

Supplemental Information

Effect of Relative Humidity, NO_x, and Ammonia on Physical Properties of Naphthalene Secondary Organic Aerosol

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Section S1. Chamber OH Steady-State Concentration Estimation

The rate of depletion of NAP was used to estimate the OH steady-state concentration in the chamber. The rate of change of NAP ($\frac{d[VOC]}{dt}$) is given by Eq. S1.

$$\frac{d[VOC]}{dt} = -k_{OH}[OH]_{SS}[VOC] + k_{wall} \quad (S1)$$

Here, $[VOC]$ is the concentration of NAP, $k_{OH} = 2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, taken from Calvert et al., 2022,¹ is the bimolecular rate constant for the reaction of NAP with the OH radical, and $[OH]_{SS}$ is the steady-state OH radical concentration in the chamber. The change in NAP concentration due to wall loss is represented by k_{wall} . The wall loss correction is neglected in this estimation as it is relatively small for NAP (compared to NH_3). The steady-state OH concentration calculated here should therefore be regarded as an upper limit although it should be within 10% from the actual value. The gas-phase concentration of NAP was monitored using the ^{13}C isotope $[^{13}\text{CC}_9\text{H}_8 + \text{H}]^+$, measured with a Proton Transfer Time of Flight Mass Spectrometer (PTR-ToF-MS; Ionicon model 8000, Innsbruck, Austria). The results from this analysis, shown in Figure S1, suggest $OH_{SS} \approx 4 \times 10^6 \text{ molecules cm}^{-3}$.

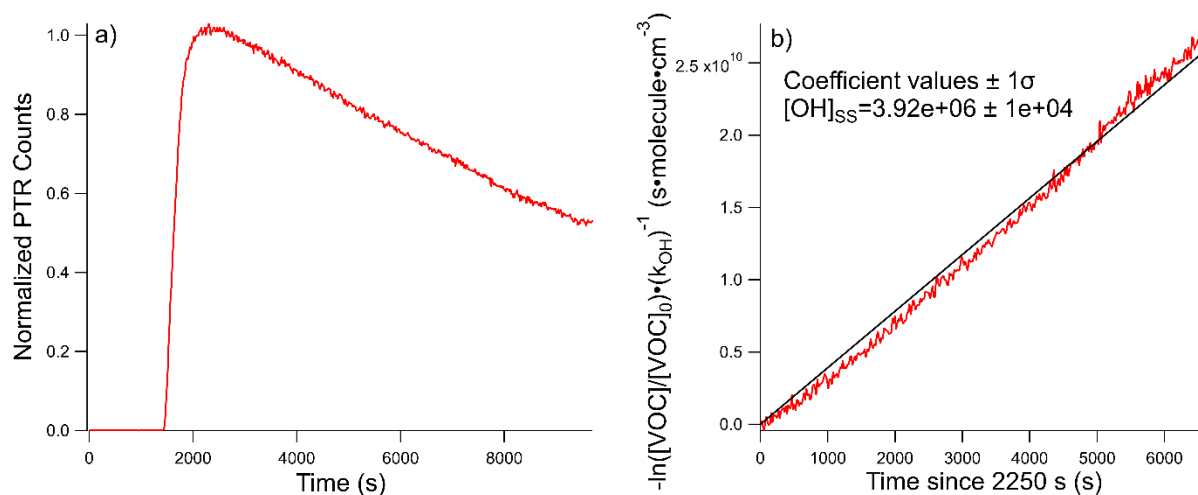


Figure S1. PTR-ToF-MS data ($[^{13}\text{CC}_9\text{H}_8 + \text{H}]^+$ trace) used to estimate the OH steady-state concentrations during SOA formation. Panel (a) shows the PTR counts normalized to the value at 2250 s where the fit in Panel (b) begins. Panel (b) shows the integration and subsequent linearization of equation S1 such that the slope is equivalent to OH_{SS} .

Section S2. Correction for the Incomplete Extraction in MAC_{bulk} Measurements

The total mass of SOA, m , sitting on the filter is estimated from the SMPS or gravimetric measurements. When we extract the SOA material from the filter, we dissolve a certain portion of it (m_1) in a volume of solvent (V_1) in the first extraction, and a certain portion (m_2) in a volume of solvent (V_2) in the 2nd extraction. We do not know the SOA masses that went into extracts 1 and 2 but we are going to assume that the two extractions fully dissolve the SOA material (this treatment can easily be extended to three or more extractions):

$$m = m_1 + m_2 \quad (\text{S2})$$

The corresponding (unknown) mass concentrations in the extracts are:

$$C_1 = \frac{m_1}{V_1} \quad (\text{S3})$$

$$C_2 = \frac{m_2}{V_2} \quad (\text{S4})$$

If extract # 2 has no measurable absorbance ($A_1 \gg A_2 \sim 0$), as is the case with methanol or acetonitrile extracted SOA, the calculations are simple. It means that everything extracted on the first trial, so we can assume $m = m_1$ and (b is the cell path length):

$$MAC(\lambda) = \frac{A_1(\lambda) \times \ln(10)}{b \times C_1} = \frac{A_1(\lambda) \times \ln(10) \times V_1}{b \times m_1} \quad (\text{S5})$$

However, for water-extracted SOA we find the absorbance of extract #2, while small, is not negligible. Assuming absorbance has a linear dependence on concentration (this was explicitly verified by recording spectra of progressively diluted samples), and further assuming that the $MAC(\lambda)$ from the 1st and 2nd extractions has the same wavelength dependence, we can relate the absorbance in extracts 1 and 2 to $MAC(\lambda)$ as follows.

$$m = m_1 + m_2 = \frac{A_1(\lambda) \times \ln(10) \times V_1}{b \times MAC(\lambda)} + \frac{A_2(\lambda) \times \ln(10) \times V_2}{b \times MAC(\lambda)} \quad (\text{S6})$$

Or equivalently:

$$MAC(\lambda) = \frac{\ln(10)}{b \times m} (A_1(\lambda) \times V_1 + A_2(\lambda) \times V_2) \quad (\text{S7})$$

If the volumes used at each step are the same ($V = V_1 = V_2$), this simplifies to:

$$MAC(\lambda) = \frac{\ln(10) \times V}{b \times m} (A_1(\lambda) + A_2(\lambda)) \quad (\text{S8})$$

Equivalently, we can calculate $MAC(\lambda)$ from the results of the 1st extraction measurement only (which is advantageous, because it has higher signal-to-noise ratio than the 2nd extraction measurement):

$$MAC(\lambda) = \frac{\ln(10) \times V}{b \times m_1} A_1(\lambda) \quad (S9)$$

Where the unknown mass of m_1 is estimated from

$$m_1 = m \times \frac{\langle A_1(\lambda) \rangle}{\langle A_1(\lambda) \rangle + \langle A_2(\lambda) \rangle} \quad (S10)$$

Equations (S9) and (S10) are the ones we used in this paper for aqueous solutions, wherein the absorbances were averaged over the wavelength range 285 to 585 nm.

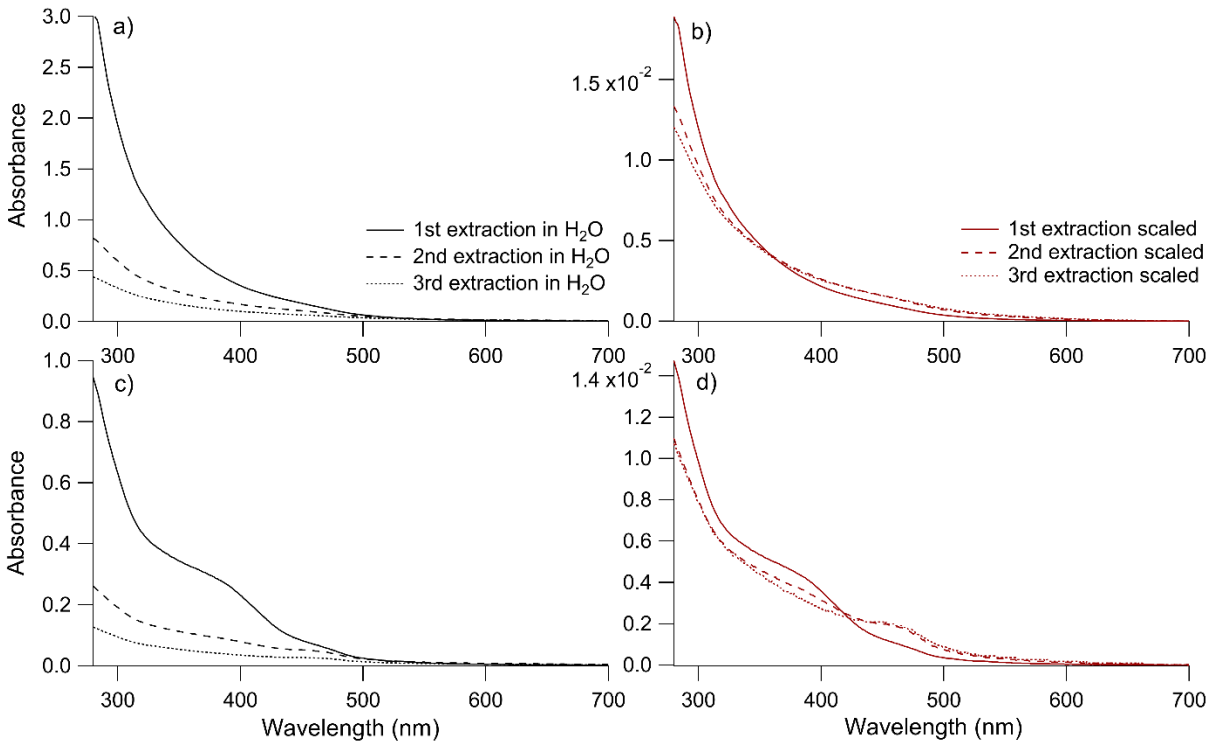


Figure S2. A typical result for our experiment plotting absorbances A_1 , A_2 , A_3 for three successive extractions of the NAP SOA sample in **water**, using absorbance data from the high-NO_x, low-RH (panels a and b) and high-NO_x, high-RH (panels c and d) studies, both with NH₃ present. In the panels b) and d) of this figure, the traces from panels a) and c) are scaled to the sum of their absorbance to show that the absorption spectra of the 1st and 2nd extract have a similar (although not identical) wavelength dependence making it possible for us to assume the same $MAC(\lambda)$ values in the denominators of equation (S6).

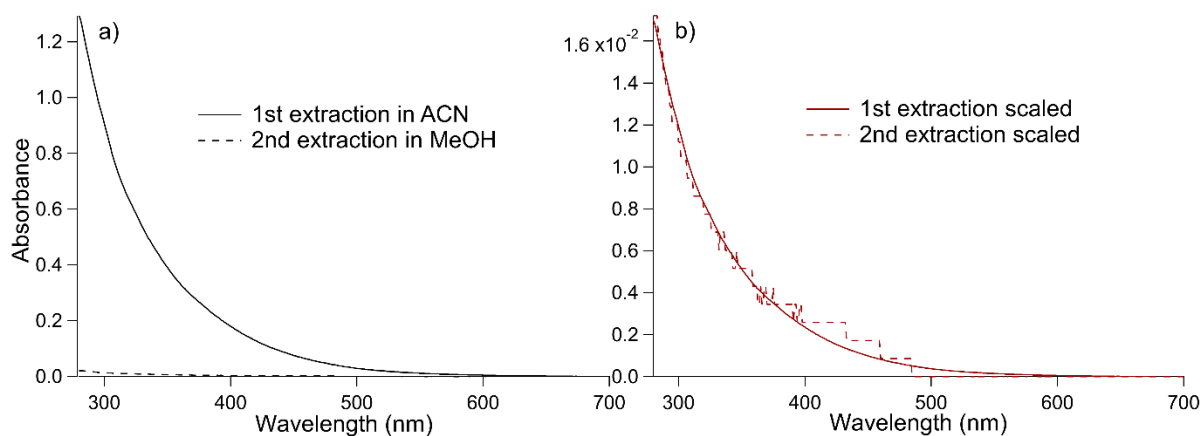


Figure S3. A test of extraction efficiency from the Teflon filters using acetonitrile and methanol. After the filter was extracted using acetonitrile, it was extracted a second time using an equivalent volume of methanol. Panel a) shows the results of the extraction in the two solvents. Panel b) shows the same data scaled to the total absorbance of each trace to emphasize shape changes as described in Figure S2. Assuming that the integrated absorbance from 280 to 700 nm is a good metric for the amount of SOA extracted, 98% of the organic-solvent soluble SOA was extracted from the filter using acetonitrile.

Section S3. Supporting Figures

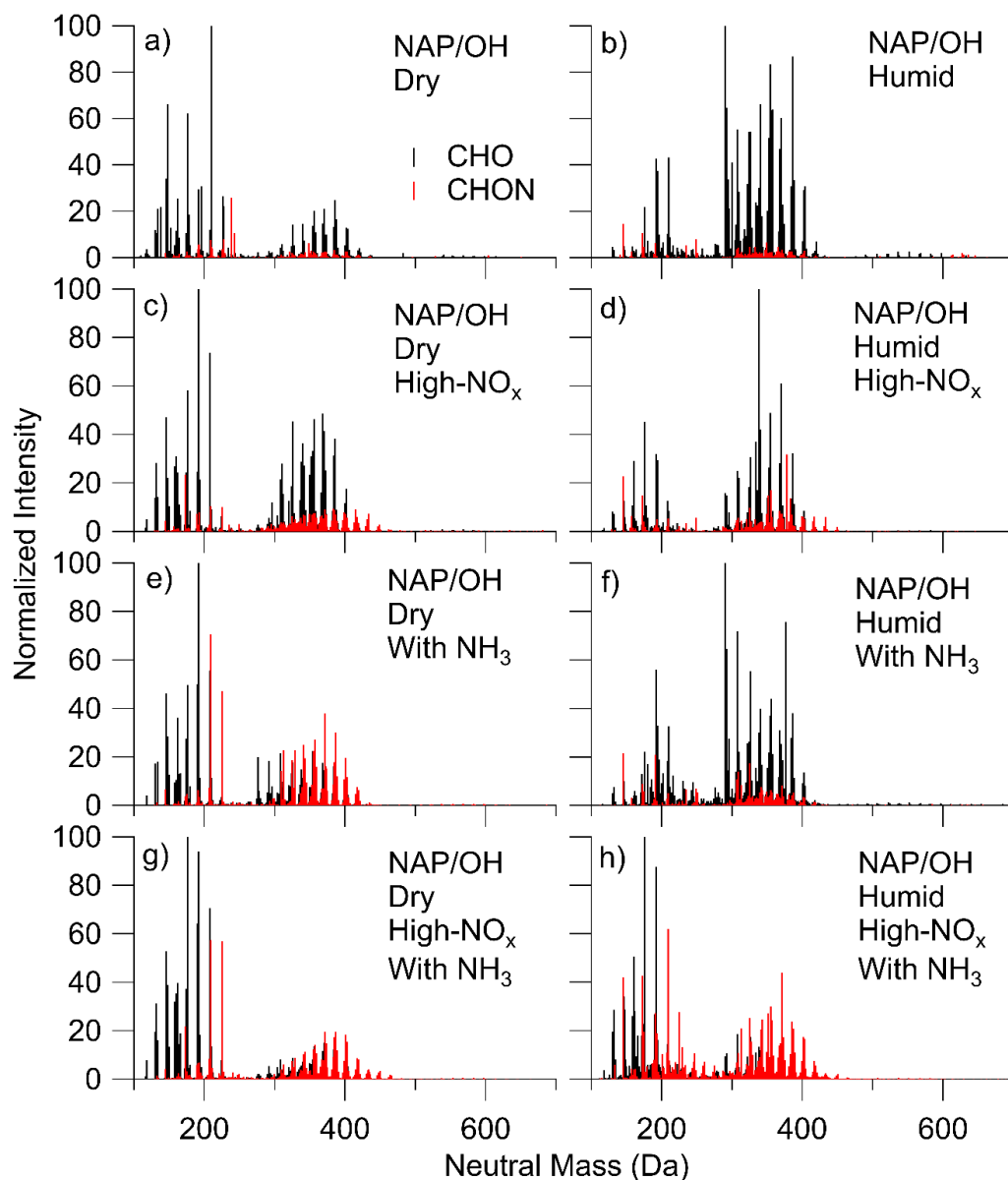


Figure S4. Nano-DESI mass spectra for each set of conditions normalized to the highest peak in the spectrum. The panels show NAP SOA prepared under (a) dry, low-NO_x conditions without ammonia, (b) humid, low-NO_x conditions without ammonia, (c) dry, high-NO_x conditions without ammonia, (d) humid, high-NO_x conditions without ammonia, (e) dry, low-NO_x conditions with ammonia, (f) humid, low-NO_x conditions with ammonia, (g) dry, high-NO_x conditions with ammonia, and (h) humid, high-NO_x conditions with ammonia. CHO peaks are shown in black and CHON peaks are shown in red.

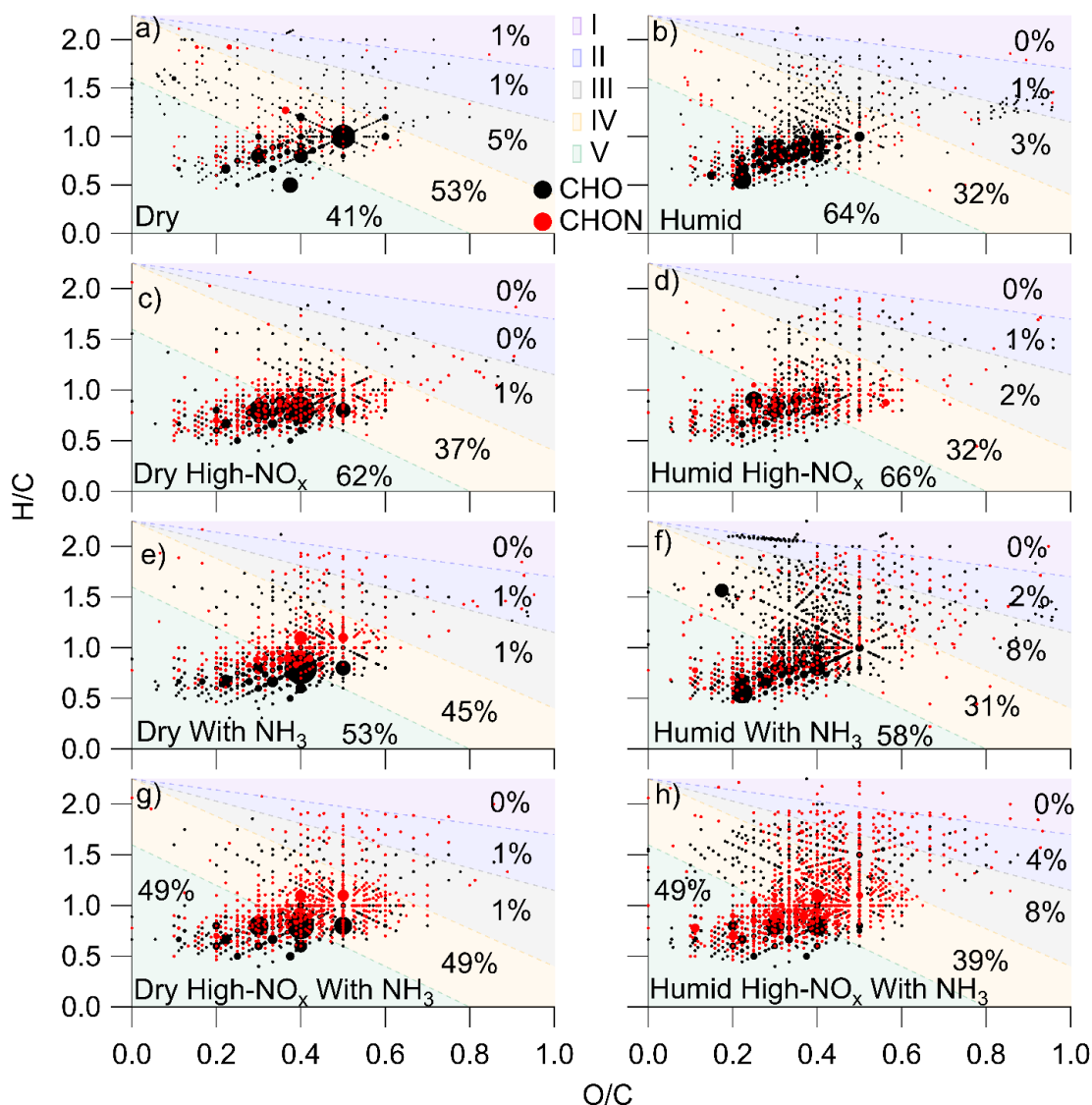


Figure S5. Maximum Carbonyl Ratio (MCR) - Van Krevelen diagrams for each set of conditions from nano-DESI-HRMS data. The panels show NAP SOA prepared under (a) dry, low- NO_x conditions without ammonia, (b) humid, low- NO_x conditions without ammonia, (c) dry, high- NO_x conditions without ammonia, (d) humid, high- NO_x conditions without ammonia, (e) dry, low- NO_x conditions with ammonia, (f) humid, low- NO_x conditions with ammonia, (g) dry, high- NO_x conditions with ammonia, and (h) humid, high- NO_x conditions with ammonia. Point area corresponds to the relative abundance of the compound represented. Each point represents the summed relative intensity of each compound with that corresponding H/C and O/C ratio. CHO peaks are shown in black and CHON peaks are shown in red. Each panel is divided into 5 areas with limits take from Zhang et al.² (2021) – very highly oxidized compounds (I in purple), highly oxidized compounds (II in blue), intermediately oxidized (III in gray), oxidized unsaturated (IV in orange), and highly unsaturated (V in green). Percentages portray the percentage of total intensity falling within that MCR area.

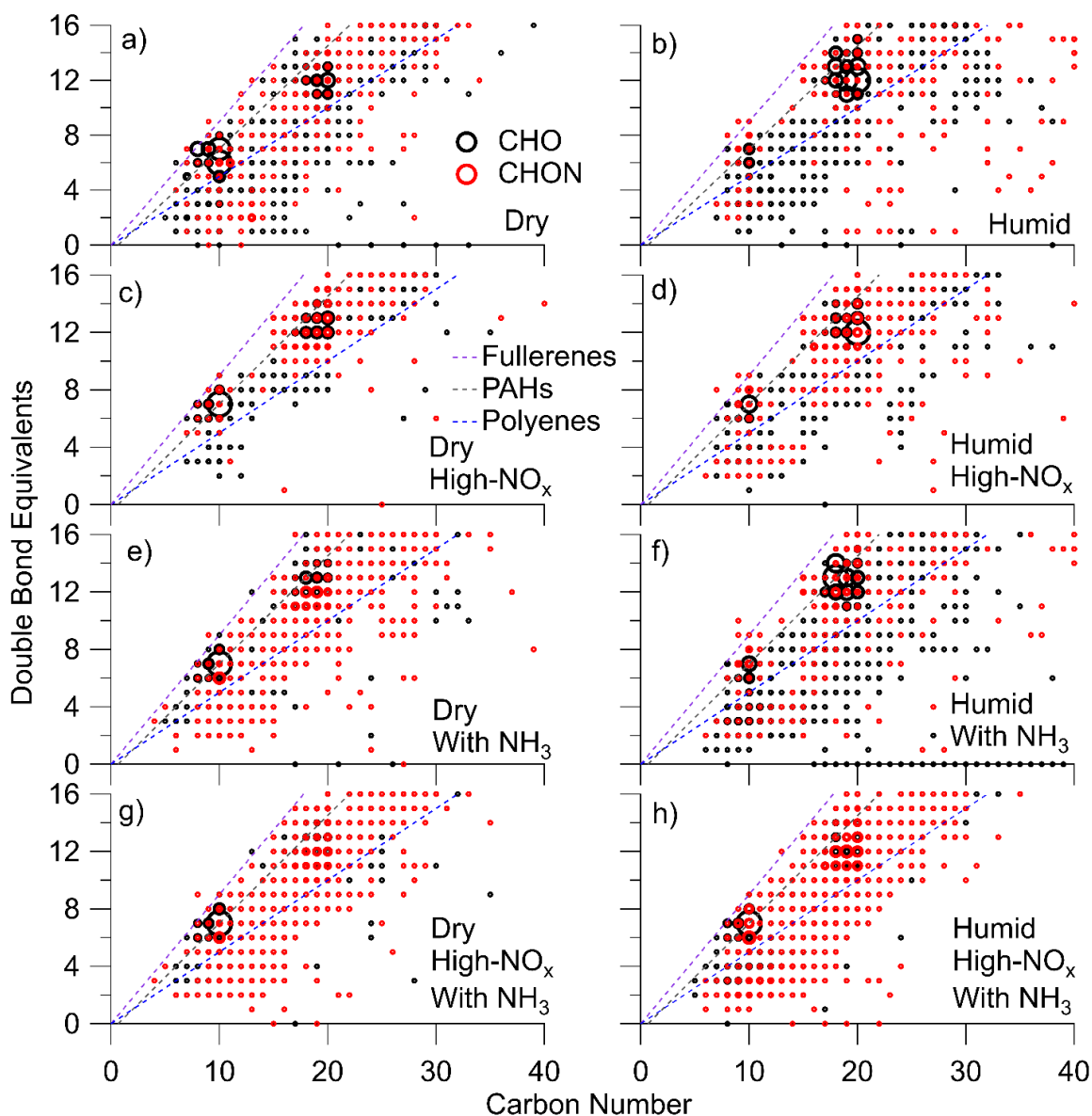


Figure S6. Double bond equivalent plots for each set of conditions from nano-DESI-HRMS data. The panels show NAP SOA prepared under (a) dry, low- NO_x conditions without ammonia, (b) humid, low- NO_x conditions without ammonia, (c) dry, high- NO_x conditions without ammonia, (d) humid, high- NO_x conditions without ammonia, (e) dry, low- NO_x conditions with ammonia, (f) humid, low- NO_x conditions with ammonia, (g) dry, high- NO_x conditions with ammonia, and (h) humid, high- NO_x conditions with ammonia. Circle area corresponds to the relative abundance of the compound represented. Red circles represent CHON compounds, and black circles represent CHO compounds. Dashed lines show upper compositional boundaries for fullerenes (purple), polycyclic aromatic hydrocarbons (gray), and polyenes (blue).

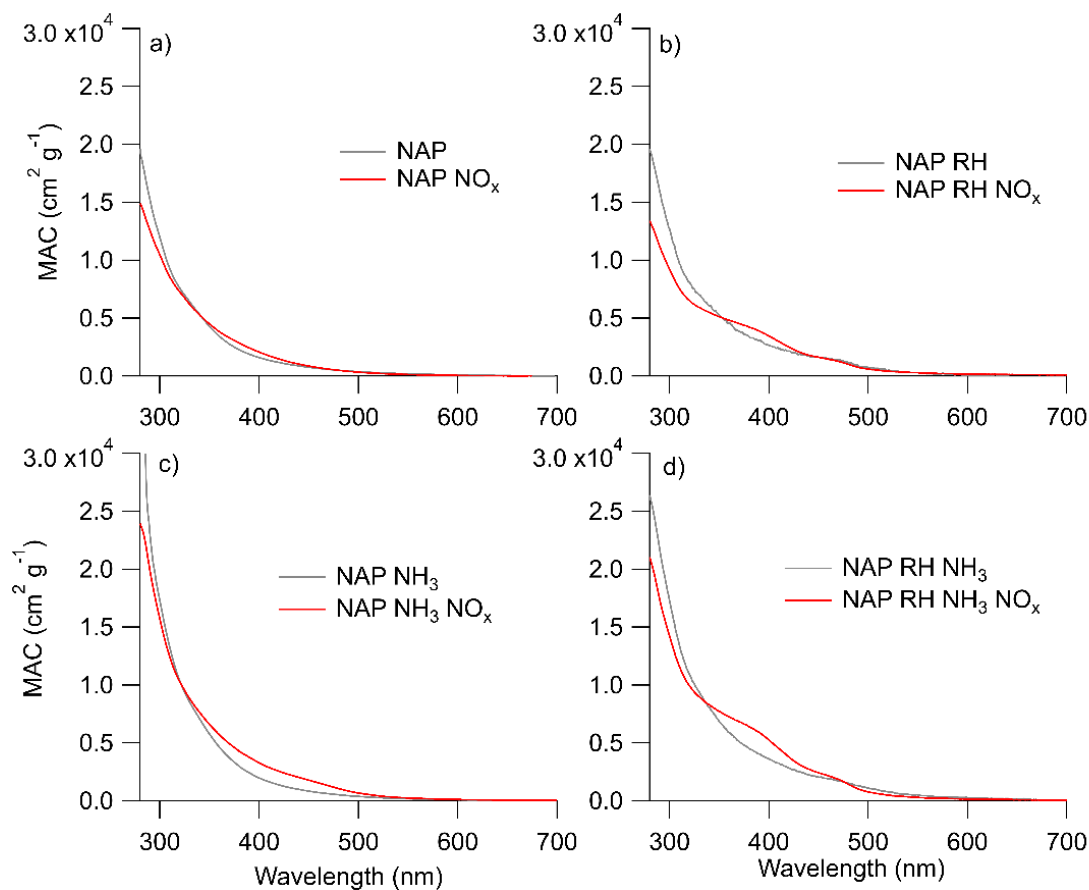


Figure S7. UV-Vis data comparing high- and low- NO_x conditions. Low- NO_x conditions are shown in gray and high- NO_x conditions are shown in red. Panel a) shows NAP SOA prepared at low RH and without ammonia, panel b) shows NAP SOA prepared at high RH and without ammonia, panel c) shows NAP SOA prepared at low RH with ammonia, and panel d) shows NAP SOA prepared at high RH with ammonia. UV-vis are for samples 9-16, which were collected in water (see Section S2).

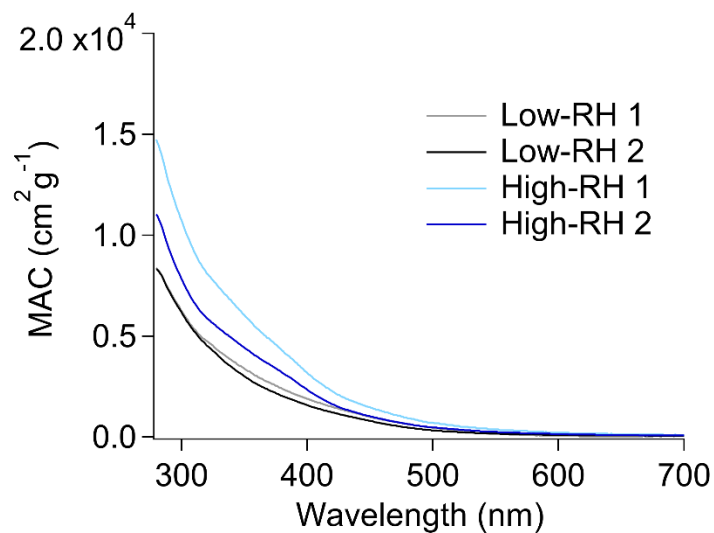


Figure S8. MAC_{bulk} for Samples 17-20, which were collected in methanol. Note: these samples were prepared at different NO_x concentrations than the previous samples, so some variation in spectral shape is expected.

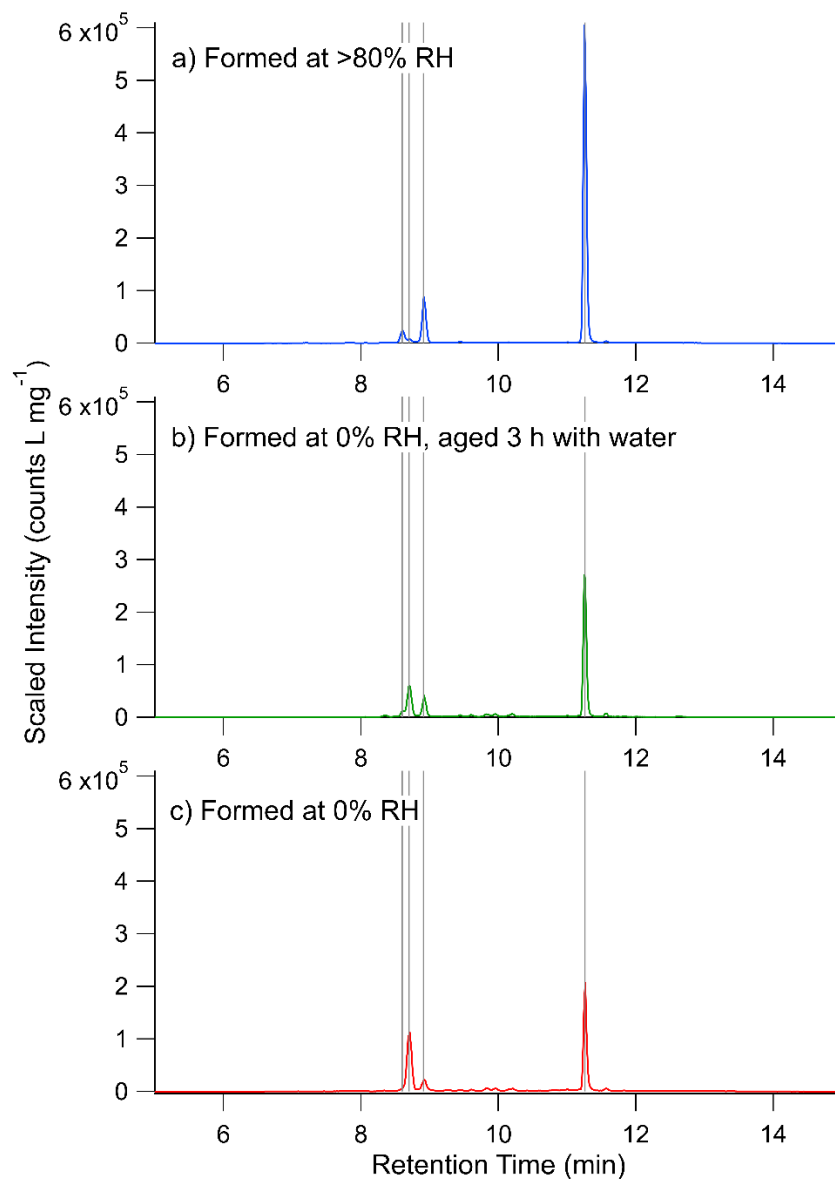


Figure S9. Negative mode UPLC-MS EIC trace of mass 188.035, corresponding to all structural isomers of nitro-naphthol. Panel a) shows fresh SOA prepared at >80% RH, panel b) shows SOA prepared at 0% RH and aged 3 h in a solution of 50% water by volume, and panel c) shows fresh SOA prepared at 0% RH. EIC counts are scaled to the mass concentration of the mass spectrometry sample.

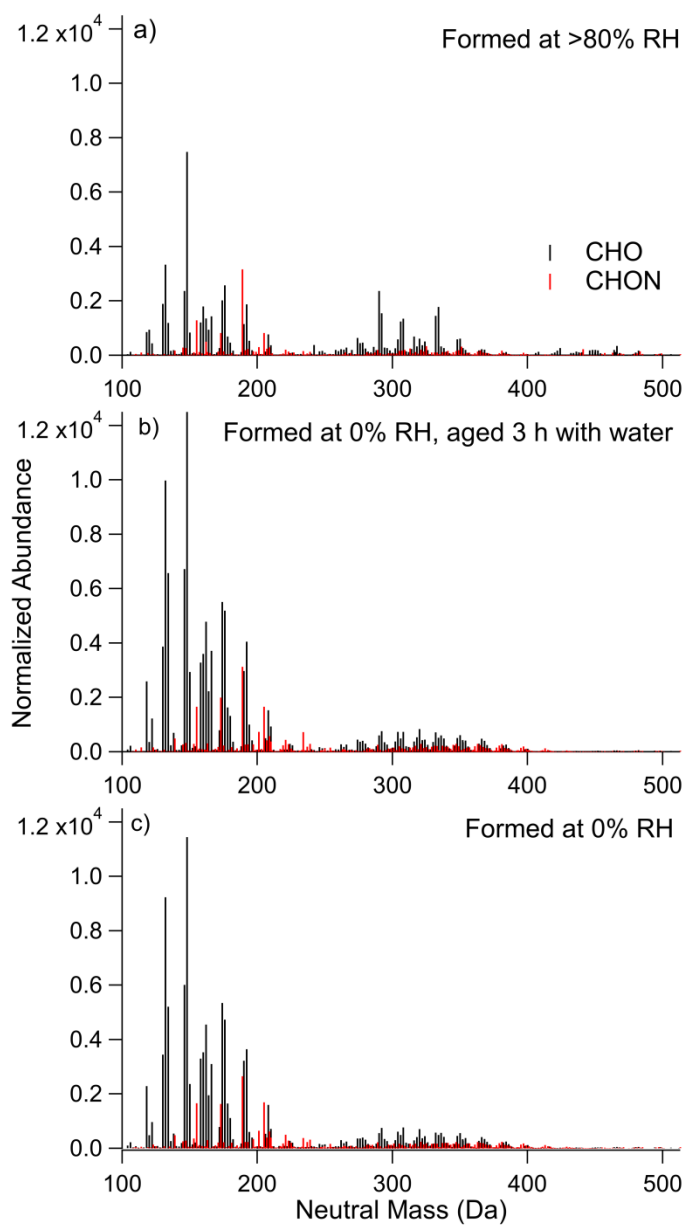


Figure S10. ESI-HRMS for Filters 21-23. Abundance is normalized to the SOA mass concentration in the mass spectrometry samples.

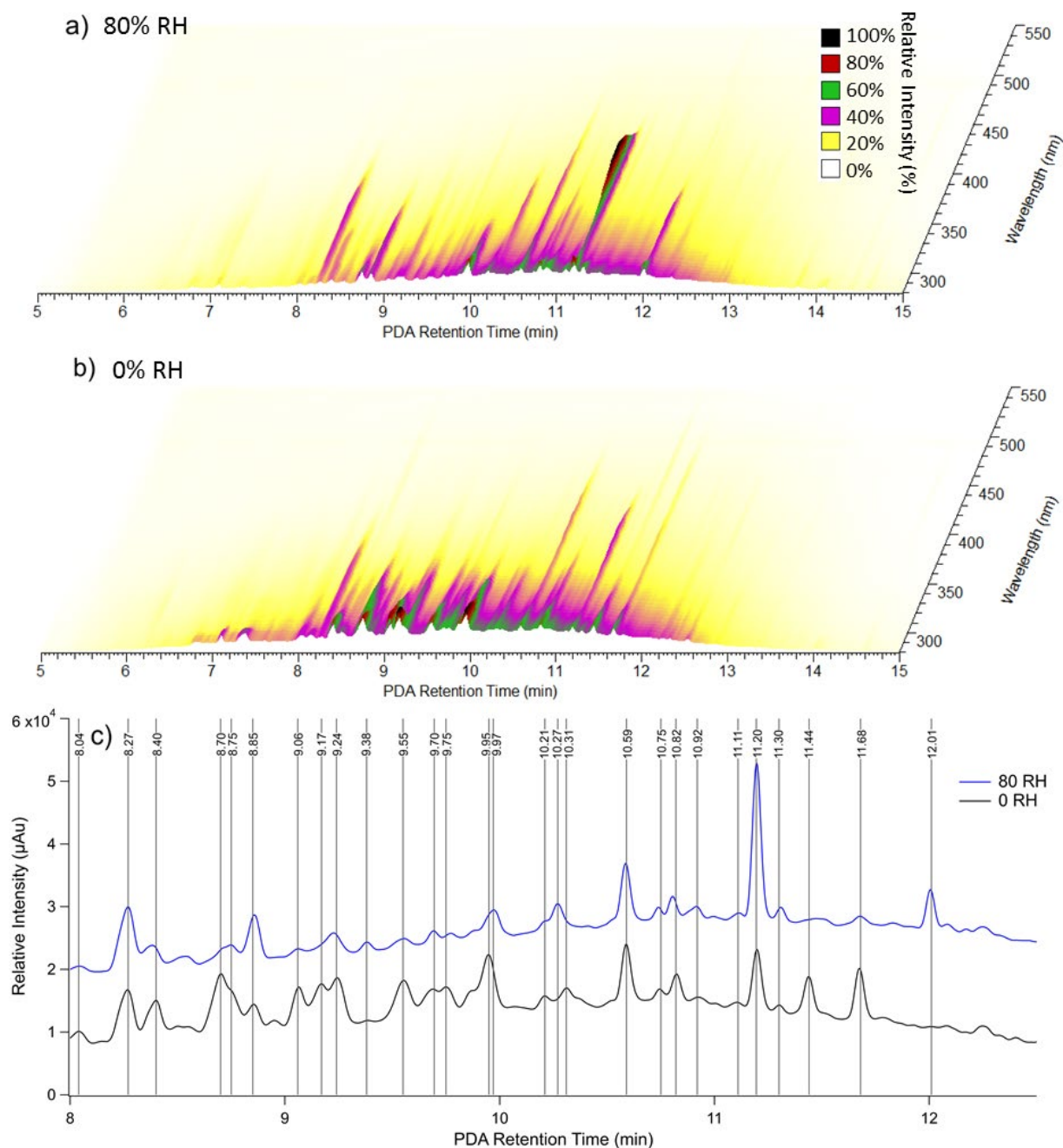


Figure S11. UPLC-PDA chromatograms for (a) NAP SOA prepared at 80% RH and (b) NAP SOA prepared at 0% RH. The retention time of the UPLC column is on the x-axis, the wavelength of absorption is on the y-axis, and the relative intensity, i.e., the absorption spectrum, is on the z-axis. Panels (a) and (b) are repeated from Figure 6. Panel (c) shows UPLC-PDA chromatograms integrated from 280 to 680 nm with the retention times of identified absorbers marked with vertical lines. Formulas corresponding to the marked retention times are provided in Table S1.

Table S1. Assignments for PDA data. Formulas provided were observed as the major mass under both dry and humid conditions unless otherwise marked. In these cases, the first formula was observed under dry conditions, while the second formula was observed under humid conditions.

PDA Retention Time (min)	Formula (Formula with High-RH if different)	0% RH intensity ($\times 10^3$)	80% RH intensity ($\times 10^3$)
8.04	C ₇ H ₅ NO ₅	2.9	2.2
8.27	C ₆ H ₅ NO ₄	7.3	9.7
8.40	C ₁₀ H ₇ NO ₆	5.0	3.1
8.70	C ₇ H ₅ NO ₅	8.4	NA
8.75	C ₁₀ H ₈ O ₄	NA	2.8
8.85	C ₁₀ H ₇ NO ₃	3.8	5.1
9.06	C ₁₀ H ₈ O ₃	5.1	0.8
9.17	C ₁₀ H ₆ O ₃	5.4	NA
9.24	C ₆ H ₅ NO ₄	6.4	3.9
9.38	C ₁₀ H ₇ NO ₃	0.2	0.9
9.55	C ₆ H ₄ N ₂ O ₆	6.2	2.1
9.70	C ₁₈ H ₁₄ O ₆	4.2	2.0
9.75	C ₇ H ₅ NO ₄	3.9	1.4
9.95	C ₁₀ H ₇ NO ₂	8.2	NA
9.97	C ₂₀ H ₁₄ O ₅	NA	5.5
10.21	C ₉ H ₆ O ₂	1.6	0.9
10.27	C ₈ H ₆ N ₂ O ₂	NA	3.8
10.31	C ₉ H ₇ NO ₅	2.8	NA
10.59	C ₁₀ H ₇ NO ₄	6.5	6.5
10.75	C ₈ H ₆ O ₄	1.3	1.1
10.82	C ₈ H ₆ N ₂ O ₅	2.7	2.4
10.92	C ₁₈ H ₁₂ O ₄	0.6	1.7
11.11	C ₁₀ H ₆ N ₂ O ₆ (C ₁₉ H ₁₂ O ₄)	7.9	1.0
11.20	C ₁₀ H ₇ NO ₃	5.6	16.4
11.30	C ₁₀ H ₅ N ₃ O ₈ (C ₁₈ H ₁₂ O ₅)	0.5	1.7
11.44	C ₈ H ₆ N ₂ O ₅	3.8	1.6
11.68	C ₁₀ H ₆ N ₂ O ₅	4.9	1.9
12.01	C ₁₈ H ₁₀ O ₄	NA	4.2

Footnote: NA stands for not applicable

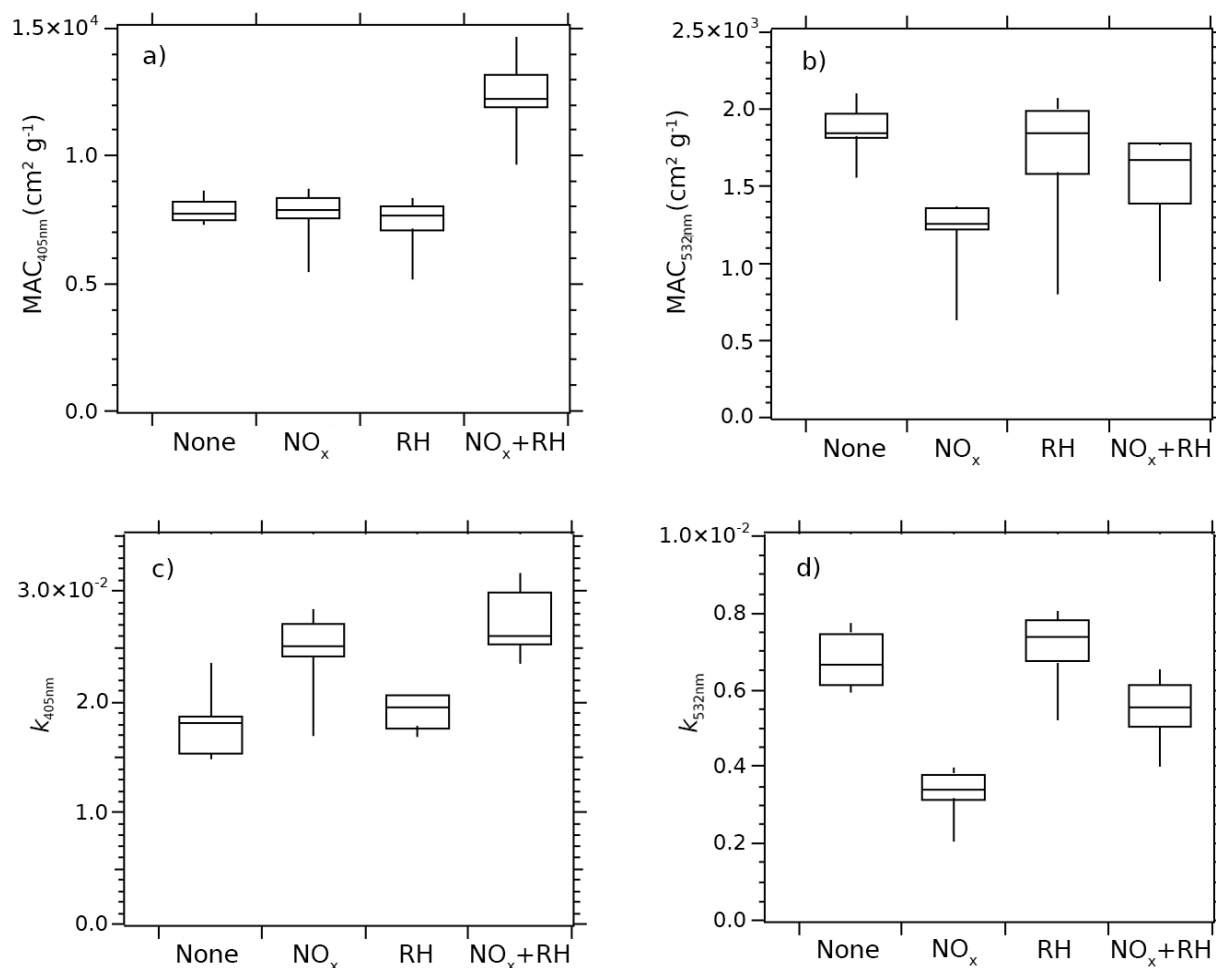


Figure S12. CRD-PAS data for samples 1 through 4. Panel a) shows MAC values at 405 nm, panel b) shows MAC values at 532 nm, panel c) shows the imaginary refractive index (*k*) at 405 nm, and panel d) shows the imaginary refractive index (*k*) at 532 nm. Labels on the X-axis correspond to parameters (either RH or NO_x) which are elevated during SOA formation. Note all trails for which CRD-PAS data were collected contain ammonia. Daily data sets included Figures S12-S15.

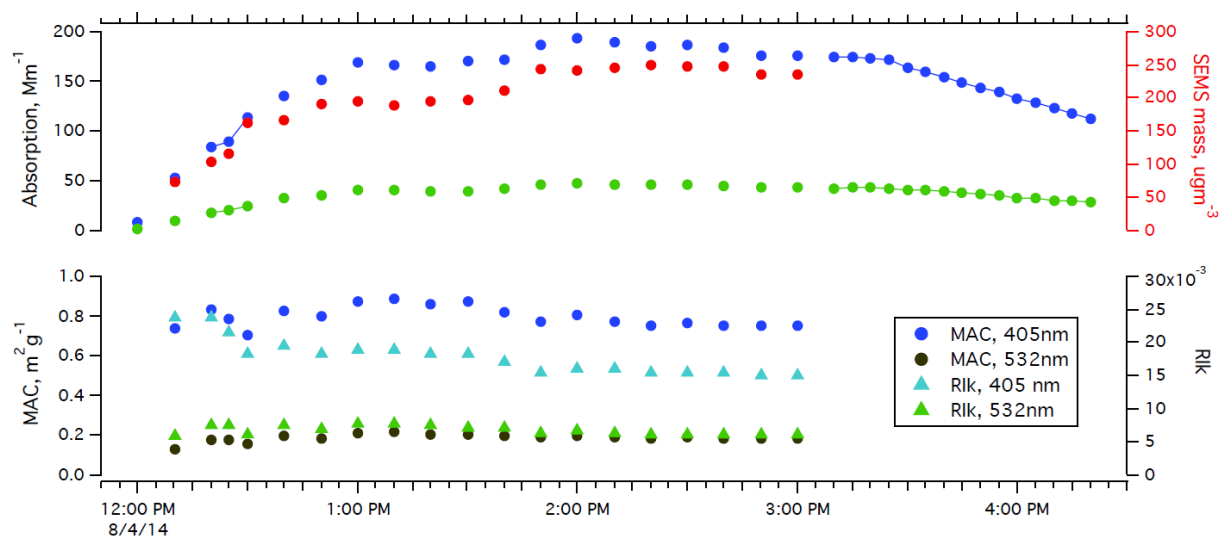


Figure S13. CRD/PAS data from the low- NO_x , low-RH, high- NH_3 study (Sample #1)

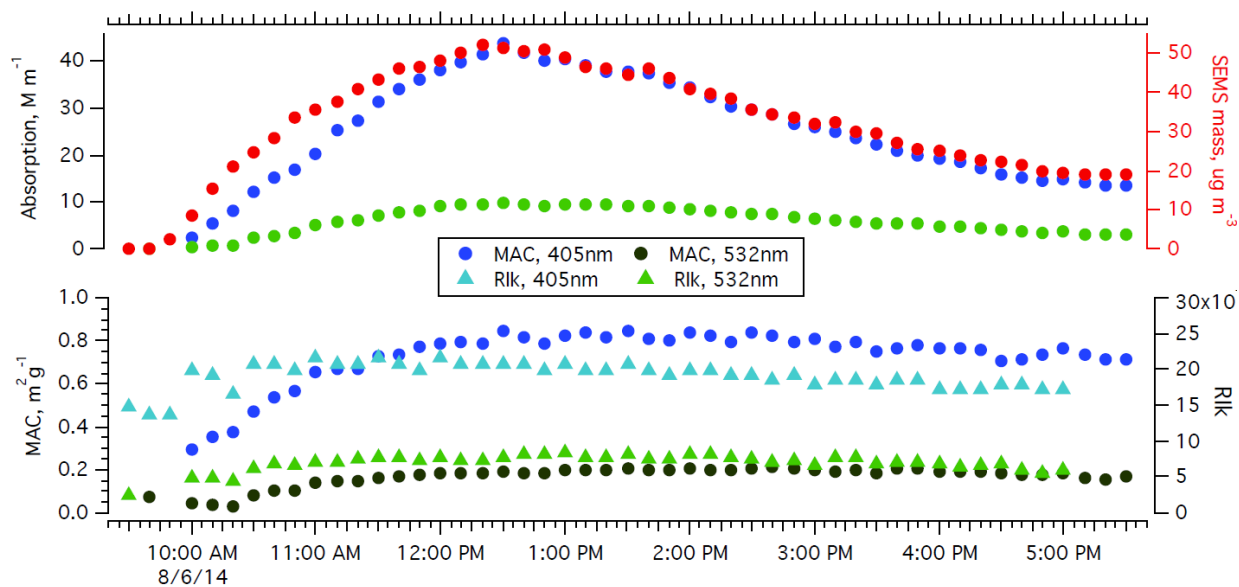


Figure S14. CRD/PAS data from the low- NO_x , high-RH, high- NH_3 study (Sample #2)

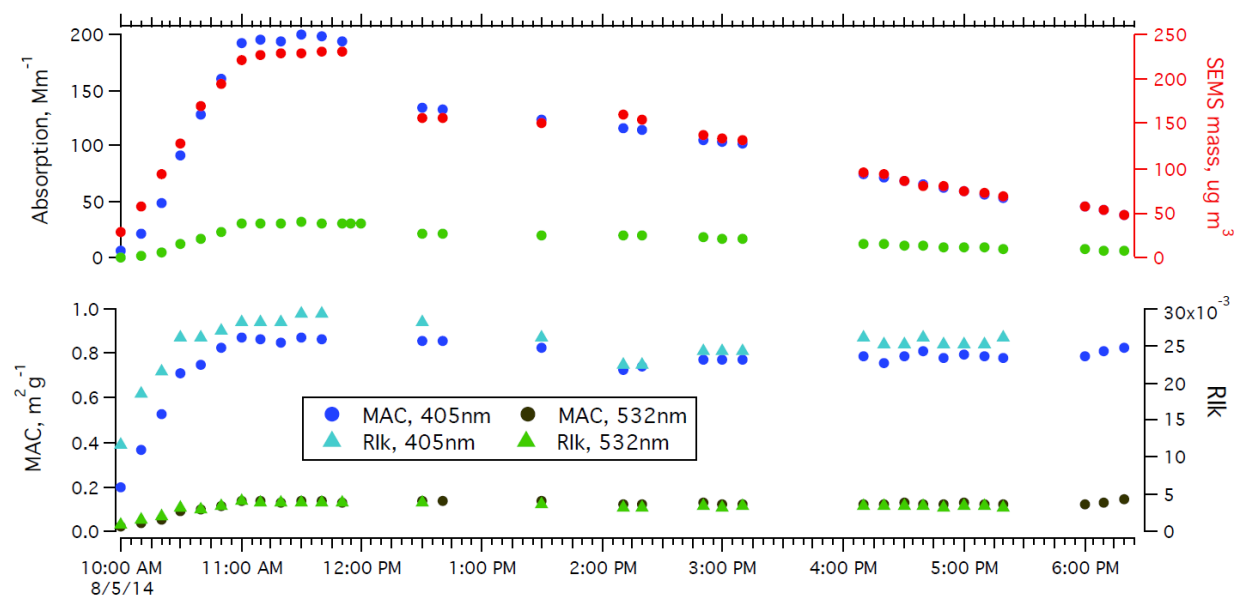


Figure S15. CRD/PAS data from the high-NO_x, low-RH, high-NH₃ study (Sample #3)

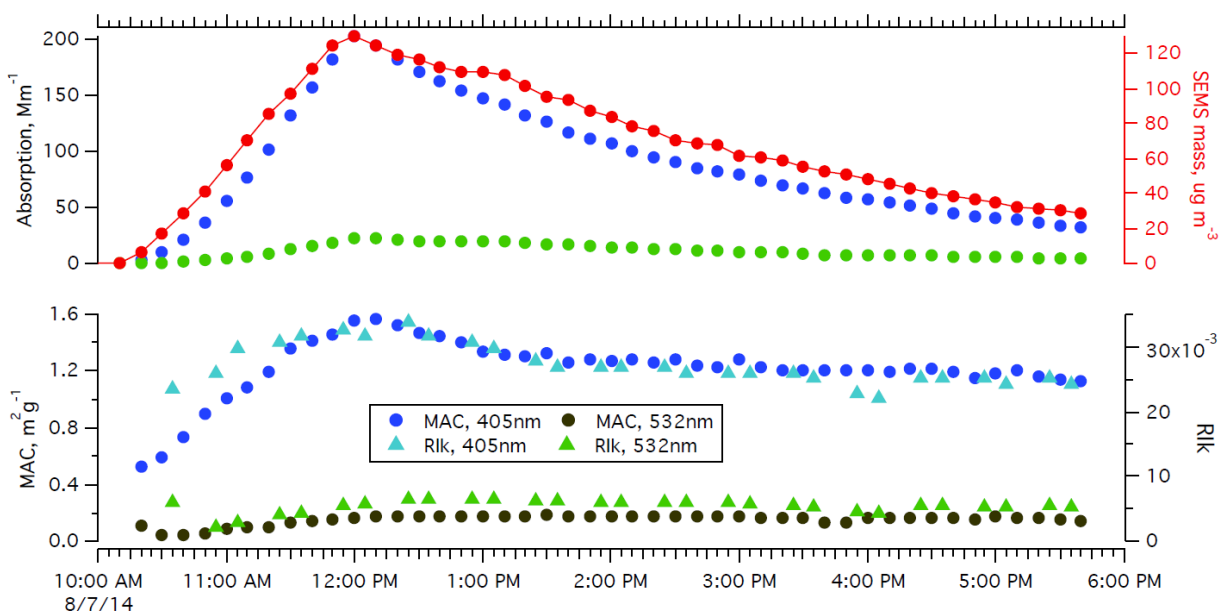


Figure S16. CRD/PAS data from the high-NO_x, high-RH, high-NH₃ study (Sample #4)

References

- (1) Calvert, J. G.; Atkinson, R.; Becker, K.; Kamens, R.; Seinfeld, J.; Wallington, T.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*; Oxford University Press: New York, 2002.
- (2) Zhang, Y.; Wang, K.; Tong, H.; Huang, R. J.; Hoffmann, T. The Maximum Carbonyl Ratio (MCR) as a New Index for the Structural Classification of Secondary Organic Aerosol Components. *Rapid Commun. Mass Spectrom.* **2021**, 35 (14), e9113. <https://doi.org/10.1002/RCM.9113>.