Supporting Information

Photodegradation of Secondary Organic Aerosols by Long-Term Exposure to Solar Actinic Radiation

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QCM Experiments Summary

Table S1: C_f is the QCM sensitivity factor determined for every sample by dividing the frequency reduction of the loaded crystal by the SOA mass on the crystal. In the experimental conditions column, "dry-long term" means hours or days of exposure of SOA to UV radiation under dry conditions, an RH value means shorter term exposure to quantify the initial photodegradation rate in humidified air, and control means irradiation under 405 nm LED.

SOA Type	Wavelength of the irradiation source (nm)	Mass on Crystal after Annealing (µg)	C_f (Hz/µg)	Experimental Conditions	Maximum FMLR (h^{-1})
LIM/O$_3$	305	2337	21.60	Dry Long-term	0.031
LIM/O$_3$	305	1729	12.33	Dry Long-term	0.034
LIM/O$_3$	305	1319	12.12	Dry Long-term	0.036
LIM/O$_3$	305	457	14.28	Dry Short-term	0.014
LIM/O$_3$	305	452	14.34	42% RH	0.026
LIM/O$_3$	305	858	10.41	60% RH	0.043
LIM/O$_3$	305	556	13.74	78% RH	0.054
LIM/O$_3$	305	1712	12.35	Long-term 63% RH	0.050
APIN/O$_3$	305	856	10.18	Dry Long-term	0.055
APIN/O$_3$	305	1373	10.85	Dry Short-term	0.027
APIN/O$_3$	305	1466	13.57	42% RH	0.053
APIN/O$_3$	305	1473	12.52	62% RH	0.062
APIN/O$_3$	405	1365	13.28	Dry Control	n/a
APIN/O$_3$	Dark	1934	10.61	Dark Control	n/a
APIN/O$_3$	254	3429	13.56	Dry Long-term	0.933
TOL/OH	254	53	13.89	Dry Long-term	0.368
TOL/OH	305	185	10.83	Dry Long-term	0.008
TOL/OH/NO$_x$	305	194	24.21	Dry Long-term	0.020

Correction for Dark Evaporation

The correction for the spontaneous dark evaporation competing with photodegradation is not trivial since the chemical composition of the SOA material is changing with time. However, it can be done with a simplifying assumption of a time-invariant evaporation rate constant (k_{evap}). This assumption is consistent with our observations of slow first-order mass loss in control experiments shown in Figure S1.

We assume that the Fractional Mass Loss Rate (*FMLR*) obeys the first-order kinetics with the time-invariant evaporation rate constant k_{evap} and time-dependent photodegradation rate constant *J(t)*:

$$FMLR_{total}(t) = -\frac{1}{m}\frac{dm}{dt} = k_{evap} + J(t)$$

The subscript "total" refers to the fact that both UV irradiation and evaporation contribute to the mass loss. Based on the above equation, *FMLR* can be corrected for evaporation by directly subtracting results of a dark experiment from results of an irradiated experiment done on an identical sample:

$$FMLR_{UV}(t) = J(t) = FMLR_{total}(t) - FMLR_{dark}(t) = FMLR_{total}(t) - k_{evap}$$

The value of k_{evap} can be determined from a separate experiment (e.g., Figure S1) or from the short segment of the data collected before the irradiation started.

Percent Mass Loss (*PML*) is related to *FMLR(t)* as follows:

$$-\int \frac{dm}{m} = \int FMLR(t)dt$$

$$m(t) = m_0 \times exp\left[-\int_0^t FMLR(t)dt\right]$$

$$PML(t) = 100 \times \frac{m_0 - m(t)}{m_0} = 100 \times \left[1 - exp\left[-\int_0^t FMLR(t)dt\right]\right]$$

Since we assume that k_{evap} is constant, the equation for time-dependent mass becomes:

$$m(t) = m_0 \times exp[-k_{evap} \times t] \times exp\left[-\int_0^t J(t)dt\right]$$

PML under the conditions of both UV irradiation and evaporation, just UV irradiation and just evaporation are, respectively:

$$PML_{total}(t) = 100 \times \left[1 - exp[-k_{evap} \times t] \times exp\left[-\int_0^t J(t)dt\right]\right]$$

$$PML_{UV}(t) = 100 \times \left[1 - exp\left[-\int_0^t J(t)dt\right]\right]$$

$$PML_{dark}(t) = 100 \times \left[1 - exp[-k_{evap} \times t]\right]$$

By combining the three equations for *PML* above, we arrive at the following method for getting corrected PML_{UV} from the uncorrected PML_{total}:

$$PML_{UV}(t) = \frac{PML_{total}(t) - 100 \times \left[1 - exp\left[-k_{evap} \times t\right]\right]}{e^{-k_{evap} \times t}}$$

Based on the considerations and equations above, we have corrected for the effects of evaporation by following these steps:

1. We calculated mass as a function of time, $m(t)$, directly from the QCM frequency data, which gave us $PML_{total}(t)$ directly.

$$PML_{total}(t) = 100 \times \frac{m_0 - m(t)}{m_0}$$

2. We calculated $FMLR_{total}(t)$ from the QCM data for the irradiated system with evaporation occurring inn parallel. This represents uncorrected data shown in Figures 2, 3 and 4 of the manuscript and Figures S1 and S3 of the Supporting information section.

3. We fitted the dark segments of the data collected before the irradiation started to obtain the evaporation rate constant k_{evap}. Since the evaporation process is slow, we used a linear fit as follows:

$$PML_{dark}(t) = 100 \times \left[1 - exp\left[-k_{evap} \times t\right]\right] \approx 100 \times k_{evap} \times t$$

The k_{evap} values determined for this study were:

SOA Type	k_{evap} (h^{-1})
APIN/O$_3$	5.55 x 10^{-4}
LIM/O$_3$	3.74 x 10^{-4}
TOL/OH/NO$_x$	7.52 x 10^{-4}
TOL/OH	2.41 x 10^{-4}

4. With the values of k_{evap} determined, we corrected *FMLR* using the following equation. Corrected results are shown in Figures 2 and 4 of the manuscript.

$$FMLR_{UV}(t) = FMLR_{total}(t) - k_{evap}$$

5. Finally, we corrected *PML* using the following equation. Corrected results are shown in Figures 2 and 4 of the manuscript.

$$PML_{UV}(t) = \frac{PML_{total}(t) - 100 \times \left[1 - exp\left[-k_{evap} \times t\right]\right]}{e^{-k_{evap} \times t}}$$

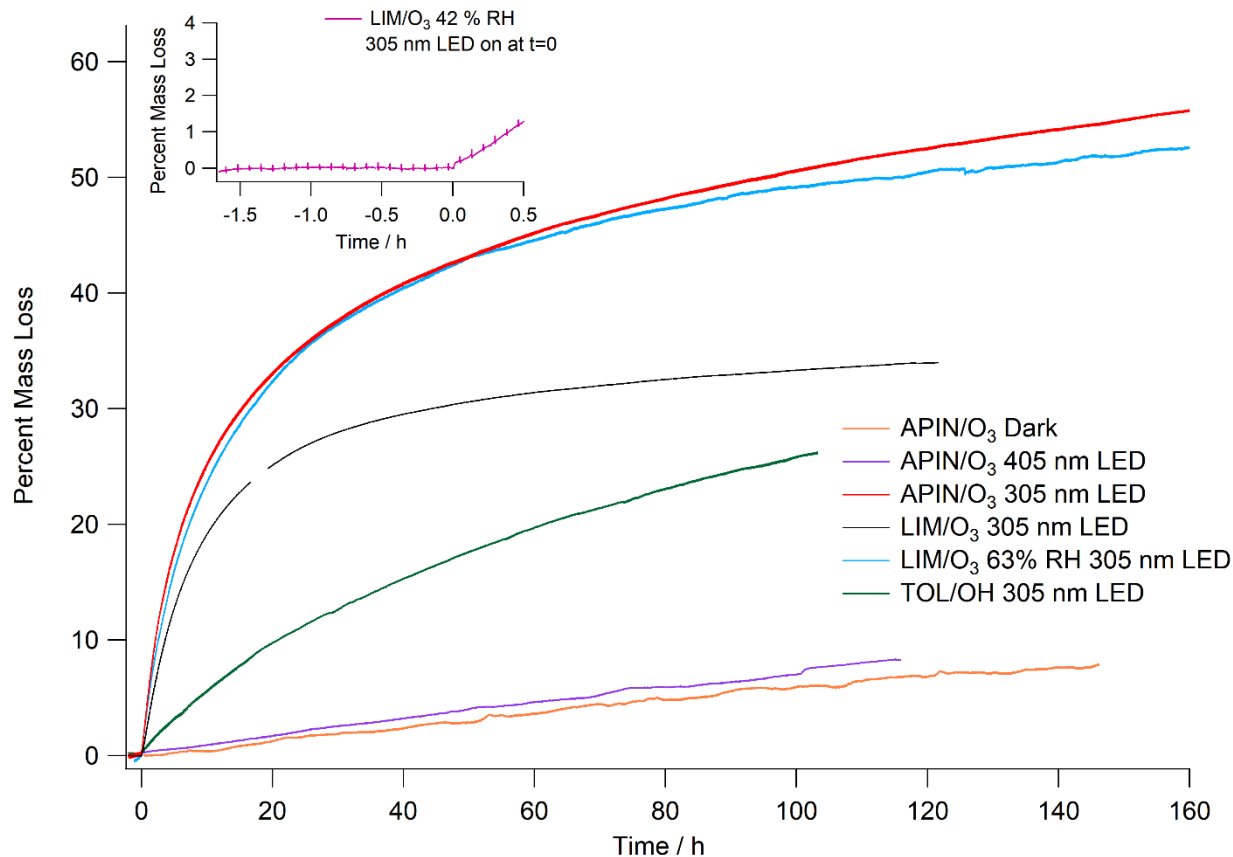# Control Experiments & Long Term LIM/O$_3$ Degradation under Humid Conditions

Figure S1: Control experiments showed that mass loss under both dark and under 405 nm LED irradiation conditions were similar and smaller compared to the mass loss due to photodegradation. APIN/O$_3$ (highest mass loss) and TOL/OH (lowest mass loss) SOA trials are shown for comparison to the control experiments. The inset shows LIM/O$_3$ SOA under 42 % RH has a minimal percent mass loss compared to when the LED is turned on at the zero-hour mark. The data shown here are not yet corrected for evaporative loss and represent a combination of evaporation and degradation effects (*PML$_{total}$*).

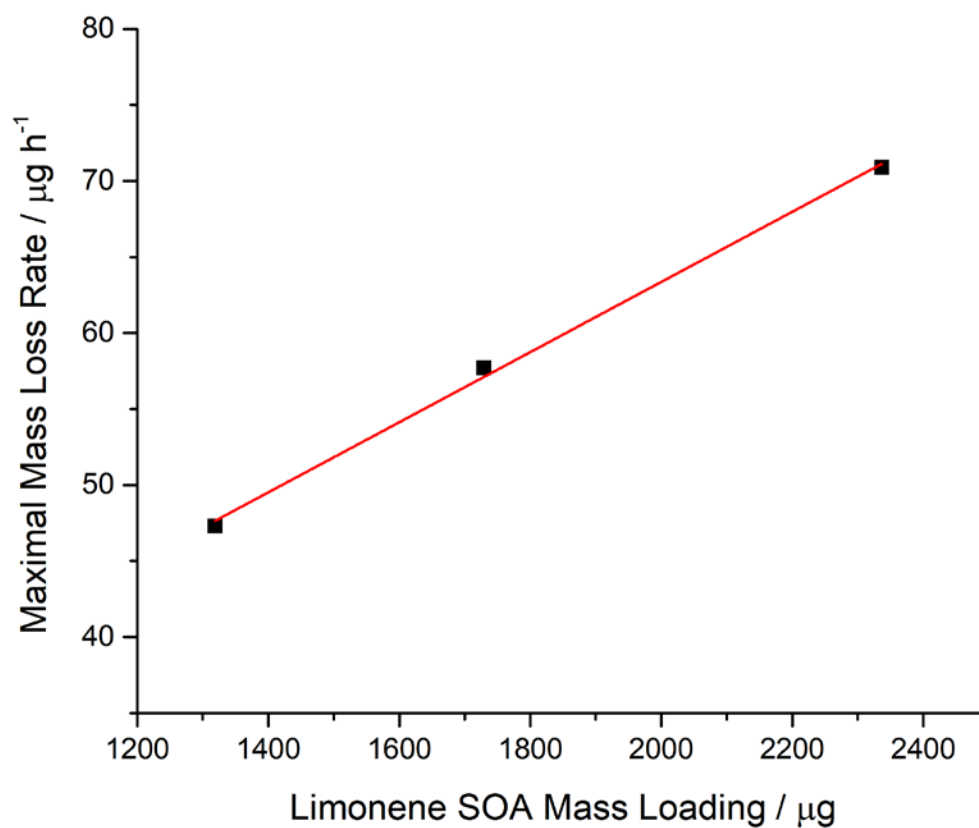# Dependance of the Mass Loss Rate on the QCM Loading

Figure S2: The maximum mass loss rate from the QCM measurement scaled linearly with the mass of SOA deposited on the QCM crystal during 305 nm irradiation experiments with LIM/O_3 SOA. This made it possible to normalize the mass loss rate by the mass loading on the crystal to calculate the fractional mass loss rate (*FMLR*).

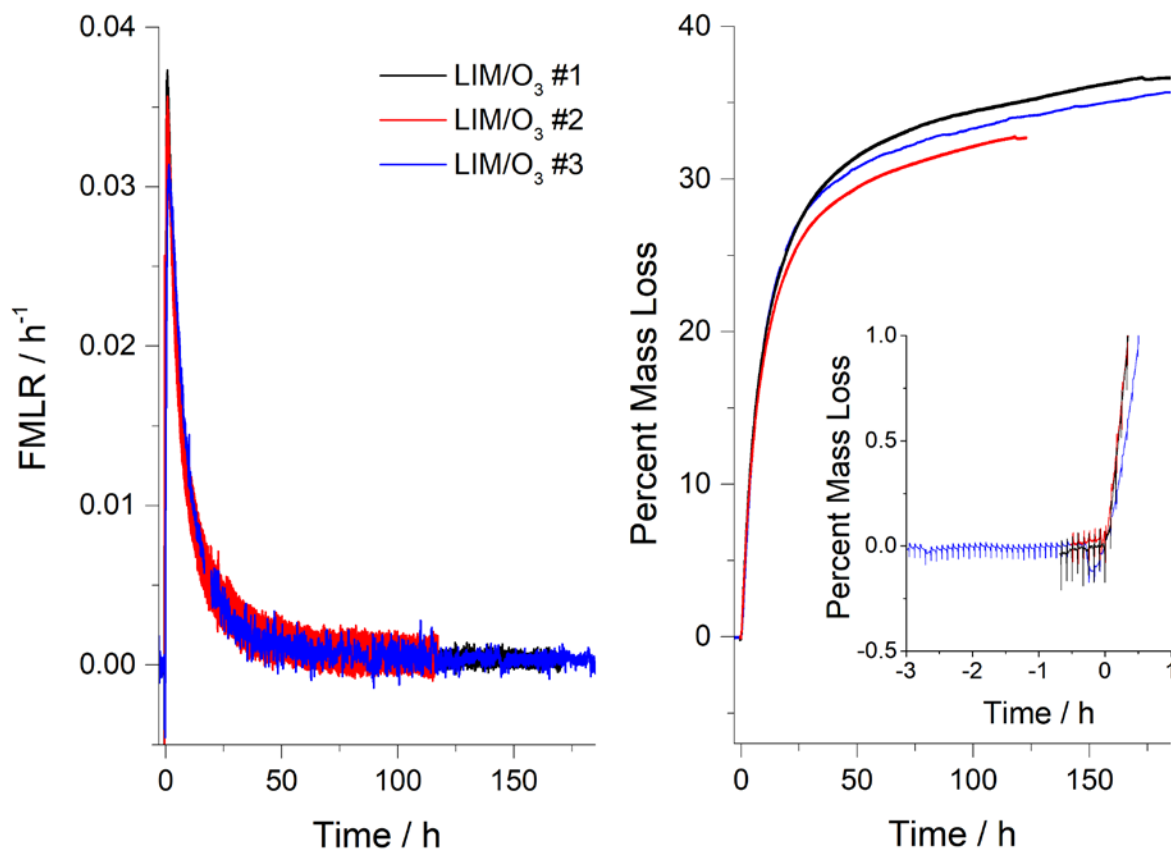# Assessing Reproducibility for Limonene Ozonolysis SOA Samples

Figure S3: Repeated experiments with LIM/O₃ SOA samples photodegraded under 305 nm LED radiation. The three samples had different mass loadings resulting in different absolute mass loss rates, but normalization to the mass loading resulted in similar FMLR values and time dependence. The inset zooms on the date at negative times (before the LED was turned on) and shows that the mass loss due to evaporation was minimal compared to the effects of irradiation. Periodic spikes in the data were due to the clean air generator periodic purges. The data shown here are not yet corrected for evaporative loss and represent a combination of evaporation and degradation effects (*FMRL*$_{total}$ and *PML*$_{total}$).

Spectral Flux Density in Los Angeles

We used the following parameters from the Quick TUV calculator mentioned in the main text:

• Latitude/Longitude: 34°/-118°

• Date and Time: June 20, 2017 – data from each hour in the day were acquired and averaged to obtain a *24-hour average* spectral flux density

Or 19:00:00 GMT, representative of the summer solstice maximum

• 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: 1.0/1.0/1.0
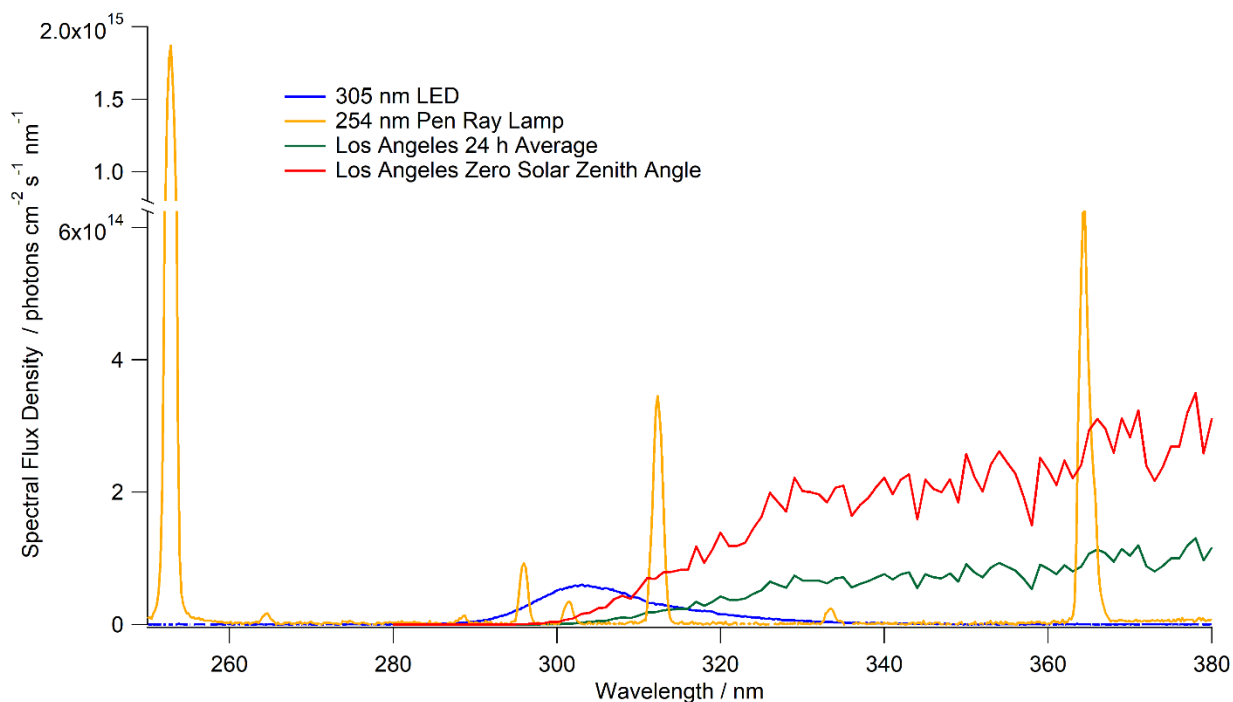
• 4 streams transfer model.

Figure S4: Spectral flux density of the M300L4 305 nm LED, Spectroline 11SC-1 Pen Ray Lamp, Los Angeles summer solstice maximum, and the 24-hour average Los Angeles solar flux. Los Angeles spectral flux densities were obtained using the TUV model.[1]

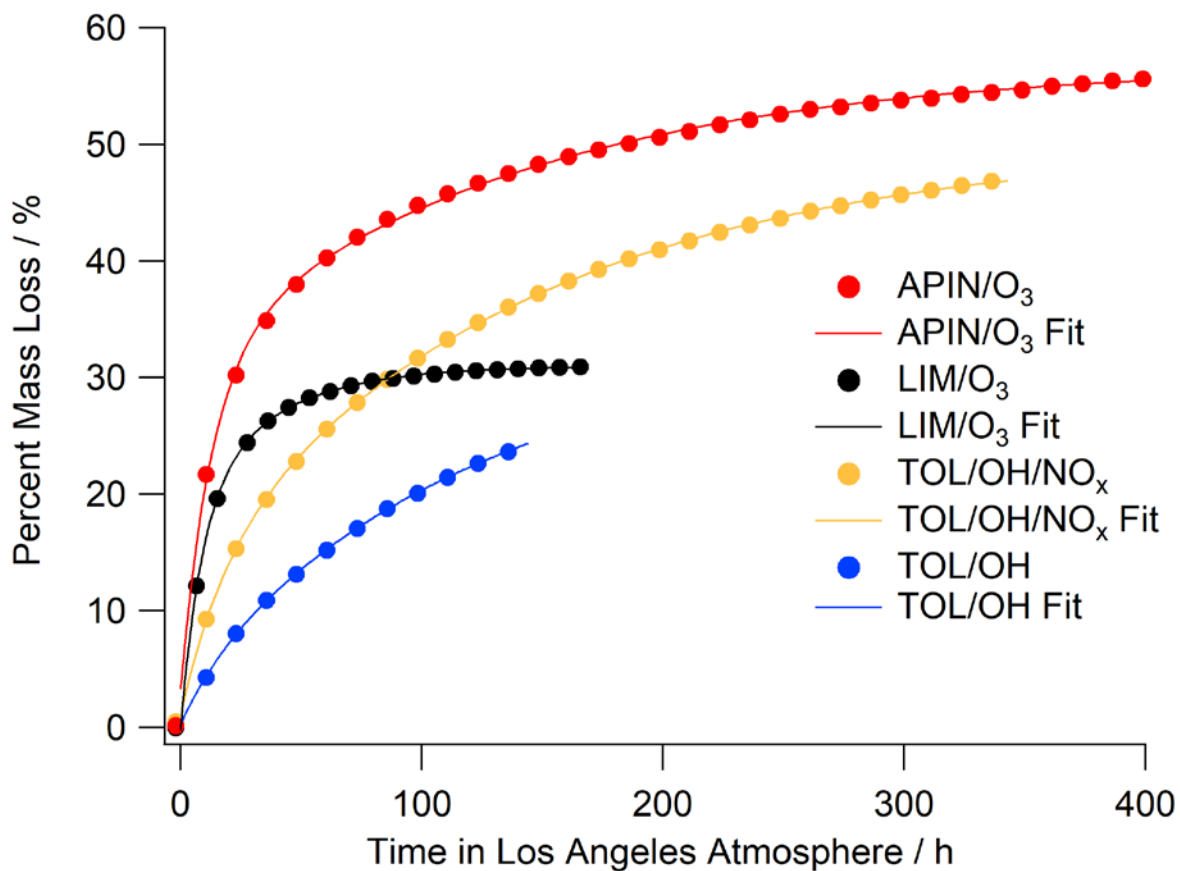**Fitting Percent Mass Loss Scaled to 24 -Hour Average Los Angeles Flux**

Figure S5: The UV degradation percent mass loss profiles (PML$_{UV}$) were scaled to the 24 hour average Los Angeles flux (J_{NO2} = 4.05 x 10^{-3} s^{-1}) and fit to a bi-exponential function.

$$y = y_0 + A_1 e^{\frac{-x}{\tau_1}} + A_2 e^{\frac{-x}{\tau_2}}$$

SOA Type	$y_0 \pm$ 95% CI	$A_1 \pm$ 95% CI	$\tau_1 \pm$ 95% CI	$A_2 \pm$ 95% CI	$\tau_2 \pm$ 95% CI
APIN/O$_3$	56.884 ± 0.003	-28.292 ± 0.008	12.876 ± 0.008	-25.357 ± 0.005	138.59 ± 0.06
LIM/O$_3$	30.976 ± 0.006	-18.556 ± 0.080	8.571 ± 0.041	-12.692 ± 0.082	34.728 ± 0.185
TOL/OH/NO$_x$	50.176 ± 0.002	-11.967 ± 0.003	17.98 ± 0.01	-36.962 ± 0.002	141.77 ± 0.03
TOL/OH	33.661 ± 0.016	-3.498 ± 0.009	16.275 ± 0.044	-29.914 ± 0.007	123.53 ± 0.15

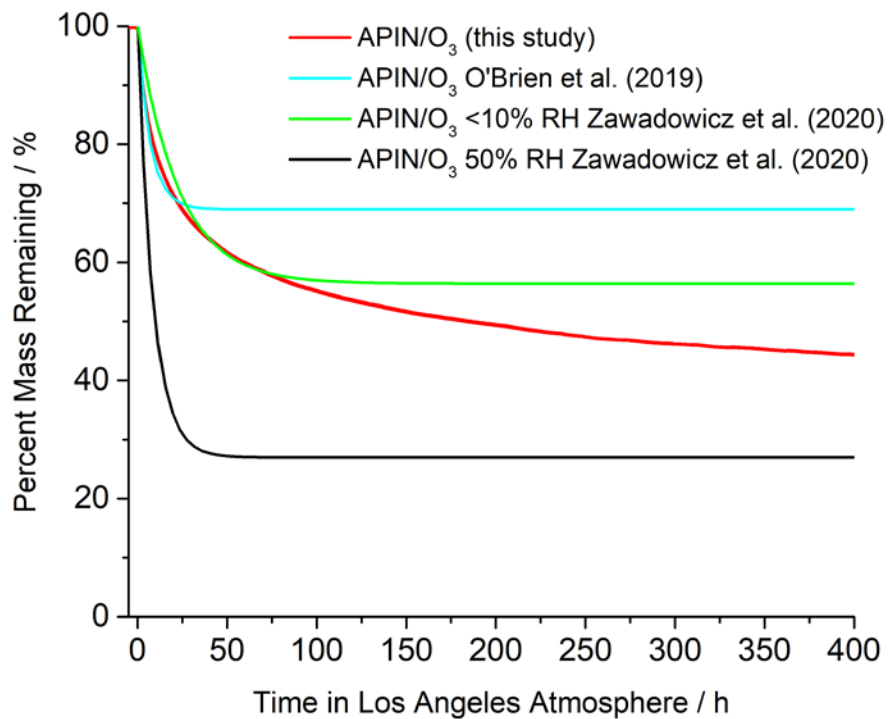## Comparison with Previous Studies

Figure S6: Converting the APIN/O_3 percent mass loss to a percent mass remaining allows for comparison with the extent of APIN/O_3 photodegradation as found by O'Brien et al. (2019)[2] and Zawadowicz et al. (2020).[3] It is important to note that the Zawadowicz et al. (2020) study did not report a recalcitrant fraction under dry conditions due to the uncertainty in the fit. In order to compare our study with theirs under dry conditions we assumed the recalcitrant fraction to be the average between our study (43.8%) and the O'Brien et al. study (69%). The Zawadowicz et al. (2020) study also found increased photodegradation rates under humid conditions, also included in Figure S6.

References

1. Madronich, S. Tropospheric ultraviolet and visible (TUV) radiation model. https://www2.acom.ucar.edu/modeling/tropospheric-ultraviolet-and-visible-tuv-radiation-model (accessed February 25, 2020)
2. O'Brien, R. E. & Kroll, J. H. Photolytic Aging of Secondary Organic Aerosol: Evidence for a Substantial Photo-Recalcitrant Fraction. *J. Phys. Chem. Lett.* **10**, 4003–4009 (2019).
3. Zawadowicz, M. A. *et al.* Photolysis Controls Atmospheric Budgets of Biogenic Secondary Organic Aerosol. **54**, 3861–3870 (2020).