Supporting Information

Aqueous Photochemistry of Secondary Organic Aerosol of α-Pinene and α-Humulene in the Presence of Hydrogen Peroxide or Inorganic Salts

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Light Flux Characterization

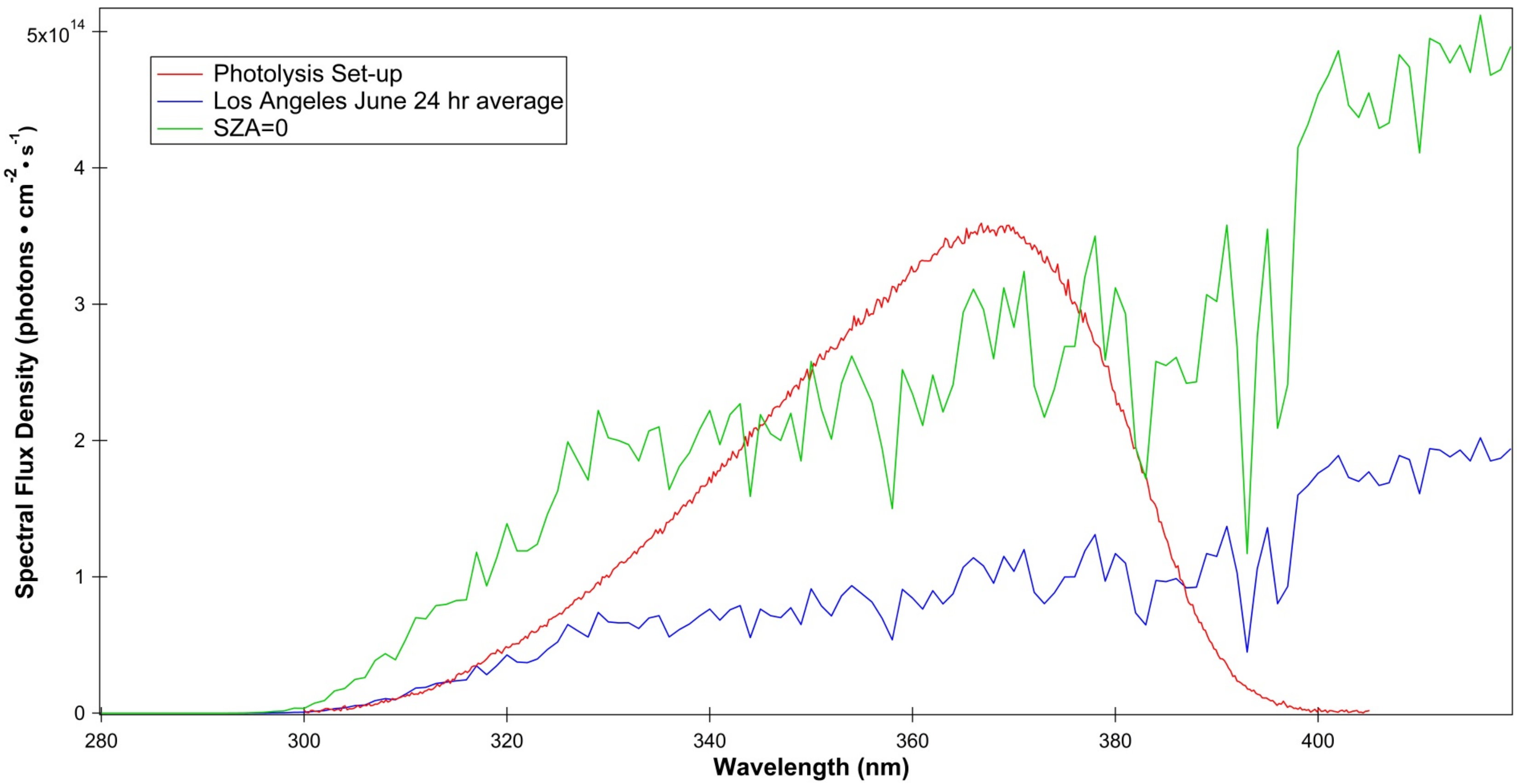

Figure S1. The spectral flux densities over the range of the electromagnetic spectrum of the photolysis set-up used in these experiments (in red), the 24-hour averaged solar spectrum in Los Angeles, California (Latitude/Longitude: 34°/118°) for the month of June (in blue), and the solar spectrum at a solar zenith angle (SZA) of zero (in green). The "Quick TUV" calculator [Madronich, S. ACOM: Quick TUV http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/ (accessed Jul 11, 2019)] was used to estimate the spectral flux densities. The parameters used for the Quick TUV calculator were:

- Latitude/Longitude: 34°N 118°W or SZA = 0

- Date and Time: June 20, 2017
- Overhead Ozone: 300 du
- Surface Albedo: 0.1
- Ground Altitude: 0 km
- Measured Altitude: 0 km
- Clouds Optical Depth/Base/Top: 0.00/4.00/5.00
- Aerosols Optical Depth/S-S Albedo/Alpha: 0.235/0.990/1.000
- Sunlight Direct Beam/Diffuse Down/Diffuse Up: 1.0/1.0/0.0
- 4 streams transfer model.

Table S1. The integrated fluxes and the number of hours equivalent to one hour under our photolysis set-up for the 24 hour average solar flux in June in Los Angeles and the maximal achievable flux at the SZA = 0. The calculation was performed by integrating the flux in Figure S1 for the three UV wavelength ranges that may potentially drive photochemistry. The values on the last two columns represent the ratios of UV lamp's integrated flux to the solar integrated flux.

Wavelength range of comparison	Integrated flux from the UV lamp (photons cm^{-2} s^{-1})	Integrated flux from the 24-average sunlight in Los Angeles (photons cm^{-2} s^{-1})	Integrated flux from the sun at SZA=0 (photons cm^{-2} s^{-1})	One hour under lamp is equivalent to hours under 24-average sunlight in Los Angeles:	One hour under lamp is equivalent to hours under SAZ=0 sunlight
UVB (280 – 315 nm)	1.46E14	1.72E14	6.86E14	0.85	0.22
UVB + UVA 2 (280 – 340 nm)	2.40E15	1.54E15	4.83E15	1.56	0.50
Full UV (280 – 400 nm)	1.54E16	7.24E15	2.03E16	2.13	0.76

OH Steady State Concentration Calculation

Approximate OH steady state concentrations ($[OH]_{SS}$) resulting from photolysis of H_2O_2 and NO_3^- under irradiated conditions were calculated from the measured radiation flux and known absorption cross sections and quantum yields of photolysis. First, the rate constants for OH production were found using the following equation:[1]

$$J_x = \int 2.303 \times 10^3 \times F_\lambda \times \varepsilon_{x,\lambda} \times \phi_{OH,\lambda} d\lambda \quad (x = NO_3^- \text{ or } H_2O_2)$$

where F_λ represents the surface area normalized photon flux (mol-photon $cm^{-2}s^{-1}nm^{-1}$) with values shown in Figure S1, $\varepsilon_{x,\lambda}$ is the base-10 molar absorptivity coefficient for x ($M^{-1}s^{-1}$), and $\phi_{OH,\lambda}$ is the OH quantum yield. Values for $\varepsilon_{x,\lambda}$ and $\phi_{OH,\lambda}$ were retrieved from the literature.[2–5] Calculated *J* values can be found in Table S2. Next, OH formation rates were calculated by multiplying the production rate constant by the concentration of x to give k_x. Finally, $[OH]_{SS}$ was found by multiplying the OH production rate by the OH lifetime (τ), where τ can be found via the following equation:

$$\tau = (k_{SOA}[SOA] + k_{H_2O_2}[H_2O_2])^{-1}$$

In the case of nitrate photolysis, the H_2O_2 term will go to zero. We assumed the reaction of OH with SOA to be diffusion limited, and so used 1×10^{10} $M^{-1}s^{-1}$ for k_{SOA}. The rate constant for OH reaction with H_2O_2 is 2.7×10^7 $M^{-1}s^{-1}$.[6] SOA concentrations were estimated using the average molar mass for each condition. The final $[OH]_{SS}$ are shown in Table S2 below. They are too small to compete with direct photolysis under our experimental conditions.

Table S2. Values of interest for OH steady state concentration calculation.

SOA System	J_x (s^{-1})	R_{OH} formation ($M\ s^{-1}$)	[SOA] (mM)	τ (s)	Theoretical $[OH]_{SS}$ (M)
APIN + H_2O_2	1.8×10^{-6}	1.8×10^{-11}	0.66	1.5×10^{-7}	2.7×10^{-18}
APIN + $NaNO_3$	1.3×10^{-7}	2.0×10^{-11}	0.76	1.3×10^{-7}	2.7×10^{-18}
APIN + NH_4NO_3	1.3×10^{-7}	2.0×10^{-11}	0.77	1.3×10^{-7}	2.6×10^{-18}
HUM + H_2O_2	1.8×10^{-6}	1.8×10^{-11}	0.30	3.7×10^{-7}	6.0×10^{-18}
HUM + $NaNO_3$	1.3×10^{-7}	2.0×10^{-11}	0.28	3.5×10^{-7}	7.0×10^{-18}
HUM + NH_4NO_3	1.3×10^{-7}	2.0×10^{-11}	0.28	3.5×10^{-7}	7.0×10^{-18}

HUM SOA Extraction Efficiency

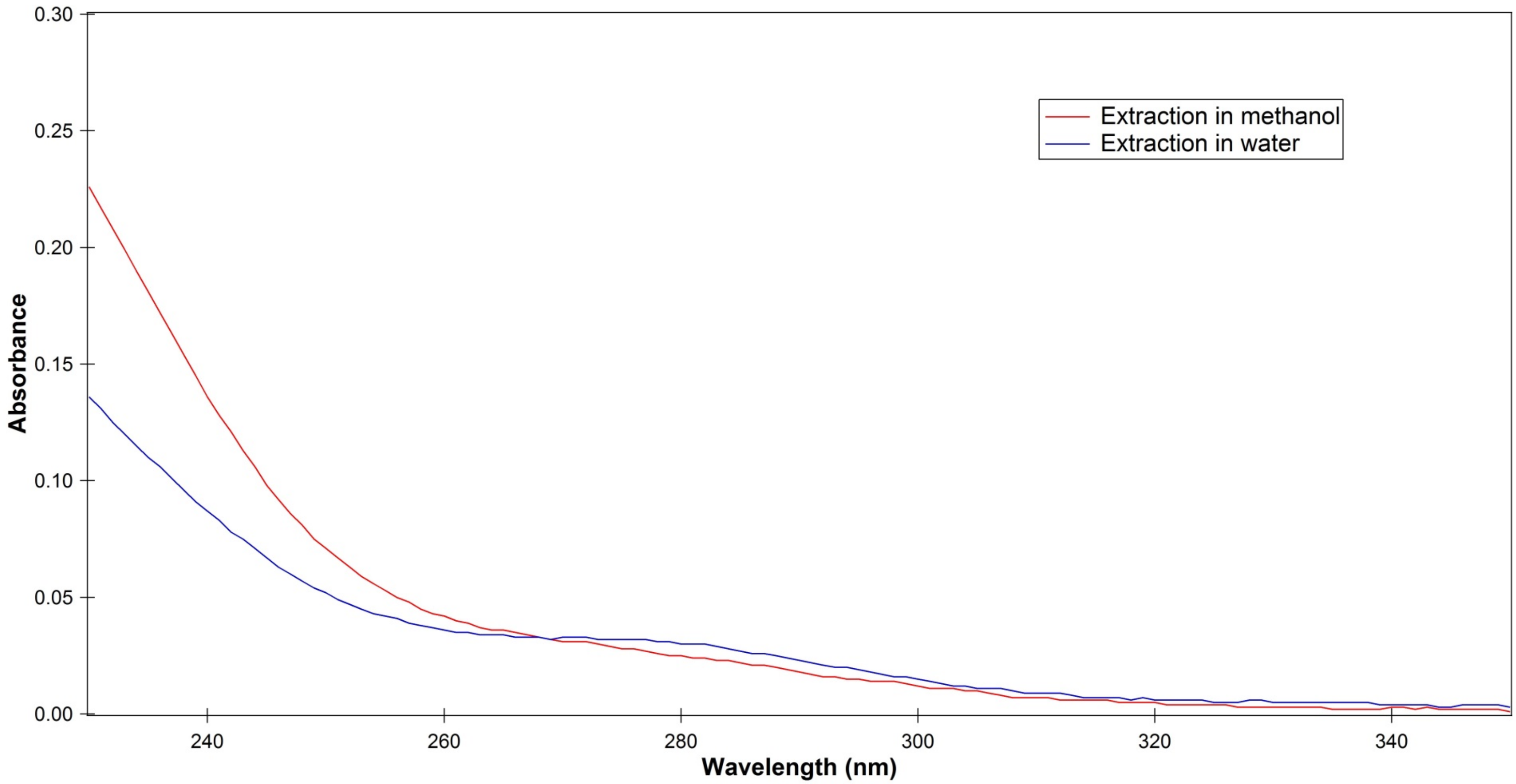

Figure S2. A test for the extraction efficiency of HUM SOA in water. A filter with HUM SOA was first sonicated in 10 mL water for 10 min and an absorbance spectrum of the extract taken. Then the filter was removed from water and sonicated in 10 mL of methanol for 10 min. Based on the comparison of integrated absorbance over the 230-350 nm range, we estimate that approximately 40% of the SOA was dissolved in water, and the rest dissolved in methanol. This is to be contrasted with dissolution of APIN SOA, for which the initial water extraction dissolved more than 90% of the material based on the study of Updyke et al.[7] (2012, see supporting information Figure # S3).

Mass Spectra Results

Mass spectra are shown for α-pinene (APIN) and α-humulene (HUM) SOA formed via ozonolysis and aged in four different aqueous systems (nanopure water, water containing H_2O_2, water containing $NaNO_3$, or water containing NH_4NO_3) and in the dark or with photolysis. Panels in the figures are organized into 0, 1, 2, 3, and 4 hours with photolysis on the top, and 0, 1, 2, 3, and 4 hours in the dark on the bottom. Nitrogen-containing peaks are shown in red.

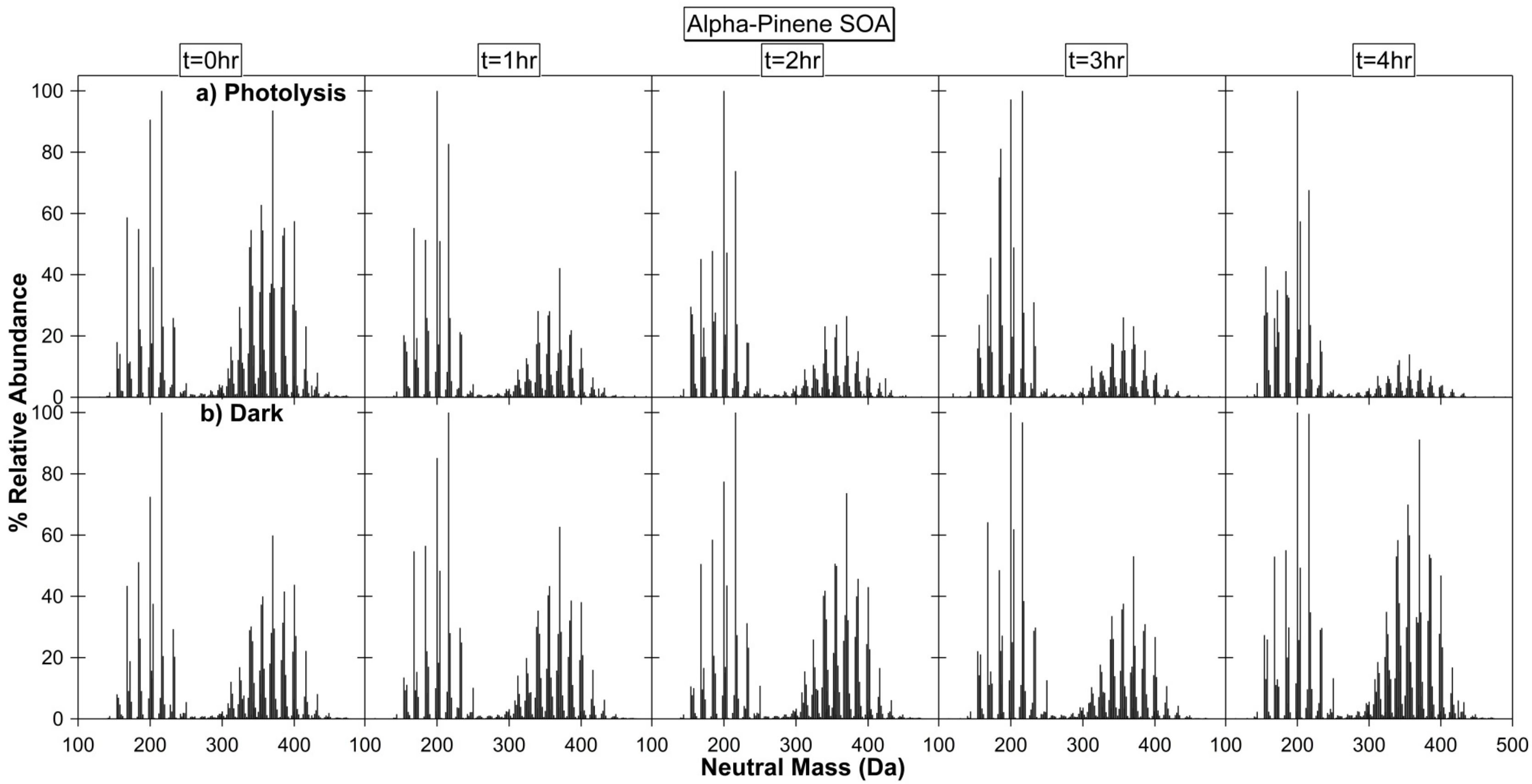

Figure S3. Mass spectra for the APIN SOA aged in nanopure water. Panel (a) shows aging with photolysis and panel (b) shows dark aging.

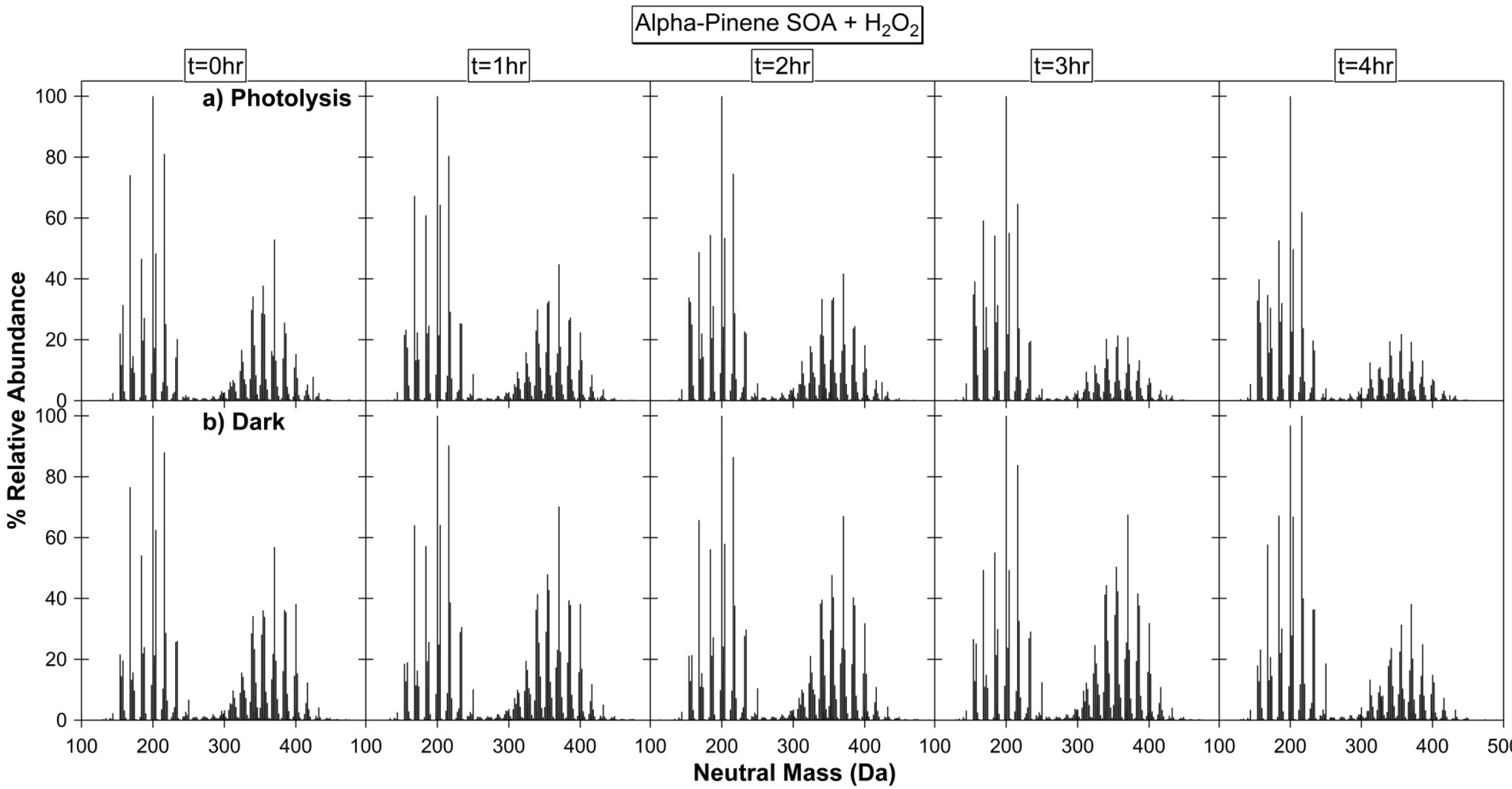

Figure S4. Mass spectra for the APIN SOA aged with 0.01 mM H_2O_2. Panel (a) shows aging with photolysis and panel (b) shows dark aging.

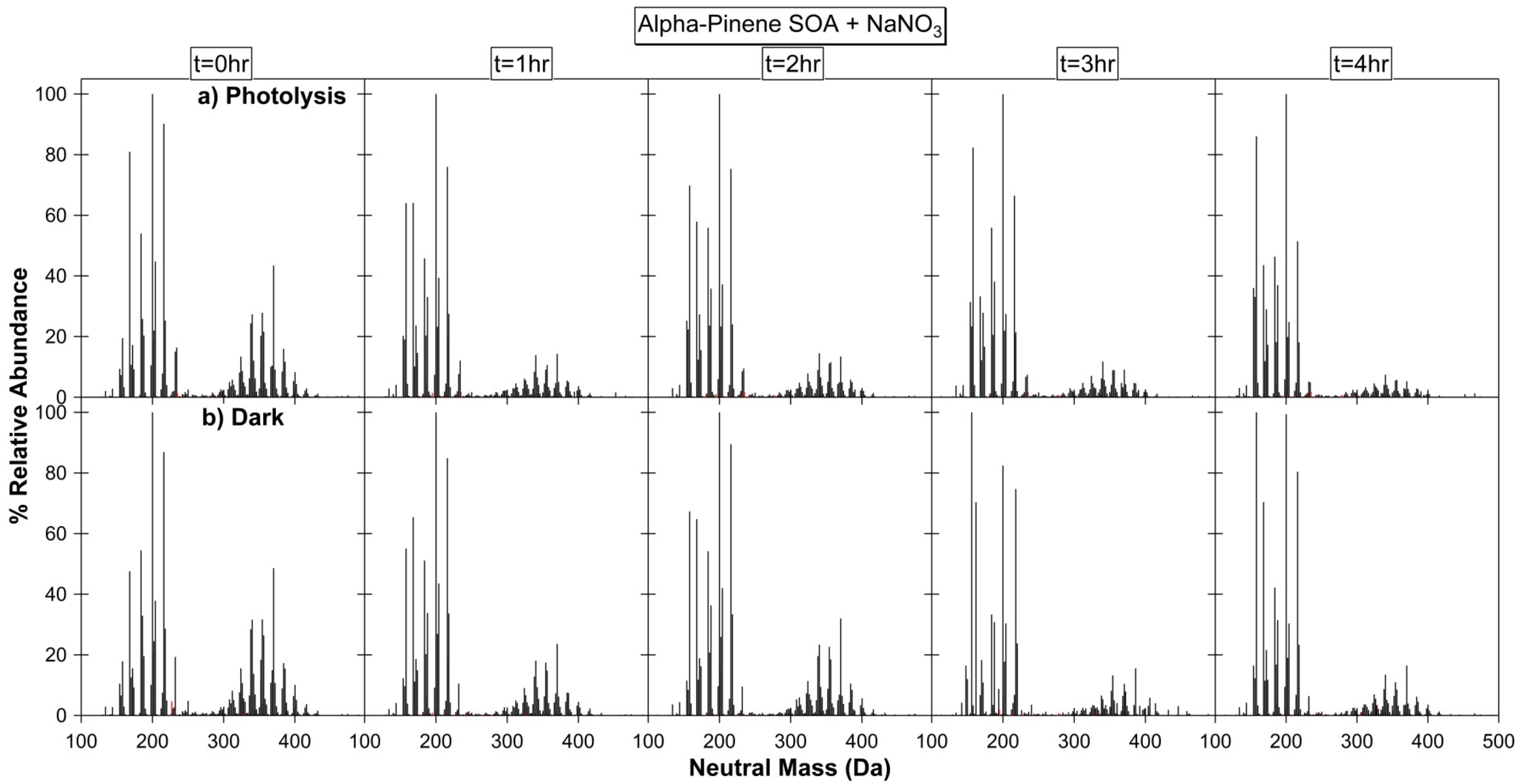

Figure S5. Mass spectra for the APIN SOA aged with 0.15 mM $NaNO_3$. Panel (a) shows aging with photolysis and panel (b) shows dark aging.

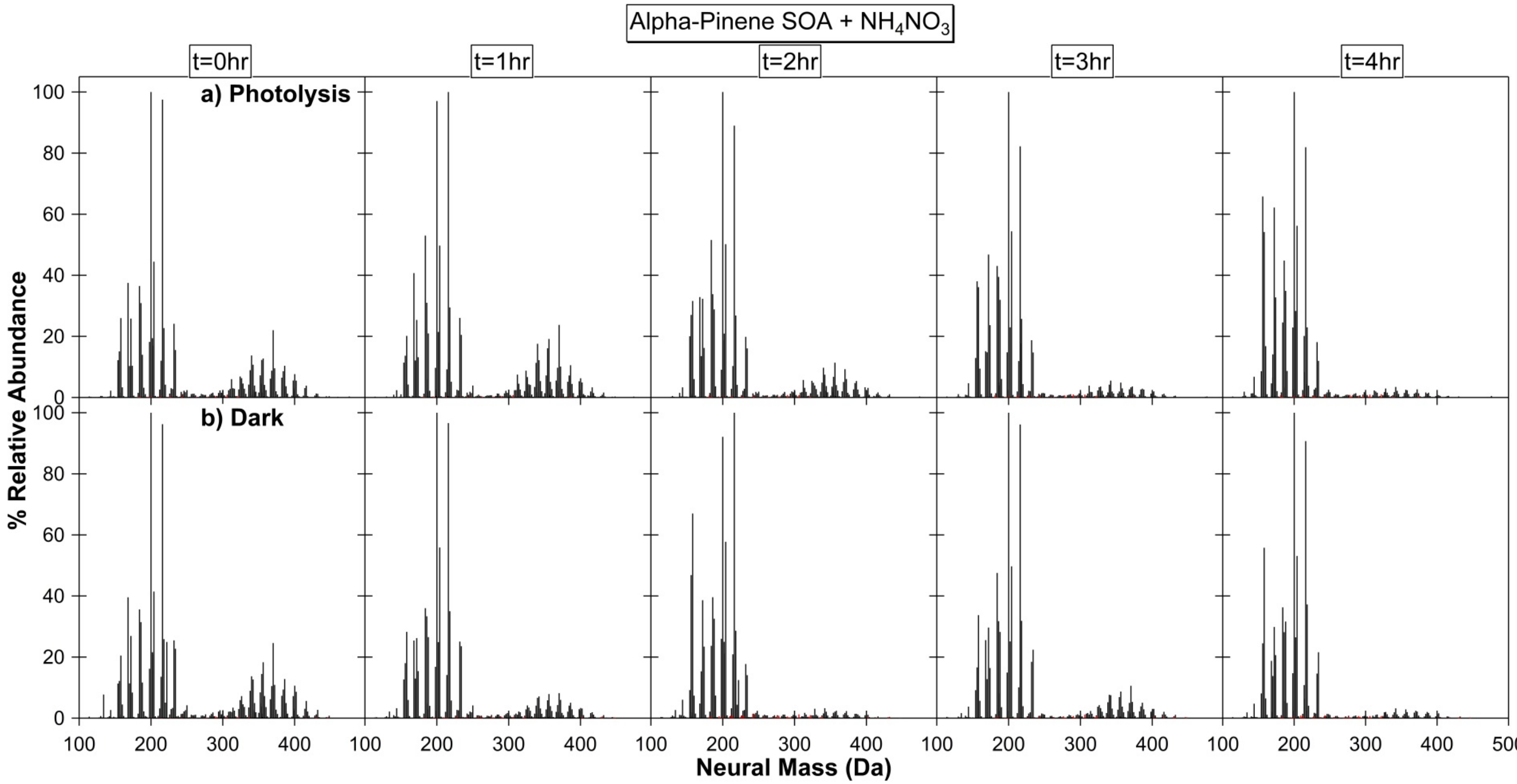

Figure S6. Mass spectra for the APIN SOA aged with 0.15 mM NH_4NO_3. Panel (a) shows aging with photolysis and panel (b) shows dark aging.

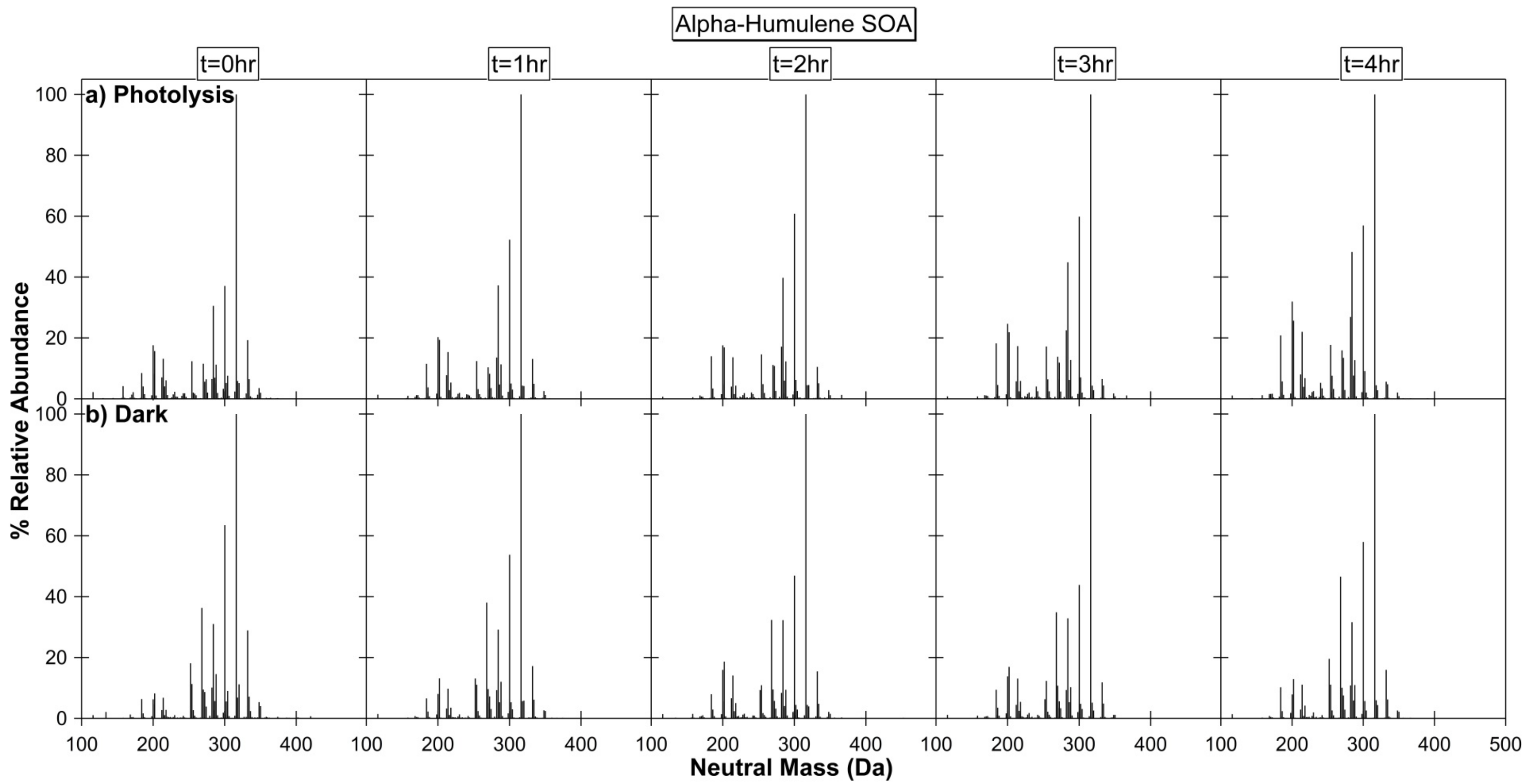

Figure S7. Mass spectra for the HUM SOA aged in nanopure water. Panel (a) shows aging with photolysis and panel (b) shows dark aging.

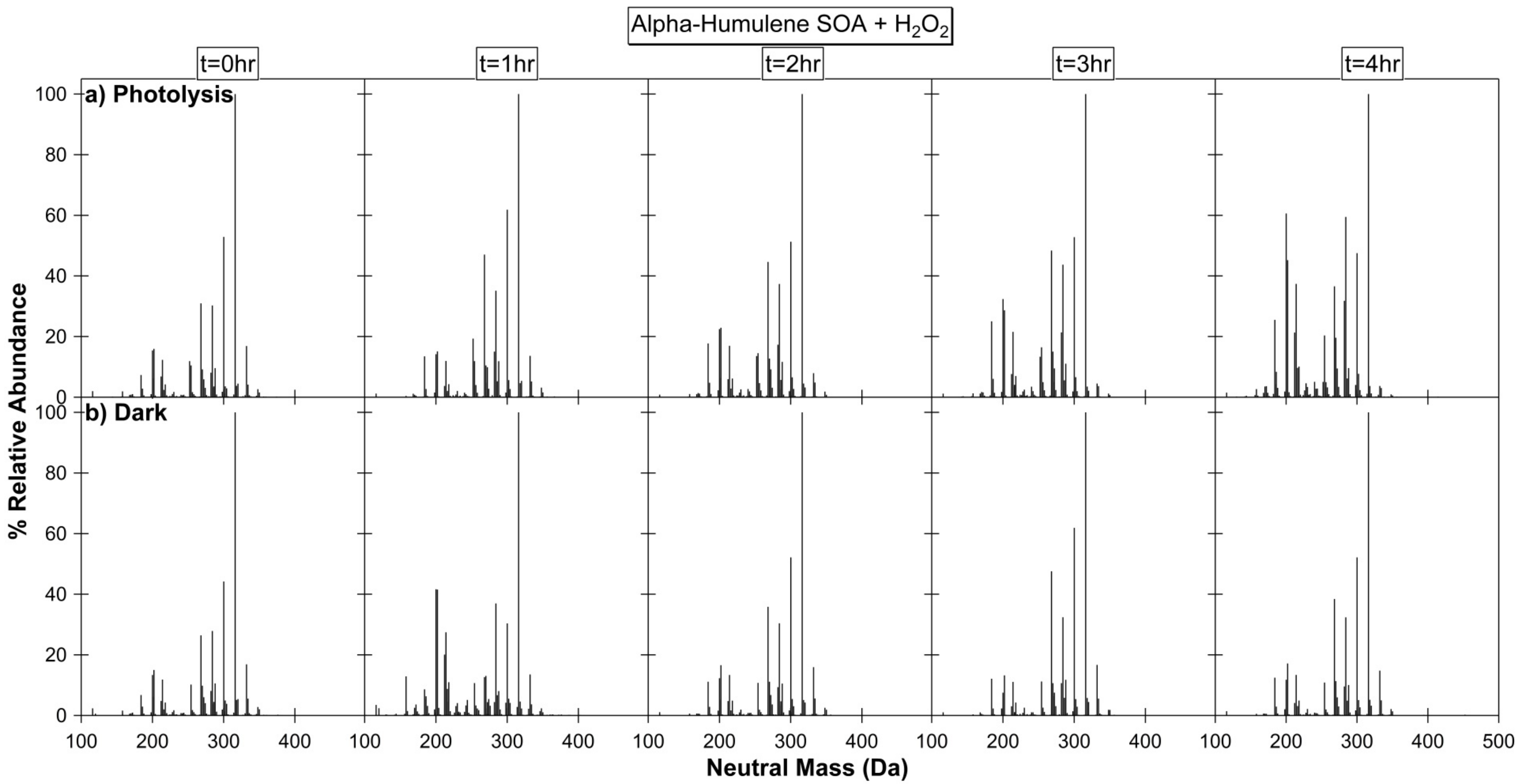

Figure S8. Mass spectra for the HUM SOA aged with 0.01 mM H_2O_2. Panel (a) shows aging with photolysis and panel (b) shows dark aging.

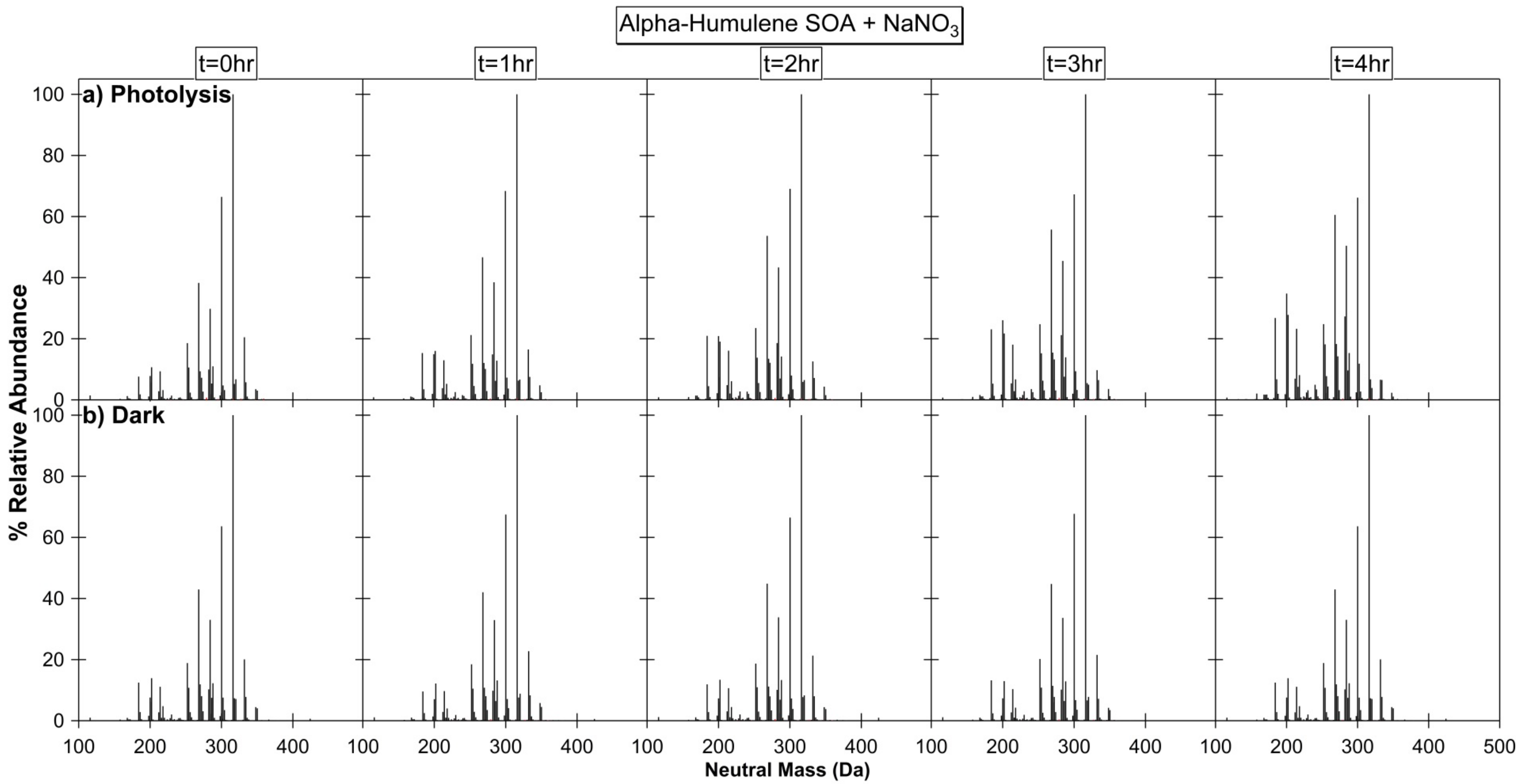

Figure S9. Mass spectra for the HUM SOA aged with 0.15 mM $NaNO_3$. Panel (a) shows aging with photolysis and panel (b) shows dark aging.

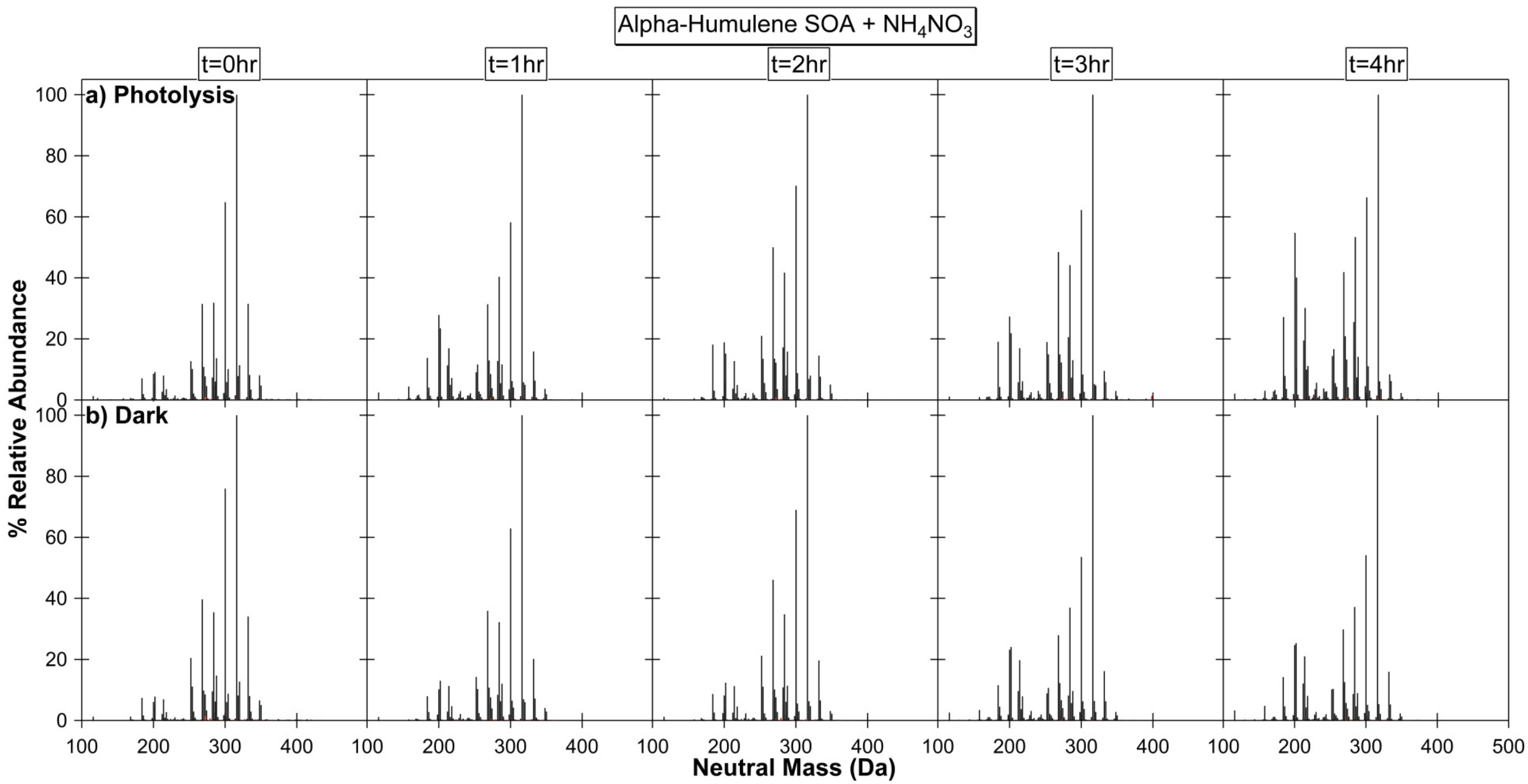

Figure S10. Mass spectra for the HUM SOA aged with 0.15 mM NH_4NO_3. Panel (a) shows aging with photolysis and panel (b) shows dark aging.

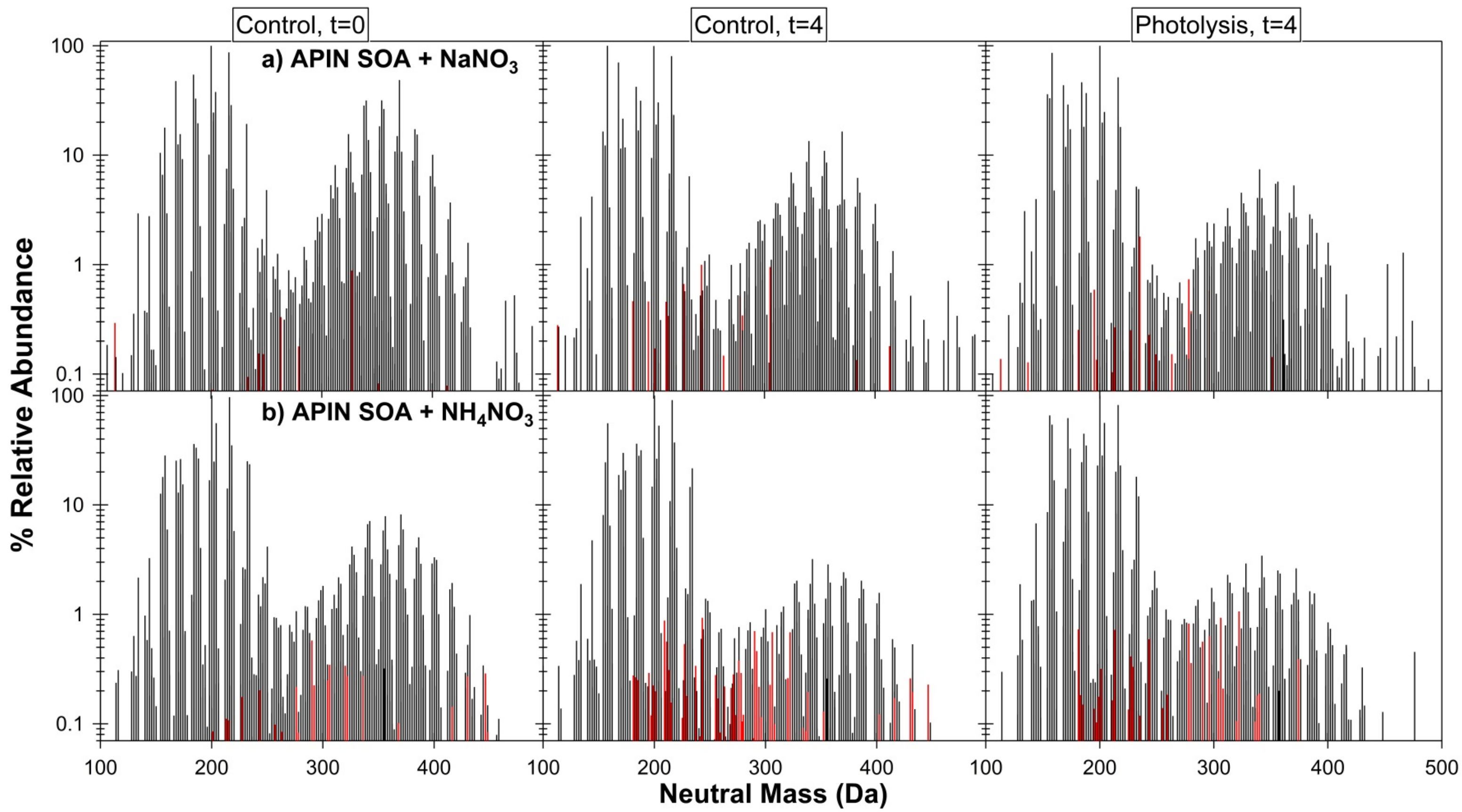

Figure S11. Mass spectra for APIN SOA aged with 0.15 mM $NaNO_3$ (a) and 0.15 mM NH_4NO_3 (b) plotted on a log scale to show NOC peaks more clearly.

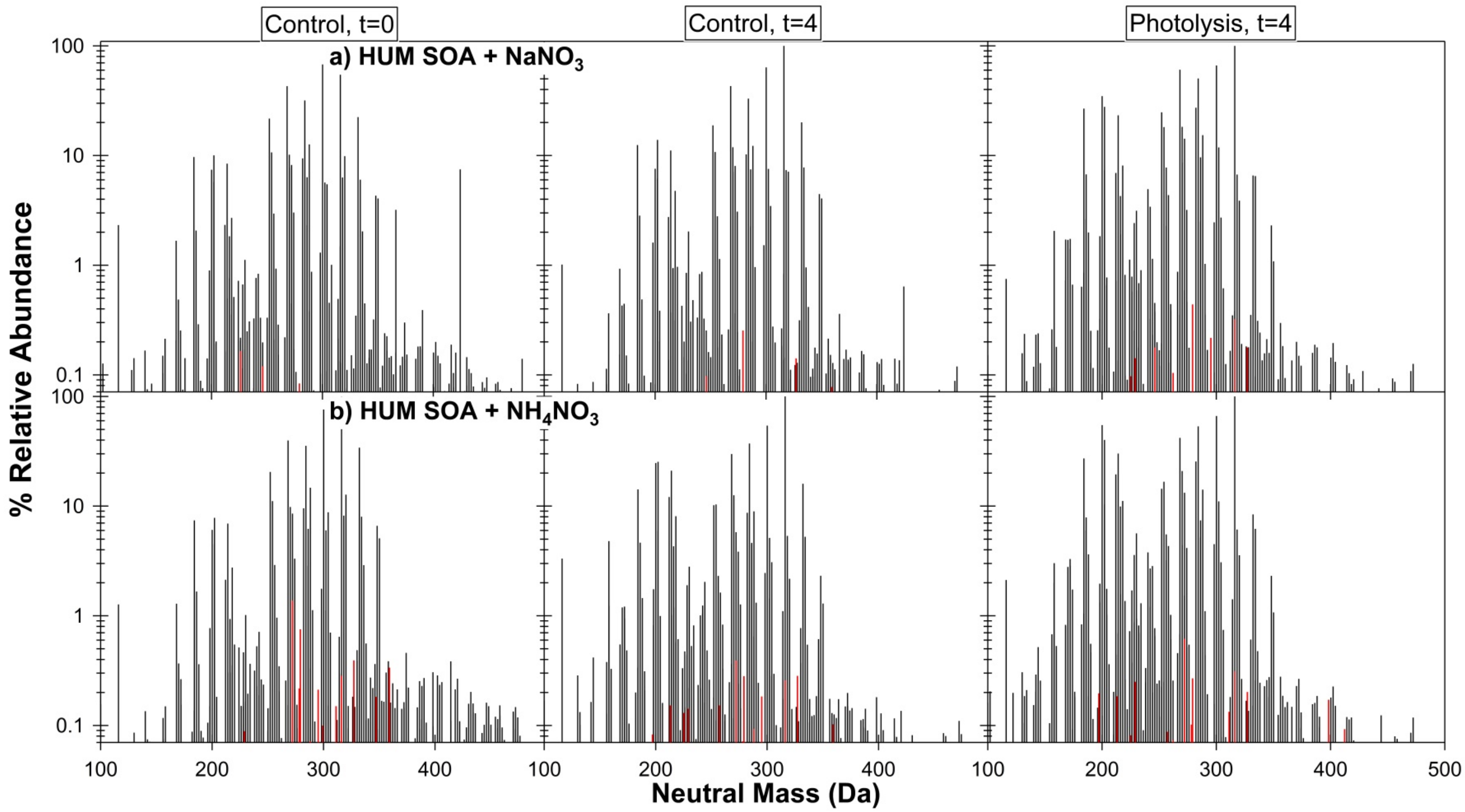

Figure S12. Mass spectra for HUM SOA aged with 0.15 mM $NaNO_3$ (a) and 0.15 mM NH_4NO_3 (b) plotted on a log scale to show NOC peaks more clearly.

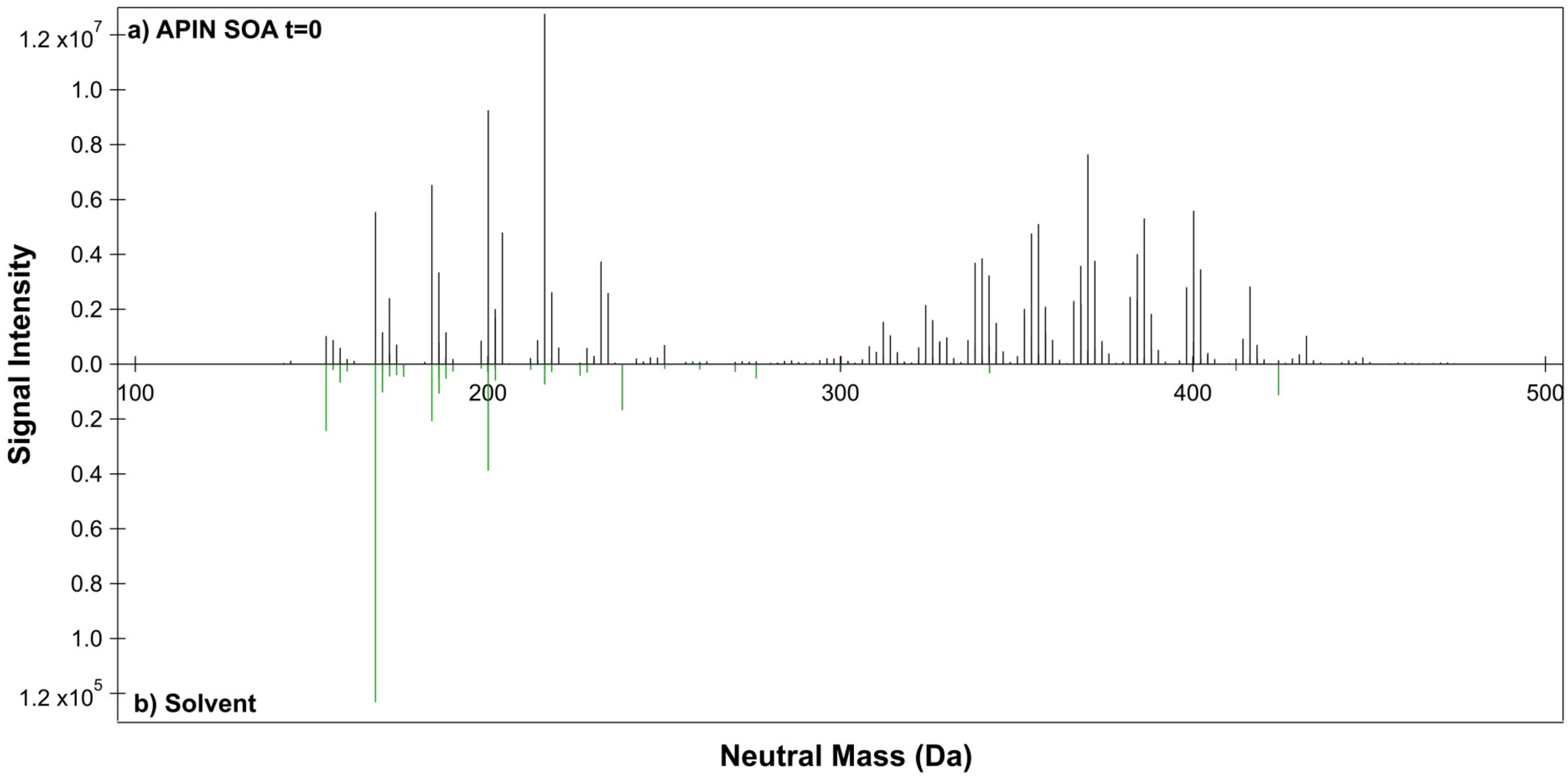

Figure S13. A comparison of a representative solvent and sample spectra. Panel a) shows the un-normalized sample spectrum for APIN SOA at t=0 before aging in pure water. Panel b) shows the solvent spectrum on the day the spectrum in panel a) was collected. Note that the scale on the solvent spectrum is two orders of magnitude smaller than that of the sample so that the solvent peaks would be visible.

References

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