

# Supplementary Material for “The Feasibility of Photosensitized Reactions with Secondary Organic Aerosol Particles in the Presence of Volatile Organic Compounds”

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8 Pages, 3 Figures, 2 Tables

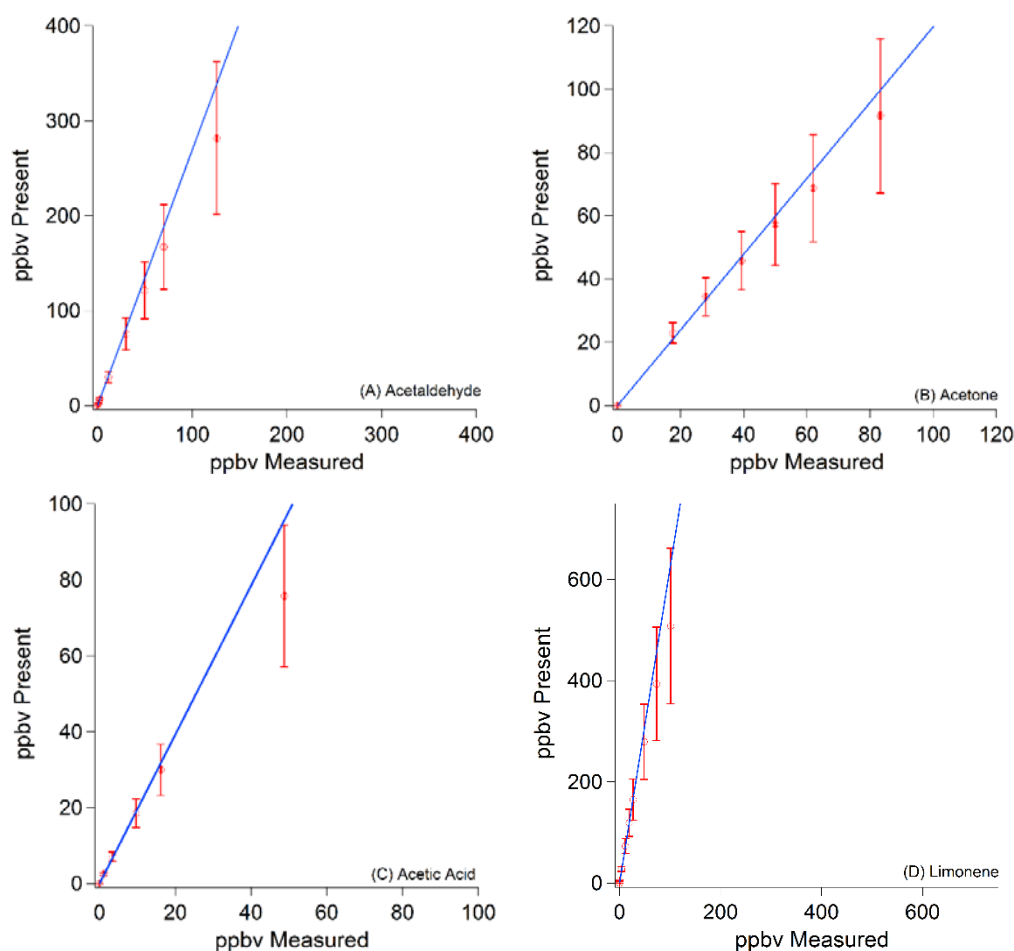
## Reagents Used for This Study

**Table S1:** The reagents used for this study, their CAS registry numbers, their sources, and their stated purity levels.

Reagent Name	CAS Registry Number	Manufacturer	Stated Purity
Hydrogen Peroxide Solution (30 wt%, water balance)	7722-84-1	Fisher	
5086 ppm Nitric Oxide in Nitrogen		Praxair	
Naphthalene	91-20-3	Fisher	98%
Dichloromethane	75-09-2	Fisher	99.9%
d-limonene ((4R)-1-Methyl-4-(1-methylethenyl)-cyclohexene)	5989-27-5	Sigma Aldrich	97%
Isoprene (2-Methylbuta-1,3-diene)	78-79-5	Sigma Aldrich	99%
Guaiacol (2-methoxyphenol)	90-05-1	Spectrum	99%

## PTR-ToF-MS Calibration

The PTR-ToF-MS was calibrated for four VOCs analyzed for this study (acetaldehyde, acetone, acetic acid, and limonene) by evaporating a known amount of a given VOC into the cleaned 5 m<sup>3</sup> chamber and monitoring the [M+1] peak, corresponding to the protonated VOC. The VOC was added to the chamber in small increments, and the corresponding PTR-ToF-MS signal was measured after each successive addition. The inlet line through which the VOC was injected into the chamber was heated throughout the experiment to 60 °C, and the PTR-ToF-MS inlet line was also heated to the same temperature to prevent losses of VOC on the steel surfaces of the inlets. (However, we could not account for losses happening on the surface of the Teflon chamber.) We created a calibration plot for each VOC comparing the actual amount of VOC in the chamber (assuming no wall losses) with that reported by the PTR-ToF-MS instrument (Figure S1). The resulting calibration factors, representing the ratio of measured to actual VOC mixing ratios, ranged from 1.2 to 6.2. Confidence intervals were calculated at the 95% level based on the uncertainty in the injection, the PTR-ToF-MS traces, and the resulting linear regression. These values are reported in Table S2.



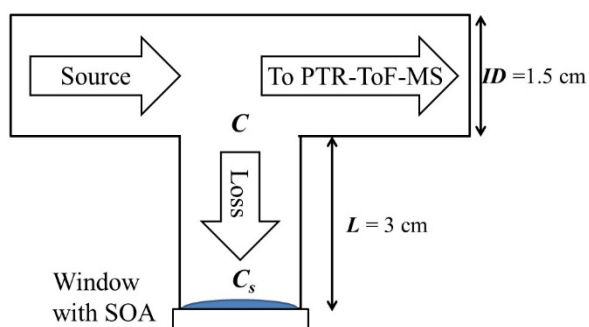
**Figure S1.** The PTR-ToF-MS calibration plots for (A) acetaldehyde, (B) acetone, (C) acetic acid, and (D) d-limonene. The horizontal axis is the PTR-ToF-MS measured mixing ratio and the vertical axis is the known amount that was injected into the chamber. Each data point has vertical and horizontal error bars corresponding to 95% confidence intervals of the amount of VOC present and measured, respectively. The vertical error bars increase with the VOC amount because of the accumulation of errors in the successive injections of the VOC in the chamber.

**Table S2:** The resulting calibration factors for each VOC. For the SOA photodegradation experiments, we multiplied the mixing ratios measured by the PTR-ToF-MS by this factor for each VOC in the main text analysis. The subscripts show the first digit that is not significant.

VOC	Calibration Factor	95% Confidence Interval
Acetaldehyde	2.6 <sub>9</sub>	0.5 <sub>4</sub>
Acetone	1.2 <sub>0</sub>	0.2 <sub>7</sub>
Acetic Acid	1.9 <sub>6</sub>	0.5 <sub>3</sub>
Limonene	6.2	1.1

## Derivation of Equations Used in This Work

### Uptake Coefficient



**Figure S2.** Schematic diagram of the flow cell.

The geometry of the experiment is schematically shown in Figure S2. The flow of air containing 200 ppbv limonene goes through a cylindrical tube with  $ID = 1.5$  cm at a volume flow rate of

$F = 200 \frac{cm^3}{s}$ . The SOA sample is located on a  $CaF_2$  window at the bottom of a cylindrical side tube with length  $L = 3$  cm and inner diameter  $ID = 1.5$  cm. The PTR-ToF-MS measures the concentration of limonene exiting from the cell,  $C \left[ \frac{molec}{cm^3} \right]$ . For the mixing ratio of 200 ppbv used in these

experiments,  $C = 4.9 \times 10^{12} \frac{molec}{cm^3}$ . When the UV-LED is on, the reduction in the measured concentration is only a few percent, so the inlet and outlet concentrations of limonene can be regarded as approximately the same. A small amount of limonene is lost onto the SOA coated window establishing a gradient of concentration along the side tube. The concentration in the

immediate vicinity of the surface is  $C_s \left[ \frac{\text{molec}}{\text{cm}^3} \right]$ . The transfer of limonene to the SOA coated window is not purely diffusive - we verified this by drastically changing the flow geometry and getting the same final result for the uptake coefficient. Nevertheless, we attempt to model the diffusion through the side tube with normal diffusion equations below.

The number of molecules delivered by the air flow per second,  $Source \left[ \frac{\text{molec}}{s} \right]$ , can be related to the volume flow rate set by the mass flow controller,  $F$ , and the limonene concentration in the inlet flow as follows:

$$Source = F \times C \quad (1)$$

Under the steady state conditions, the net flux of limonene molecules through the flow,  $J \left[ \frac{\text{molec}}{\text{cm}^2 \cdot s} \right]$ , and the absolute loss rate due to the surface reaction,  $Loss \left[ \frac{\text{molec}}{s} \right]$ , can be calculated as follows:

$$J = \frac{Loss}{Area} = \frac{\gamma_{eff} \times v \times C}{4} = \frac{\gamma_{corrected} \times v \times C_s}{4} \quad (2)$$

In this equation,  $\gamma_{eff}$  is the effective uptake coefficient measured in the experiment,  $\gamma_{corrected}$  is the actual uptake coefficient,  $Area[\text{cm}^2]$  is the area of the sample that is irradiated (about  $1 \text{ cm}^2$ ), and  $v \left[ \frac{\text{cm}}{s} \right]$  is the average speed of limonene ( $MW$  is the molecular weight of limonene,  $R$  is the gas constant,  $T$  is the absolute temperature):

$$v = \sqrt{\frac{8RT}{\pi MW}} = 2.15 \times 10^4 \frac{\text{cm}}{s} \quad (3)$$

Equation (2) shows that the effective and true uptake coefficient are related

$$\gamma_{corrected} = \gamma_{eff} \times \frac{C}{C_s} \quad (4)$$

The fractional reduction in the limonene that we observe in the flow with the PTR-ToF-MS is:

$$\frac{Ion_{UVoff} - Ion_{UVon}}{Ion_{UVoff}} = \frac{Loss}{Source} = \frac{\gamma_{eff} \times v \times Area}{4 \times F} \quad (5)$$

We can rearrange and substitute measured values of PTR-ToF-MS ion currents into Eq. (5) to calculate  $\gamma_{eff}$ . We show an example of this calculation for the GUA/OH SOA system below, in which the limonene signal dropped by 1.2% during the irradiation:

$$\gamma_{eff} = \frac{Ion_{UVoff} - Ion_{UVon}}{Ion_{UVoff}} \times \frac{4 \times F}{v \times Area} = 0.012 \times \frac{4 \times 3.33 \frac{\text{cm}^3}{s}}{2.15 \times 10^4 \frac{\text{cm}}{s} \times 1 \text{cm}^2} = 7.4 \times 10^{-6} \quad (6)$$

This uptake coefficient is reasonably large, so the diffusion gradient may be substantial (if the limonene transfer to the SOA substrate is controlled by diffusion). If we assume that the concentration gradient in the tube is linear, the diffusion flux can be approximated as:

$$J = D \times \frac{(C - C_s)}{L} \quad (7)$$

$D \approx 0.2 \frac{cm^2}{s}$  is the estimated diffusion coefficient of limonene at ambient temperature and pressure.<sup>1</sup>

From this, the concentration near the SOA surface can be estimated as follows:

$$C_s = C - \frac{J \times L}{D} = C \left( 1 - \frac{\gamma_{eff} \times v \times L}{4D} \right) \quad (8)$$

And the corrected uptake coefficient becomes

$$\gamma_{corrected} = \gamma_{eff} \times \frac{1}{\left( 1 - \frac{\gamma_{eff} \times v \times L}{4D} \right)} \quad (9)$$

For the GUA/OH SOA example, the corrected uptake coefficient is

$$\gamma_{corrected} = 7.4 \times 10^{-6} \times \frac{1}{(1 - 0.60)} = 1.9 \times 10^{-5} \quad (10)$$

The correction is quite large even for this smallest observed uptake coefficient. For the rest of the SOA systems studied in this work the effective uptake coefficient becomes too large for making the diffusion correction reliably (the linear gradient approximation breaks down). Therefore, the effective uptake coefficients listed in Table 2 should be interpreted as **the lower limits for the actual uptake coefficients**. Nevertheless, as we discuss in the text, the actual values of the uptake coefficients are not likely to be much higher than the effective values listed in Table 2. Therefore, the main conclusion of the paper (that these uptake coefficients are too small to play a role in controlling loss rates of VOCs on SOA particles) is not likely to be affected by the diffusion limitations in some of our experiments.

## Loss Rate for Limonene Under Typical Ambient Conditions

We now derive the lifetimes of limonene with respect to deposition on atmospheric particles under typical atmospheric conditions (with assumed effective ambient uptake coefficient  $\gamma_{ambient} = 2 \times 10^{-6}$ ). Our calculations assume monodisperse particles with particle diameter,  $d = 3 \times 10^{-7}$  m, a particle material density,  $\rho = 1400$  kg/m<sup>3</sup>, and the particle mass concentration in air,  $C_{mass} = 15$   $\mu$ g/m<sup>3</sup>. The area to volume ratio ( $A/V$ ) for such particles is  $2 \times 10^7$  m<sup>-1</sup>. Possible diffusion limitations for the uptake are neglected in this estimation.

The combined volume of particulate matter per volume of air is ( $m^3_{air}$  is the unit for the volume of air and  $m^3_p$  is the unit for the volume of a particle):

$$C_{\text{volume}} \left[ \frac{m_p^3}{m_{\text{air}}^3} \right] = \frac{C_{\text{mass}} \left[ \frac{\mu\text{g}}{m_{\text{air}}^3} \right] \times 10^{-9} \left[ \frac{\text{kg}}{\mu\text{g}} \right]}{\rho \left[ \frac{\text{kg}}{m_p^3} \right]} = \frac{15 \frac{\mu\text{g}}{m_{\text{air}}^3} \times 10^{-9} \frac{\text{kg}}{\mu\text{g}}}{1400 \frac{\text{kg}}{m_p^3}} = 1.07 \times 10^{-11} \frac{m_p^3}{m_{\text{air}}^3} \quad (11)$$

The combined area of particulate matter per volume of air is (where  $A/V$  is the area to volume ratio for one particle, per assumptions above):

$$C_{\text{area}} \left[ \frac{m_p^2}{m_{\text{air}}^3} \right] = C_{\text{volume}} \left[ \frac{m_p^3}{m_{\text{air}}^3} \right] \times \frac{A}{V} \left[ m_p^{-1} \right] = 1.07 \times 10^{-11} \frac{m_p^3}{m_{\text{air}}^3} \times 2 \times 10^7 m_p^{-1} = 2.14 \times 10^{-4} \frac{m_p^2}{m_{\text{air}}^3} \quad (12)$$

We can also define the loss rate per unit volume air:

$$\text{Loss} \left[ \frac{\text{molec}}{m_{\text{air}}^3 \cdot s} \right] = \gamma \times \frac{\nu \left[ \frac{m}{s} \right] \times C_{\text{area}} \left[ \frac{m_p^2}{m_{\text{air}}^3} \right]}{4} \times C_{\text{VOC}} \left[ \frac{\text{molec}}{m_{\text{air}}^3} \right] \quad (13)$$

The effective first order rate constant for limonene is then:

$$k \left[ s^{-1} \right] = \frac{\text{Loss} \left[ \frac{\text{molec}}{m_{\text{air}}^3 \cdot s} \right]}{C_{\text{VOC}} \left[ \frac{\text{molec}}{m_{\text{air}}^3} \right]} = \gamma \times \frac{\nu \left[ \frac{m}{s} \right] \times C_{\text{area}} \left[ \frac{m_p^2}{m_{\text{air}}^3} \right]}{4} \quad (14)$$

Using the effective ambient  $\gamma = 2 \times 10^{-6}$ , we get:

$$k \left[ s^{-1} \right] = 2 \times 10^{-6} \times \frac{215 \frac{m}{s} \times 2.14 \times 10^{-4} \left[ \frac{m_p^2}{m_{\text{air}}^3} \right]}{4} = 2.3 \times 10^{-8} s^{-1} \quad (15)$$

This corresponds to lifetime of limonene with respect to the deposition on SOA particles of:

$$\tau \left[ s \right] = \frac{1}{k \left[ s^{-1} \right]} = \frac{1}{2.3 \times 10^{-8} s^{-1}} = 4.3 \times 10^7 s > 1 \text{yr} \quad (16)$$

If we compare this lifetime to that of limonene reacting with OH and limonene reacting with  $O_3$  in the gas phase, we arrive at the following. We assume that the typical [OH] is  $10^6$  molecules/cm<sup>3</sup> and the typical [ $O_3$ ] is  $\sim 4.8 \times 10^{11}$  molecules/cm<sup>3</sup>. Rate constants are from Atkinson.<sup>2</sup>

$$k_{\text{OH}} \left[ s^{-1} \right] = k_{\text{OH+LIM}} \times [\text{OH}] = 1.7 \times 10^{-10} \frac{\text{cm}^3}{\text{molec} \cdot s} \times 10^6 \frac{\text{molec}}{\text{cm}^3} = 1.7 \times 10^{-4} s^{-1} \quad (17)$$

$$\tau_{\text{OH}} \left[ s \right] = \frac{1}{k_{\text{OH}} \left[ s^{-1} \right]} = \frac{1}{1.7 \times 10^{-4} s^{-1}} = 5.9 \times 10^3 s = 98 \text{min} \quad (18)$$

$$k_{\text{O}_3} \left[ s^{-1} \right] = k_{\text{O}_3+\text{LIM}} \times [\text{O}_3] = 2.0 \times 10^{-16} \frac{\text{cm}^3}{\text{molec} \cdot s} \times 4.8 \times 10^{11} \frac{\text{molec}}{\text{cm}^3} = 9.6 \times 10^{-5} s^{-1} \quad (19)$$

$$\tau_{O_3} [s] = \frac{1}{k_{O_3} [s^{-1}]} = \frac{1}{9.5 \times 10^{-5} s^{-1}} = 1.0 \times 10^4 s = 174 \text{ min} \quad (20)$$

Finally, we consider the lifetime of limonene with respect to uptake onto urban surfaces. In this case, the first term in Eq. 21 is the ratio of the actual surface area to the geometric surface area over 1 m<sup>2</sup> of ground (we set it to 50 as per the maximum discussed by Asner et al.<sup>3</sup>) and the second term is the height of the boundary layer where species mix freely (we set it to 500 m). The surface concentration is now considerably larger than it was estimated for the particles:

$$C_{area} \left[ \frac{m^2_{surface}}{m^3_{air}} \right] = \frac{S_{actual}}{S_{geometric}} \times \frac{1}{h_{boundary} [m]} = 0.1 m^{-1} \quad (21)$$

If we substitute the result from Eq. (21) into Eq. (14), we arrive at the rate of limonene loss and lifetime of limonene as:

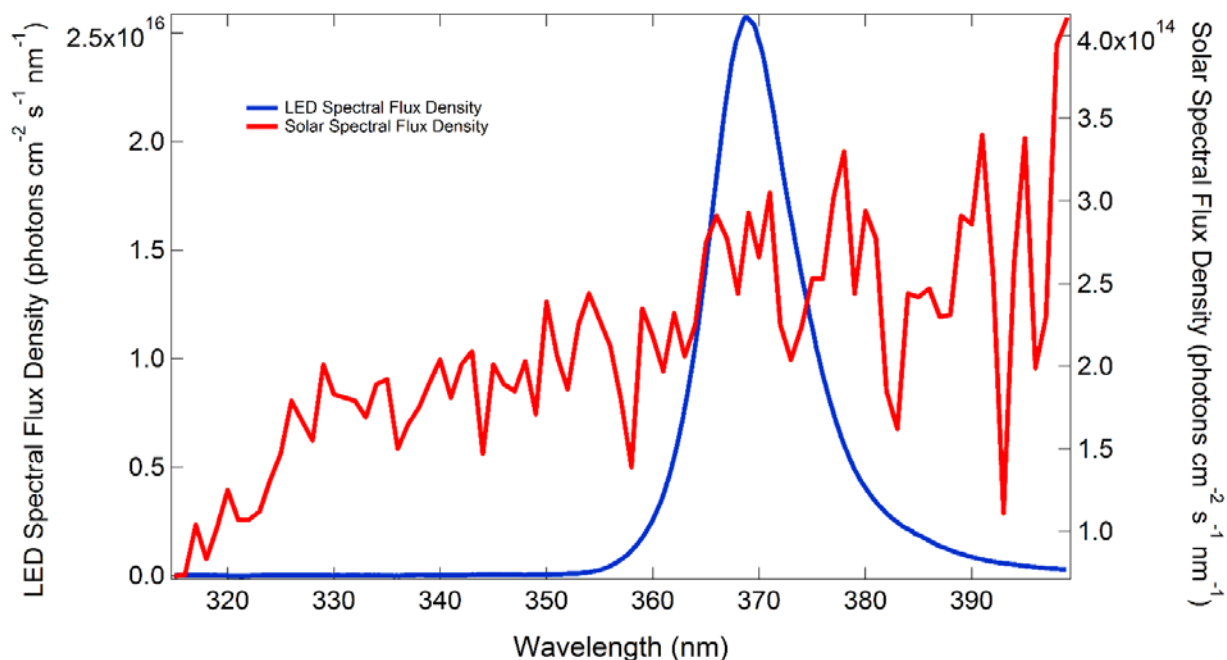
$$k [s^{-1}] = 2 \times 10^{-6} \times \frac{215 \frac{m}{s} \times 0.1 \left[ \frac{m^2_{surface}}{m^3_{air}} \right]}{4} = 1.1 \times 10^{-5} s^{-1} \quad (22)$$

$$\tau [s] = \frac{1}{k [s^{-1}]} = \frac{1}{1.1 \times 10^{-5} s^{-1}} = 9.3 \times 10^4 s = 26 \text{ hr} \quad (23)$$

This lifetime is considerably shorter but still not short enough to be competitive with the oxidation of limonene by OH or ozone in the gas phase.

## Spectral Flux Densities of LED and Sun Compared

We used the following parameters from the Quick TUV calculator mentioned in the main text: Latitude/Longitude (34°/-118°), Overhead Ozone (300 du), Surface Albedo (0.1), Ground and 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) and 4 streams transfer model. Figure S2 shows a comparison of the spectral flux densities for the sun and the lamp in the near-UV region (300-400 nm). 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 near-UV range of the electromagnetic spectrum of the LED (in blue) and the sun (in red) on the summer solstice in Los Angeles, California. The left axis corresponds to the LED, and the right axis represents the sun's flux density.

## References

1. Estimated Diffusion Coefficients in Air and Water - Extended Version. <https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion-ext.html> (accessed June 7, 2017).
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