

Supporting information

Photolytic Aging of Secondary Organic Aerosol: Evidence for a Substantial Photo-Recalcitrant Fraction

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Methods

Experiments were carried out in the MIT environmental chamber¹ : a 7.5 m³ PFA bag (Ingeniven LLC) in a temperature controlled room at 20 °C and < 5% RH in semi-batch mode. Volume was maintained by addition of clean makeup zero air (Aadco 737-13 Pure Air Generator) and the pressure in the chamber was maintained at a slightly positive pressure (20-40 mbar) by the addition of this zero air to balance the air withdrawn by the instruments.

Ammonium sulfate seeds were added with a TSI atomizer (TSI Aerosol Generator 3076), the outflow of which passed through a silica-gel drier and a Po-210 static eliminator (NRD LLC). α -pinene SOA was generated in the dark via ozonolysis. After introduction of the ammonium sulfate seed, an OH radical scavenger (C₃F₆) was added (~400 ppm). After this mixed ~ 10 min, α -pinene was added via liquid injection ((-) α -pinene 98% purity, Sigma-Aldrich). This mixed about 20 min and then ozone was added via a Penray ozone generator (Model 600, Jelight Co. Inc.) supplied with zero air at 1 liter per minute (Lpm). The ozone monitor (Model 202, 2B Technologies, Inc.) only sampled from the bag intermittently to check ozone concentrations. When ozone concentrations measured ~500 ppb, the penray was turned off (~ 3 hours). Another two hours were spent allowing α -pinene SOA to form and the Org/SO₄ ratio to stabilize. After this, for photolysis experiments the chamber lights were turned on. For dark experiments, the lights remained off for the duration.

Chamber lights include twenty-four 40 Watt UVA lamps (wavelength range 300-400 nm, peak centered at 350 nm, Figure S5) with JNO₂ of ~0.08 min⁻¹. JNO₂ was estimated in a separate set of experiments by monitoring the concentration of ozone, NO_x, and NO after the addition of NO₂ and ozone and assuming pseudo steady state:

$$J_{\text{NO}_2} = k_{\text{NO} + \text{O}_3} [\text{NO}] [\text{O}_3] / [\text{NO}_2]$$

Where [NO], [O₃], and [NO₂] are concentrations (molecules/cm³) and $k_{\text{NO} + \text{O}_3}$ is the rate constant for the reaction of ozone and NO (2×10^{-14} cm³ molecule⁻¹ s⁻¹).²

Real time particle mass spectra were collected with a high resolution, time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and aerosol size and number distribution were measured with a scanning mobility particle sizer (SMPS, TSI Inc.). Both experiments collected data for the entire experiment. Additional gas phase measurements include the ozone monitor and a NO_x monitor (Horiba APMA-370). After the first few hours, these gas-phase monitors were turned off to decrease the dilution rate in the chamber. Data analysis was performed in Igor 6.3 (Wavemetrics, Inc.) using the software packages PIKA v1.16 and SQUIRREL v1.57. Elemental composition was calculated based on molecular formulas of the ions using the updated approach of Canagaratna et al.³ A table of experimental parameters is provided below.

Absorption cross section measurements were carried out on a sample prepared as a replicate to the dark experiment 1 (experiment 1b in Table S1). A filter sample was collected for the duration of the chamber experiment. This filter was extracted with acetonitrile, blown to dryness under ultra-pure N₂ and reconstituted with H₂O. The concentration of organic in the solution was quantified using an internal standard and the SVN-AMS methodology.⁴ The absorption cross section was measured for the remaining material using a Beckman Coulter DU 800 spectrophotometer with 100 μ L quartz cuvettes.

Table S1

Experiment	Total (hr)	Irradiation (hr)	α -pinene (ppb)	Initial seed (cm ⁻³) x 10 ³	Max organic (ug/m3)	Initial yield
1a	40	34	120	200	63	0.093
1b	40	--	120	200	66	0.097
2a	40	36	120	220	62	0.091
2b	40	--	120	210	49	0.072
3a	30	25	80	180	30	0.066
3b	30	--	80	190	28	0.062

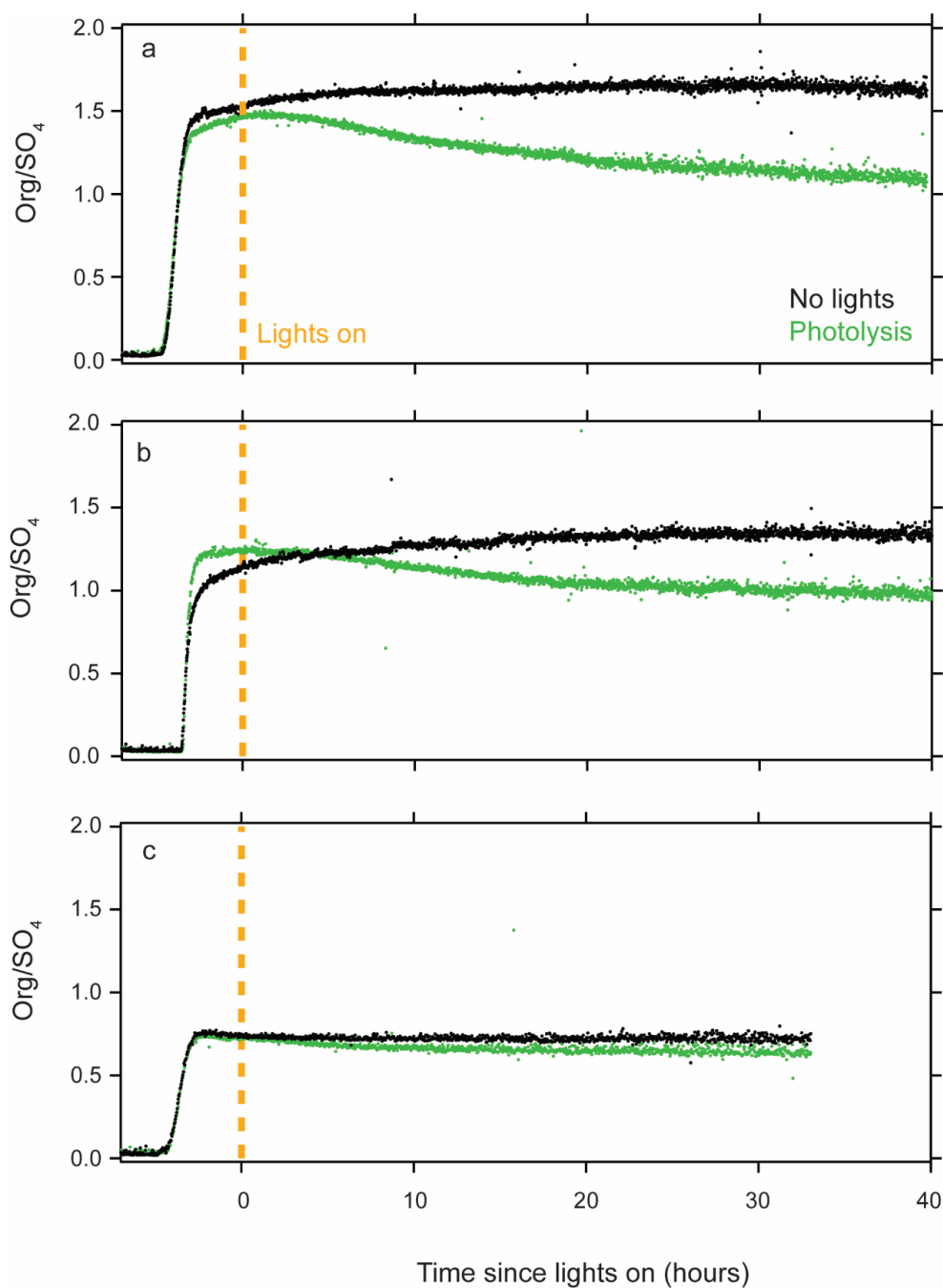


Figure S1. Org/SO₄ time series for dark and light replicates. All experiments are aligned to the equivalent time when lights were turned on. With lights on (green) a decrease in Org/SO₄ is observed as a function of time. When lights were off (black) the Org/SO₄ either stayed the same (c) or increased slightly (a and b).

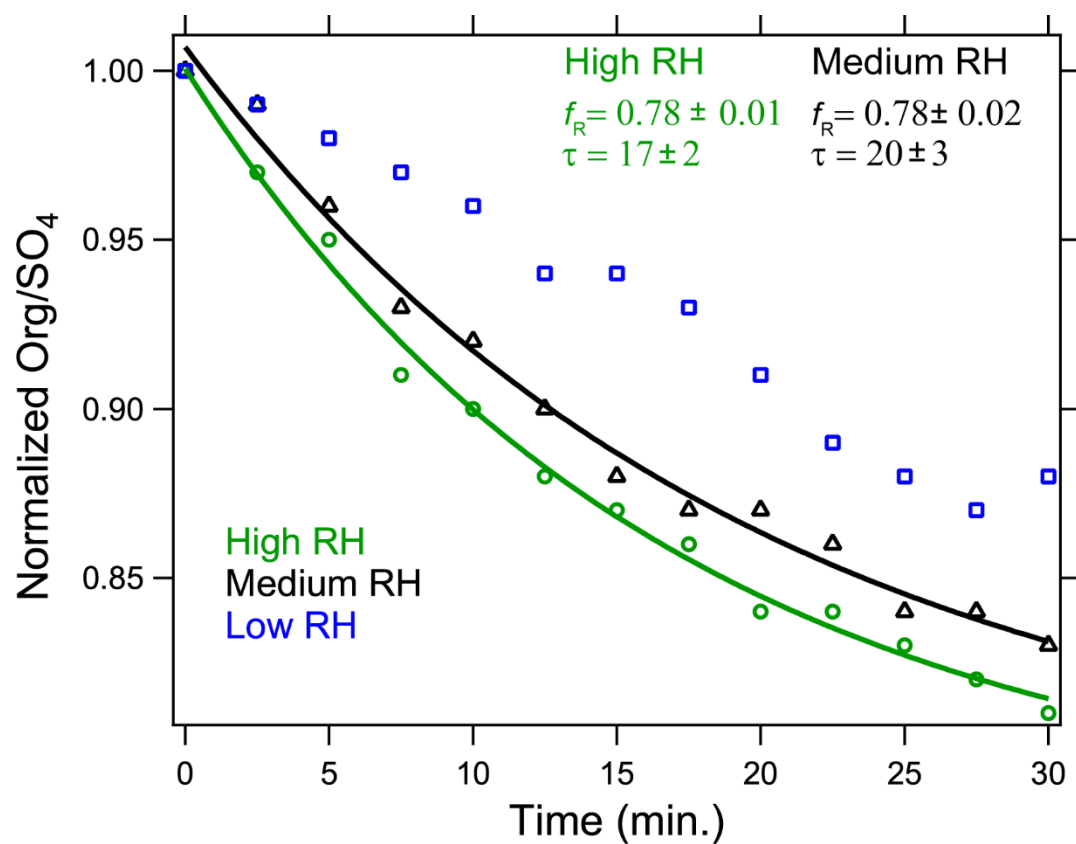


Figure S2. Exponential-offset fits applied to data from Figure S4 in Wong et al., 2014. Fits were applied to the high and medium RH experiments, the low RH experiment had too slow of a decay to fit an exponential with the 30 min. of data points.

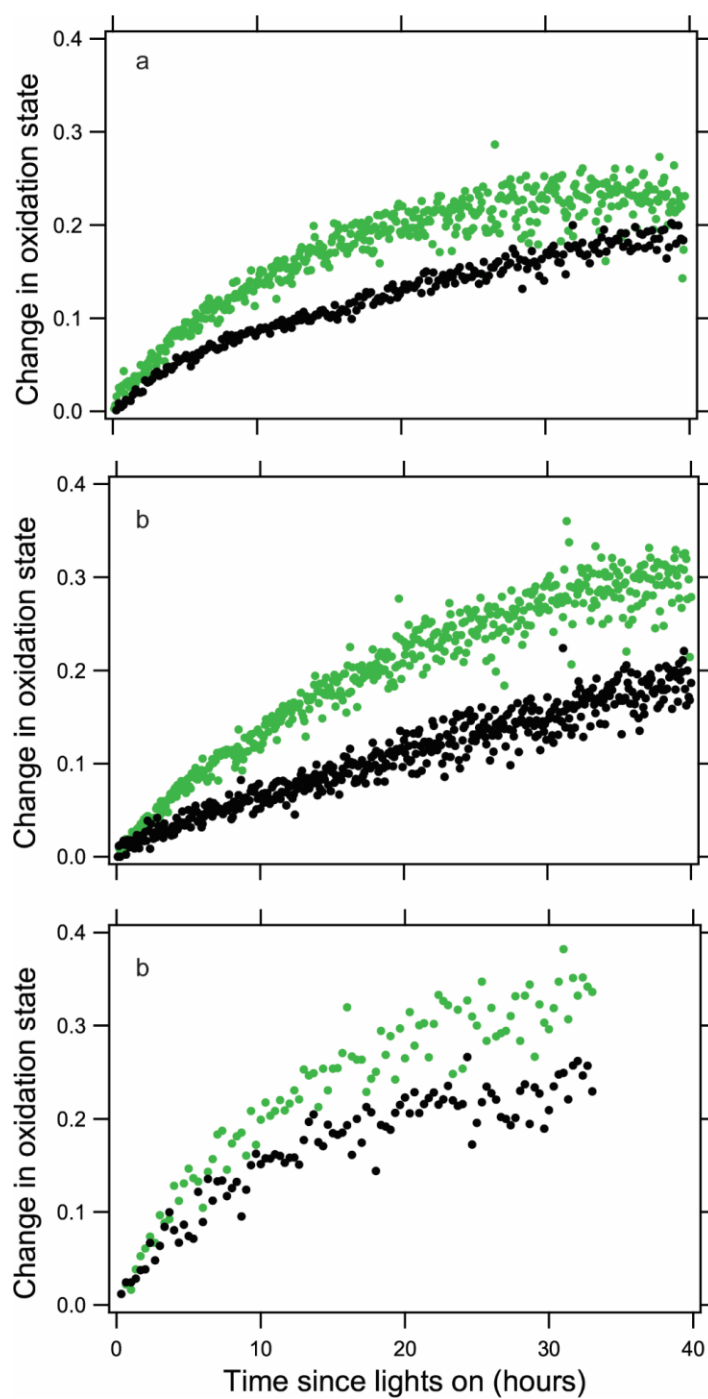


Figure S3. Change in oxidation states as a function of time in the chamber for irradiated (green) and dark (black) replicates. (a) experiment 1 (10 min averages), (b) experiment 2 (10 min. averages), (c) experiment 3 (20 min averages).

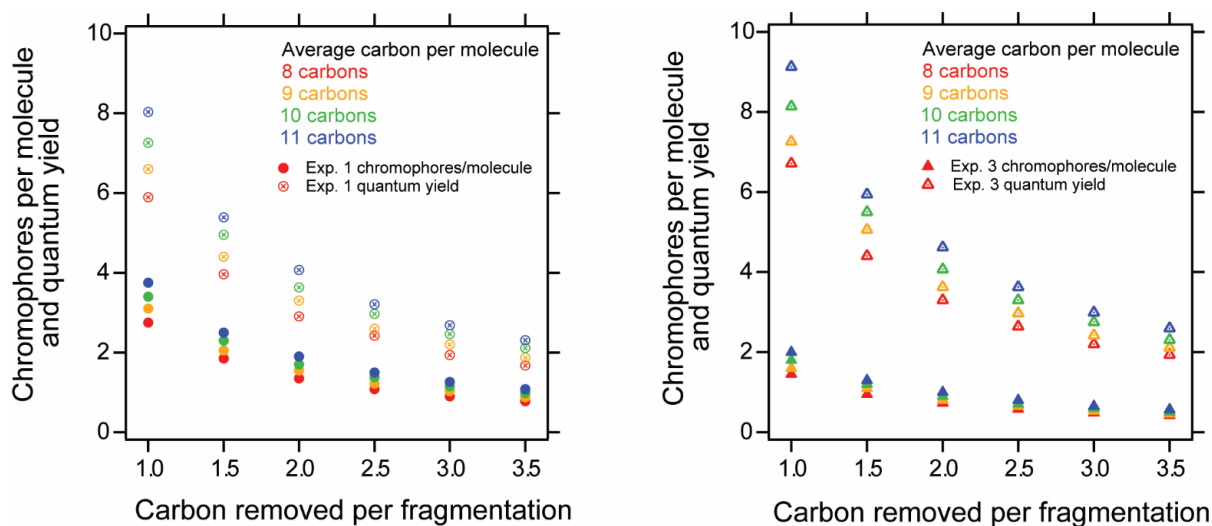


Figure S4. Chromophores/molecule and the quantum yield values from fits using 8-11 carbons for the average size of the SOA molecules and the carbons removed per fragmentation ranging from 1 to 3.5 carbons. (a) experiment 1, (b) experiment 3. Experiment 1 and 2 had very similar fits so only experiment 1 is shown.

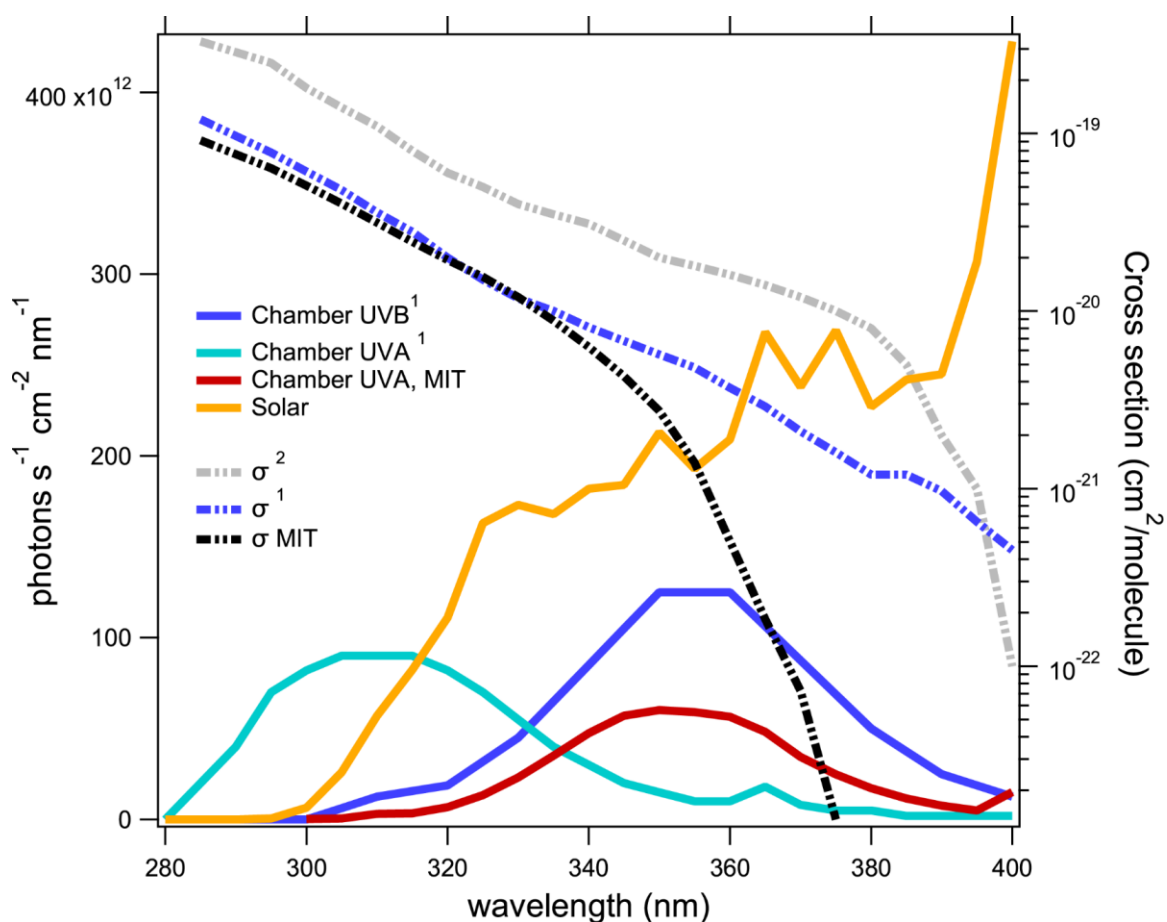


Figure S5. Photon flux (solid lines) and absorption cross sections (σ , dashed lines) for experiments carried out here (MIT) and from previous studies (blue, Wong et al., 2014; grey, Epstein et al., 2014). The solar actinic flux (yellow line) was obtained from the “Quick TUV Calculator” using the same parameters as used for Figure 1. from Wong et al., 2014, to aid comparison. The absorption cross section for the MIT chamber was collected from a replicate of experiment 1 (dark chamber). The calculated absorption cross section decreased dramatically at ~ 340 nm due to a small absorption cross section at those wavelengths and insufficient SOA concentration. Given the high degree of overlap at lower wavelengths, the absorption cross section from Wong et al., 2014 was used for model estimates.

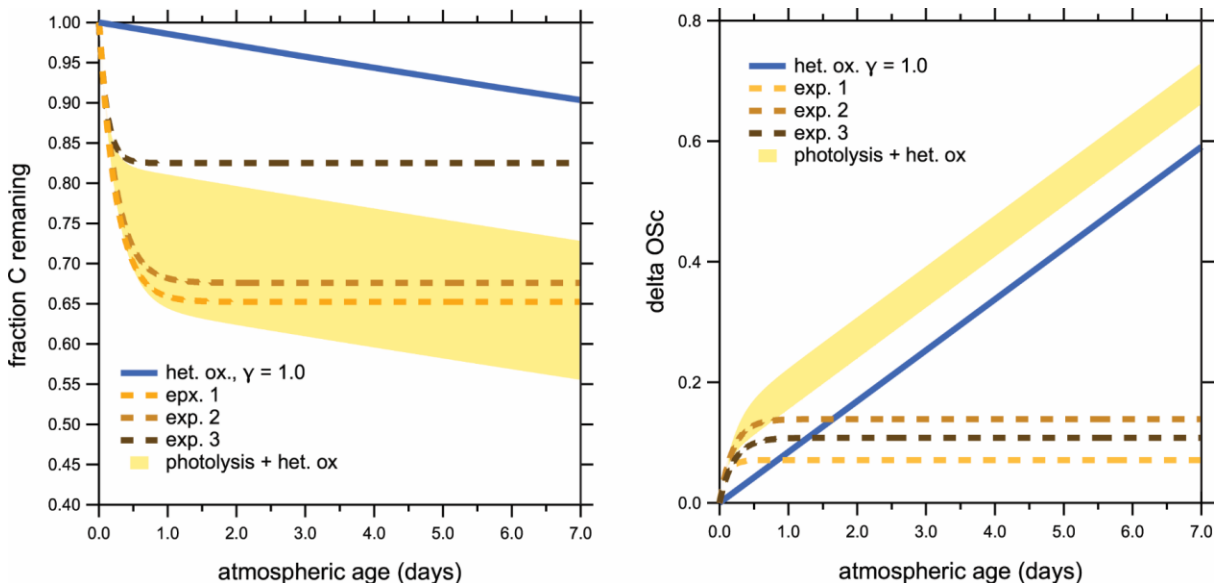


Figure S6. Predicted changes in (a) the fraction of carbon remaining and the (b) net change in carbon oxidation state as a function of particle age for photolysis (orange and brown dashed lines) and heterogeneous oxidation (blue).⁵ The shaded region shows the net change (photolysis + heterogeneous oxidation).

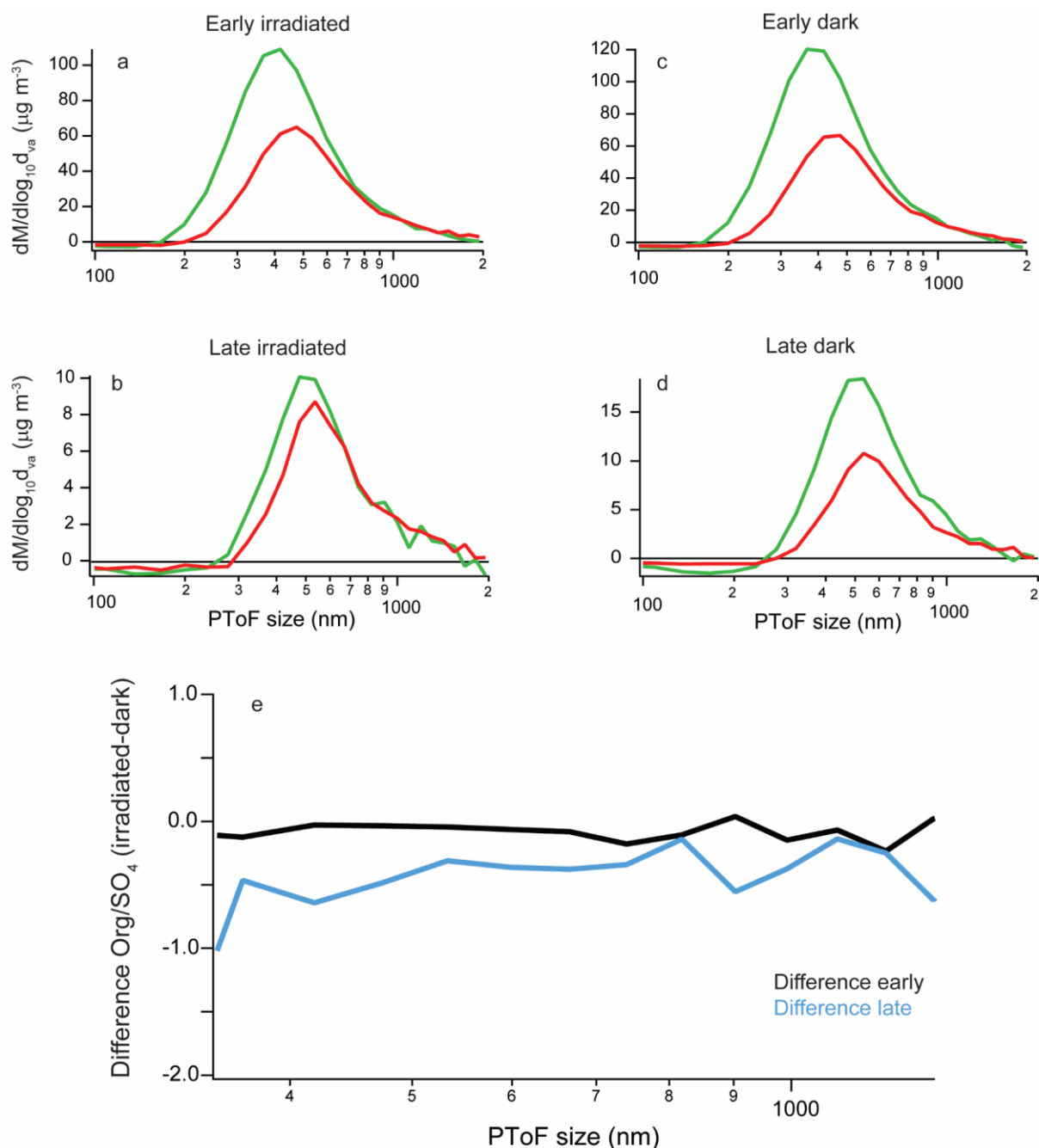


Figure S7. PToF data from experiment 1. (a-d) PToF sizes for organic (green) and sulfate (red). (a) and (b) are the photolyzed samples for experiment 1, (c) and (d) are the dark control. (e) Org/SO₄ ratios for the difference between the irradiated and dark experiments. Early times correspond to ~ 2 hours' worth of data before the lights are turned on (or would have been turned on) and late corresponds to the last few hours of the experiment. A size dependent shift in composition is observed (a vs. b and c vs. d), however, the difference is relatively constant across the particle size range measured with the pToF.

References

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