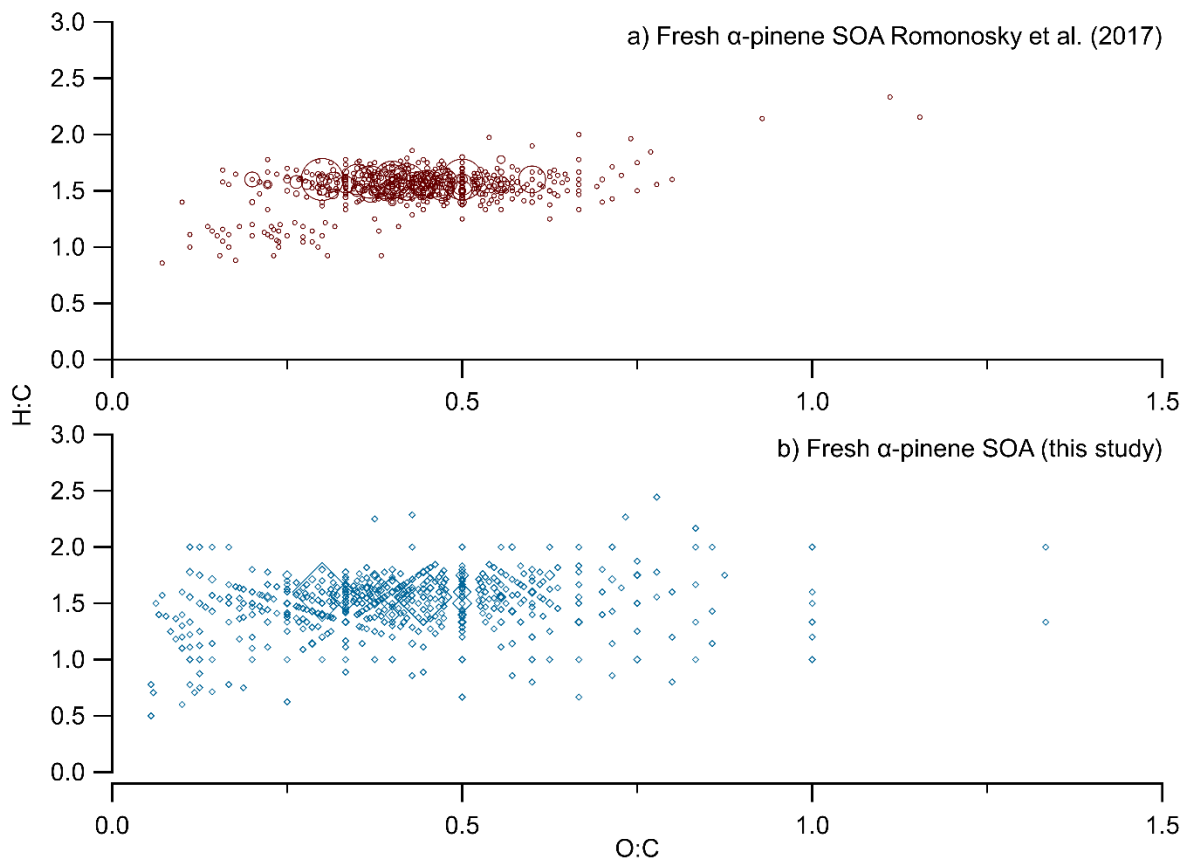


Figure S6. Van Krevelen diagram of fresh α -pinene SOA from Romonosky et al. (2017) compared to this study. Size of the markers are scaled to the normalized intensity.