Supporting Information

Photodegradation of Secondary Organic Aerosol Material Quantified with a Quartz Crystal Microbalance

Kurtis T. Malecha, Zicheng Cai, and Sergey A. Nizkorodov*

Department of Chemistry, University of California, Irvine, California 92697-2025, USA

* E-mail: nizkorod@uci.edu, Phone: +1-949-824-1262, Fax: +1-949-824-8571

Modified QCM Setup

We modified the QCM sample holder to accommodate a flow of zero air so that we could also detect the emitted OVOCs via PTR-ToF-MS in tandem. Figure S1 illustrates the modification.
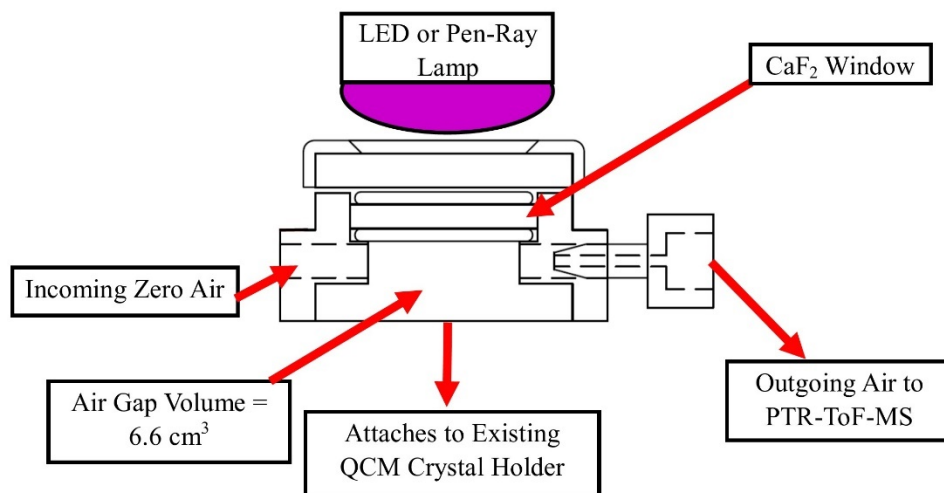

Figure S1. An experimental diagram of the QCM/PTR-ToF-MS experiment. Zero air flows at 150 sccm over the QCM crystal, and the OVOCs emitted as a result of irradiation are detected by the PTR-ToF-MS. The modified sample holder screws into the existing crystal holder, creating a sealed environment. Above the sealed mixing space (volume = 6.6 cm^3) there is a 2.54 cm CaF$_2$ window compressed with o-rings, which transmits the UV light that irradiates the SOA particles on the QCM crystal.

Sauerbrey Equation

In the commonly used form of the Sauerbrey equation, the sensitivity factor C_S has the units of Hz cm^2 μg^{-1} and is calculated as follows:

$$C_S = -\frac{\Delta f * area}{\Delta m} \tag{S1}$$

where Δf is the frequency change resulting from uniformly distributing mass Δm over the QCM active area. For a rigid thin film of the same density as quartz, the theoretical sensitivity factor should be $C_S = 56.6$ Hz cm^2 μg^{-1}. However, for softer materials and/or non-uniform films the sensitivity factor may be different, and for thick films the linear dependence of Δf on Δm can break down. We calculated the sensitivity factors for SOA films from the calibrated C_f values (defined in Equations 1 and listed in Table S1) assuming that the collected mass of SOA particles is uniformly distributed over the QCM substrate area of 5 cm^2 (confirmed by visual inspection). Figure S2 plots the sensitivity factor C_S versus the mass loading. The calculated C_S value for SOA films is of the same order of magnitude as the theoretical value. The values appear to be systematically higher for APIN/O$_3$ SOA and increase with mass loading for GUA/NO$_x$ SOA.
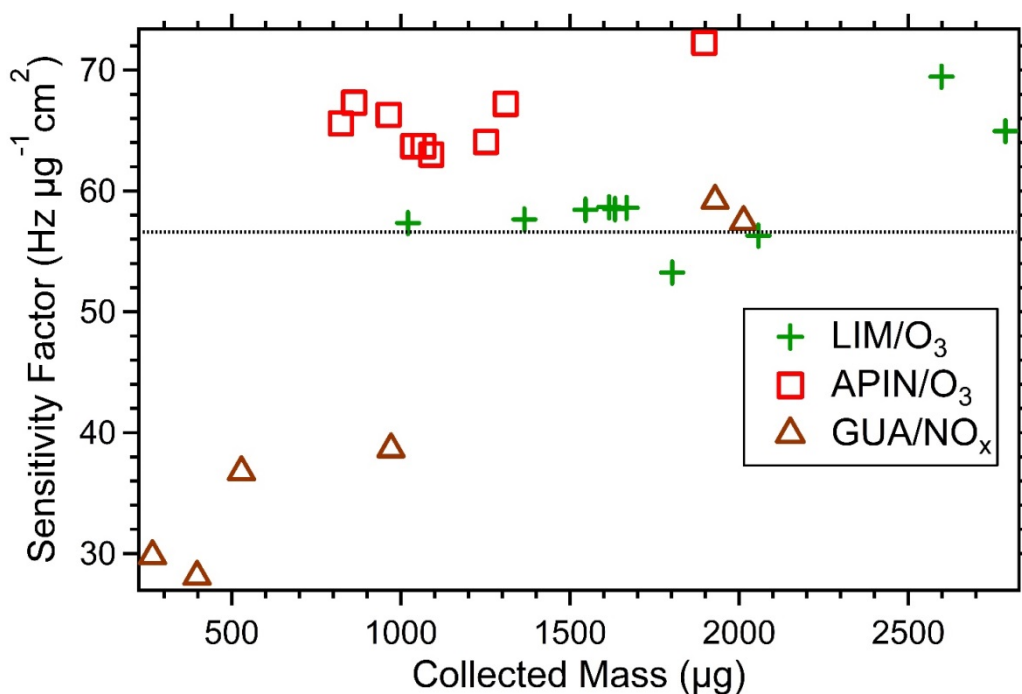
Figure S2. The sensitivity factor C_S for each SOA type is compared with the theoretical value of 56.6 Hz cm^2 µg^{-1} (dashed horizontal line). The factors are not very dependent on the mass loading until they are less than 1 mg (as discussed in the main text).

Control Experiments

Several controls were run for this study. The QCM was briefly heated for several minutes with a heat gun to an elevated temperature of 25 °C with the SOA material on it (baseline temperature of 20 °C and maximum UV-LED irradiation temperature of 22 °C), and after an initial drop in QCM frequency, the frequency returned to the initial value, suggesting minimal loss in in the SOA mass due to the heat pulse. A heat control was also run on an empty QCM crystal with similar results. Empty windows were also irradiated with the lamps, and the QCM frequency increased by fewer than 10 Hz to a steady state during irradiation. After the lamp was shut off, the QCM frequency returned to the same baseline. Finally, a QCM crystal was coated with paraffin wax (assumed to be photostable) and thereafter irradiated. As expected, this sample showed no changes in QCM frequency, suggesting no mass loss of the substrate.

Data Summary Table

Table S1. All the SOA samples examined in this study. The samples correspond to "APIN/O$_3$" = α-pinene/ozonolysis, "GUA/NO$_x$" = guaiacol (o-methoxyphenol)/high NO$_x$ conditions, and "LIM/O$_3$" = d-limonene/ozonolysis. Colum 3 contains the integrated photon fluxes for each sample. The 254 nm data's integrated flux only contains the emission line at 254 nm (other lines assumed to contribute little to no photochemistry). Column 4 contains the mass collected on the QCM crystal after the annealing step mentioned in the main text. The masses were taken in triplicate and averaged. C_f was calculated as per the main text (the product of the mass collected and C_f is equal to the change in QCM frequency between the loaded crystal and clean crystal). The mass loss rates for this study were taken during the initial part of the photodegradation, where the frequency change was linear. The PTR Mass Loss Rate was determined by summing up each of the 4 OVOCs' mass loss rates as discussed in the main text.

Sample	λ (nm)	Integrated Flux (photons cm^{-2} s^{-1})	Mass on QCM Crystal After Anneal (µg)	C_f (Hz µg^{-1})	Time Lamp On (hr)	QCM Mass Loss Rate (µg hr^{-1})	PTR Mass Loss Rate (µg hr^{-1})
APIN/O$_3$	254	2.5x10^{15}	1090	12.60	2.0	168.9	93.1
APIN/O$_3$	254	2.5x10^{15}	1037	12.74	2.0	148.9	79.5
APIN/O$_3$	254	2.5x10^{15}	1897	14.45	65.3	231.5	103.4
APIN/O$_3$	305	3.8x10^{15}	964	13.26	1.8	10.9	7.0
APIN/O$_3$	305	3.8x10^{15}	1067	12.74	1.7	35.4	16.2
APIN/O$_3$	305	3.8x10^{15}	1310	13.44	1.1	40.6	22.3
APIN/O$_3$	365	2.5x10^{15}	1252	12.81	0.9	1.0	1.1
APIN/O$_3$	365	2.5x10^{15}	823	13.12	0.8	1.5	0.9
APIN/O$_3$	365	2.5x10^{15}	862	13.46	0.7	-0.1	0.9
GUA/NO$_x$	254	2.5x10^{15}	971	7.73	1.8	23.2	2.2
GUA/NO$_x$	254	2.5x10^{15}	2013	11.49	1.0	25.5	2.5
GUA/NO$_x$	254	2.5x10^{15}	266	5.96	26.0	18.8	1.9
GUA/NO$_x$	305	3.8x10^{15}	529	7.35	17.3	3.6	0.6
GUA/NO$_x$	305	3.8x10^{15}	1929	11.84	20.7	3.7	0.5
GUA/NO$_x$	305	3.8x10^{15}	398	5.62	66.3	1.5	0.4
LIM/O$_3$	254	2.5x10^{15}	1365	11.53	1.2	165.3	70.7
LIM/O$_3$	254	2.5x10^{15}	1021	11.47	1.0	168.2	81.6
LIM/O$_3$	254	2.5x10^{15}	1667	11.72	1.6	148.5	73.2
LIM/O$_3$	254	2.5x10^{15}	1667	11.72	18.8	43.1	29.1
LIM/O$_3$	305	3.8x10^{15}	1546	1.69	0.8	56.1	24.1
LIM/O$_3$	305	3.8x10^{15}	1633	11.70	1.6	58.5	21.3
LIM/O$_3$	305	3.8x10^{15}	1616	11.73	1.4	62.7	19.7
LIM/O$_3$	365	2.5x10^{15}	2787	12.99	4.7	5.1	3.3
LIM/O$_3$	365	2.5x10^{15}	1802	10.65	1.6	-2.9	0.2
LIM/O$_3$	365	2.5x10^{15}	2598	13.89	1.4	-0.5	0.2
LIM/O$_3$	365	2.5x10^{15}	2057	11.26	1.0	2.2	0.2

Spectral Flux Densities of the Sun and the Lamps Used in this Work

We used the following parameters from the Quick TUV[1] calculator mentioned in the main text:
- Latitude/Longitude: 34°/-118°
- Date and Time: June 21, 2017, 19:00:00 GMT, representative of the summer solstice maximum flux in Los Angeles, CA
- Overhead Ozone: 300 du
- Surface Albedo: 0.1
- Ground Altitude: 0 km
- Measured Altitude: 0 km or 40 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.

Figure S3 shows a comparison of the spectral flux densities for the sun and the lamps. Each flux density is integrated over this wavelength range, and the resulting fluxes are compared in the main text.
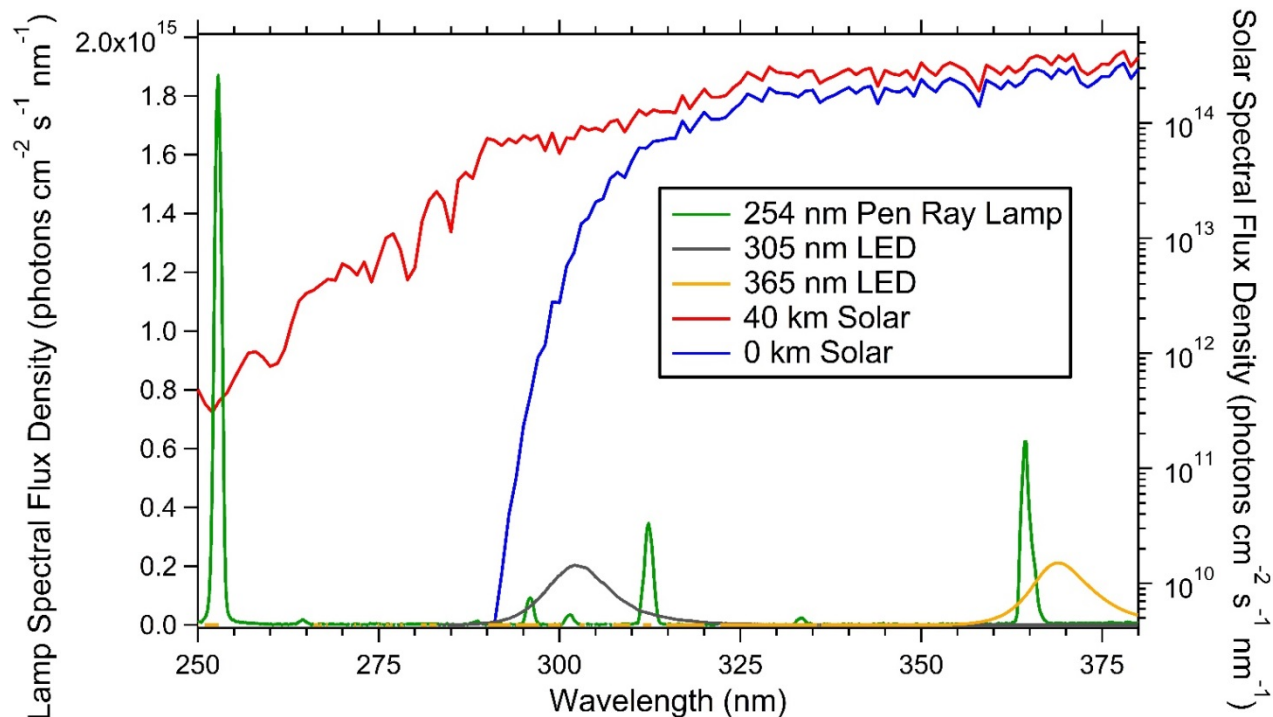

Figure S3. The spectral flux densities over the range of the electromagnetic spectrum of the pen-ray lamp (in green), 305 nm LED (in dark-gray), and 365 nm LED (in orange), and the sun at both 40 km and 0 km (in red and blue, respectively) on the summer solstice in Los Angeles, California. The left axis corresponds to the lamps, and the right axis (logarithmic scale) represents the sun's spectral flux density.

Scaling the Photodegradation Rate to Atmospheric Conditions

We assumed the following relationship between the fractional mass loss rate (FMLR) and the spectral flux of radiation:

$$FMLR = \frac{1}{m}\frac{dm}{dt} = \int F(\lambda) \cdot E(\lambda) \cdot d\lambda \qquad \text{(S2, same as Eq. 4)}$$

The right hand side of Eq. (S2) is the convolution of the spectral flux of radiation, $F(\lambda)$, and the efficiency of photodegradation, $E(\lambda)$. The latter is a combination of the effective quantum yield and absorption cross section for the SOA compounds as well as unit conversion constants. Because the lamps in this study have narrow bandwidths, we can determine the efficiency for each of the three irradiation wavelengths by rearranging Eq. (S2):

$$E(\lambda) = \frac{FMLR_{measured}(\lambda)}{\int F_{lamp}(\lambda) \cdot d\lambda} \qquad \text{(S3)}$$

The plots of the efficiency versus wavelength are presented in Figure S4 for APIN/O_3 and LIM/O_3 SOA (the mass loss rates for GUA/NO_x SOA samples were too small and could not be measured reliably at all wavelengths). Because the absorption cross sections of many molecules decay exponentially in wavelength in this wavelength range,[2-3] the efficiency was fitted to an empirical exponential function of wavelength as shown in Figure S4. The resulting function was inserted into Eq. (S3) to predict the fractional mass loss rate in the atmosphere

$$FMLR_{atmosphere} = \int F_{sun}(\lambda) \cdot E(\lambda) \cdot d\lambda \qquad \text{(S4)}$$

The solar photon fluxes used in the estimate correspond to the Summer solstice in Los Angeles at 0 km and 40 km above sea level (representative of the lower troposphere and upper stratosphere, respectively) derived from the quick TUV calculator.[1]
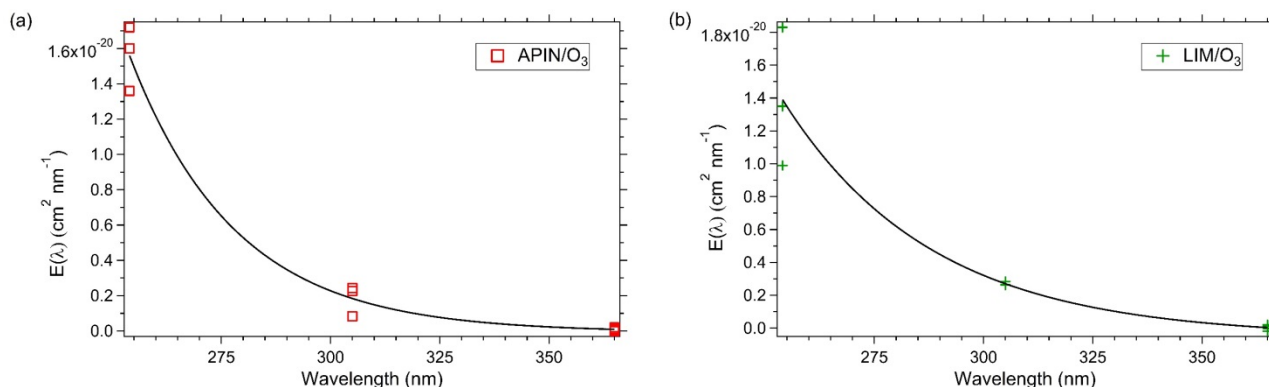

Figure S4. The efficiency factor is plotted for the (a) APIN/O_3 and (b) LIM/O_3 data. Each curve is fit to an exponential decay (solid line).

Long Irradiation Exposure Experiment

Figure S5 contains QCM data from a very long exposure of the substrate to continuous radiation. The APIN/O$_3$ sample was irradiated with 254 nm light starting right before the 2 hr mark and the UV light was left on for over 60 hours. There was no visible organic material left on the QCM crystal by the end of this experiment suggesting that the organic material completely photodegraded into volatile products.
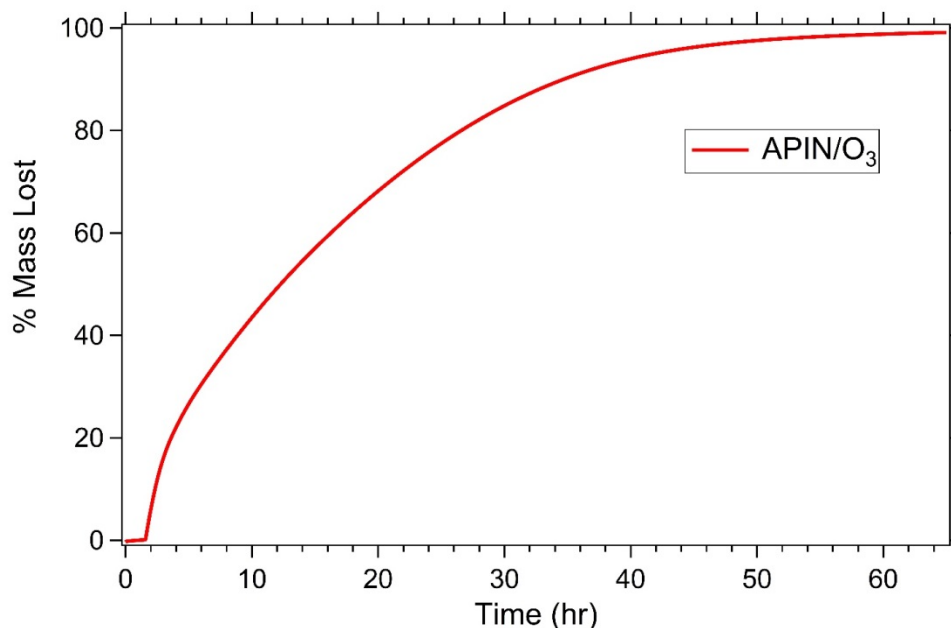

Figure S5. The present of mass lost for the APIN/O$_3$ SOA during long 254 nm irradiation. Nearly all the APIN/O$_3$ SOA sample mass was lost during this long irradiation period.

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 November 27, 2017).
2.   Calvert, J. A.; Pitts, J. N. *Photochemistry*. John Wiley: New York, 1966.
3.   Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the upper and lower atmosphere theory, experiments, and applications*. Academic Press: San Diego, CA, 2000.