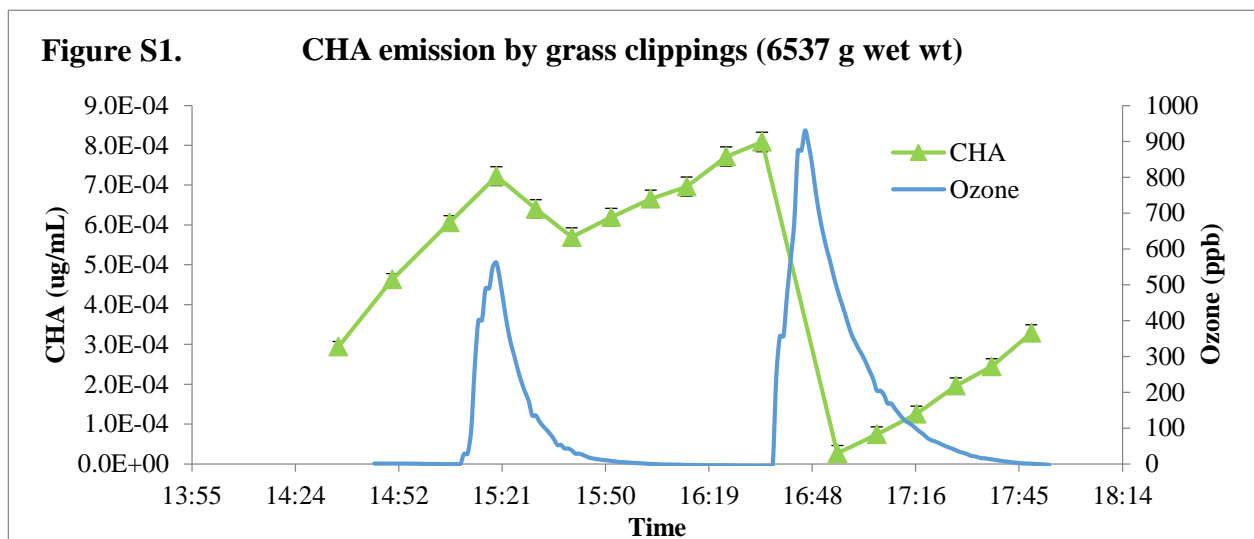


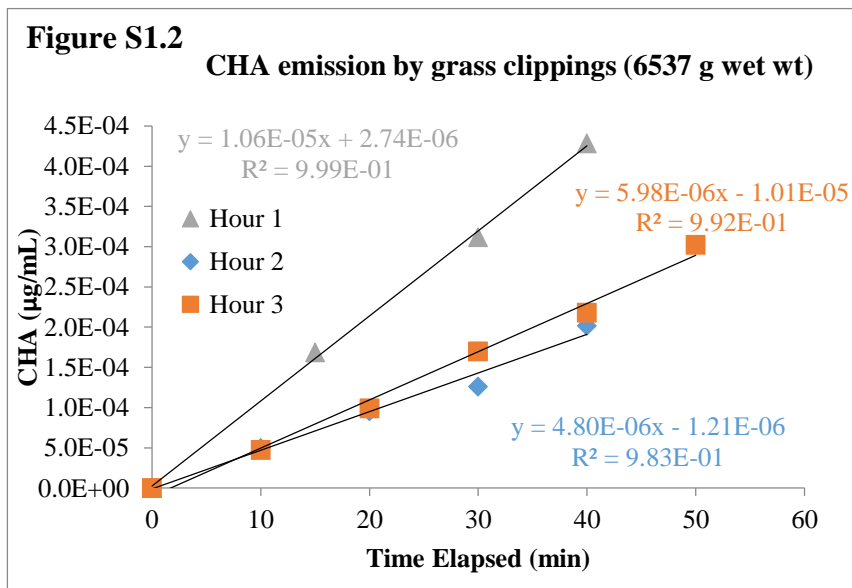
Supplemental Material

S1. GLV Emission by Grass Clippings

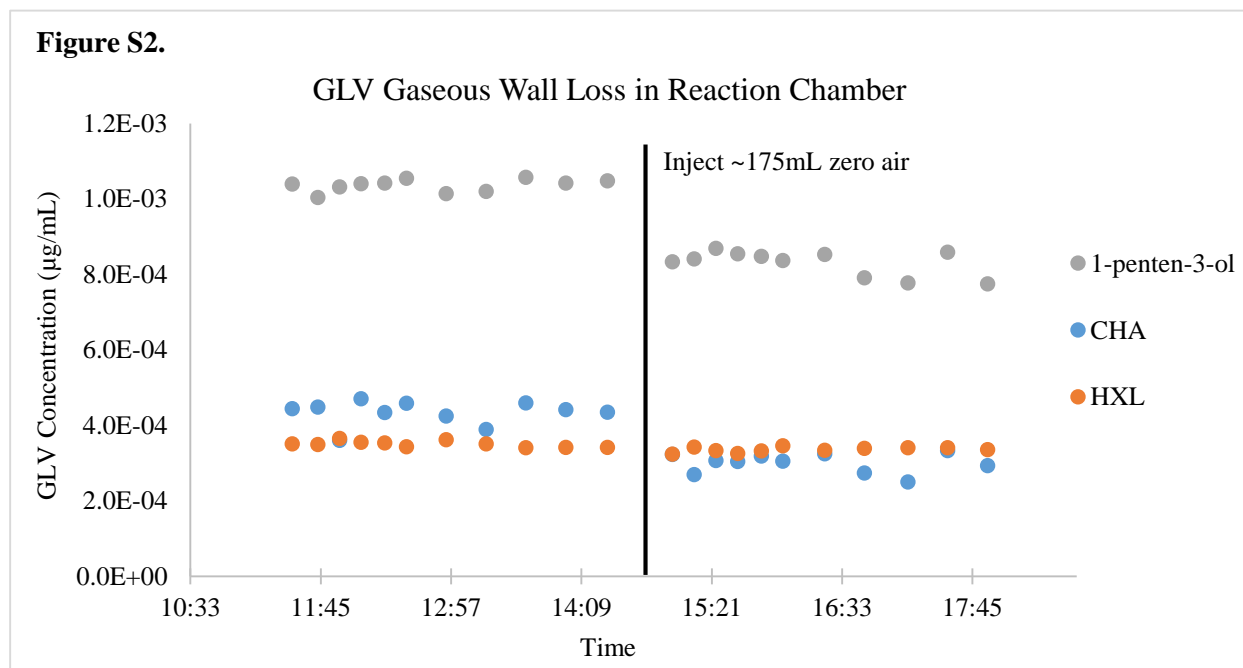
6537 g (wet weight) of grass clippings were placed inside an 8000 L Teflon reaction chamber, GLV concentration was monitored for a total of three hours (Figure S1). Except for the first sample ($6.1 \times 10^{-5} \mu\text{g/mL}$) HXL was not measured above the instrument detection limit and emission rates were not determined. After the first ~1 hour of measurement, ~500 ppb ozone was injected to the chamber as a concerted burst. CHA concentration decreased and ozone was completely consumed within 45 minutes, after which CHA concentration then increased over the course of ~1 hour, as it was re-emitted by the grass clippings. A second burst of ~950 ppb ozone was then injected and CHA concentrations again fell while ozone was consumed. Upon complete ozone consumption, CHA concentration increased for another ~1 hour. Lines between points were drawn to aid the eye.



A plot of the three, ~60 min long periods over which CHA concentration was measured versus time (Figure S1.2), yields an average CHA emission rate of $1.09 (+/- 0.5) \times 10^{-9} \mu\text{g mL}^{-1} \text{min}^{-1} \text{gram grass}^{-1}$. CHA concentration was normalized to the initial concentration during that hour to give CHA emitted as a function of time elapsed.



S2. GLV Wall Loss in Reaction Chamber



3 µL of an equimolar mix of GLVs was injected into the reaction chamber and monitored for 3 hours. At time 14:24 (as indicated by a black line in Figure B1), an additional ~175 mL of zero air was added to dilute the chamber air and the GLVs were monitored for an additional 3 hours to investigate if any observed wall loss was reversible.

A decrease in concentration from any of the GLVs in the first 3 hours of the experiment would indicate that the GLVs were partitioning/sorbing onto the chamber walls. The concentration for all GLVs, however, remained constant throughout the experiment, **indicating little or no gaseous wall loss for any of the species.**

If a GLV had shown loss to the reaction chamber walls within the first 3 hours (as evidenced by a decrease in concentration), then remained constant or increased in concentration after the dilution step, it would demonstrate *reversible* wall losses as described by Loza et al.¹ However, as stated above, we saw no evidence of wall loss of our gaseous GLVs, and therefore no reversible wall loss either.

Despite being injected at an equimolar ratio, the measured concentration for CHA and HXL ($\sim 4 \times 10^{-4}$ µg/ml) was less than that for 1-penten-3-ol (1×10^{-3} µg/ml). The disparity may be a result of the incomplete transfer of GLV into the reaction chamber (sorption to tubing from bulb to reaction chamber), although this would be expected to have occurred in calibration measurements as well, which would have accounted for losses. The reason for the difference in signal is not clear, but is inconsequential to conclusions that can be made from this experiment.

¹ Loza, C. L., Chan, A. W. H., Galloway, M. M., Keutsch, F. N., Flagan, R. C., and Seinfeld, J. H.: Characterization of Vapor Wall Loss in Laboratory Chambers, *Environ Sci Technol*, 44, 5074-5078, Doi 10.1021/Es100727v, 2010.

S3. 1-penten-3-ol Ozonolysis

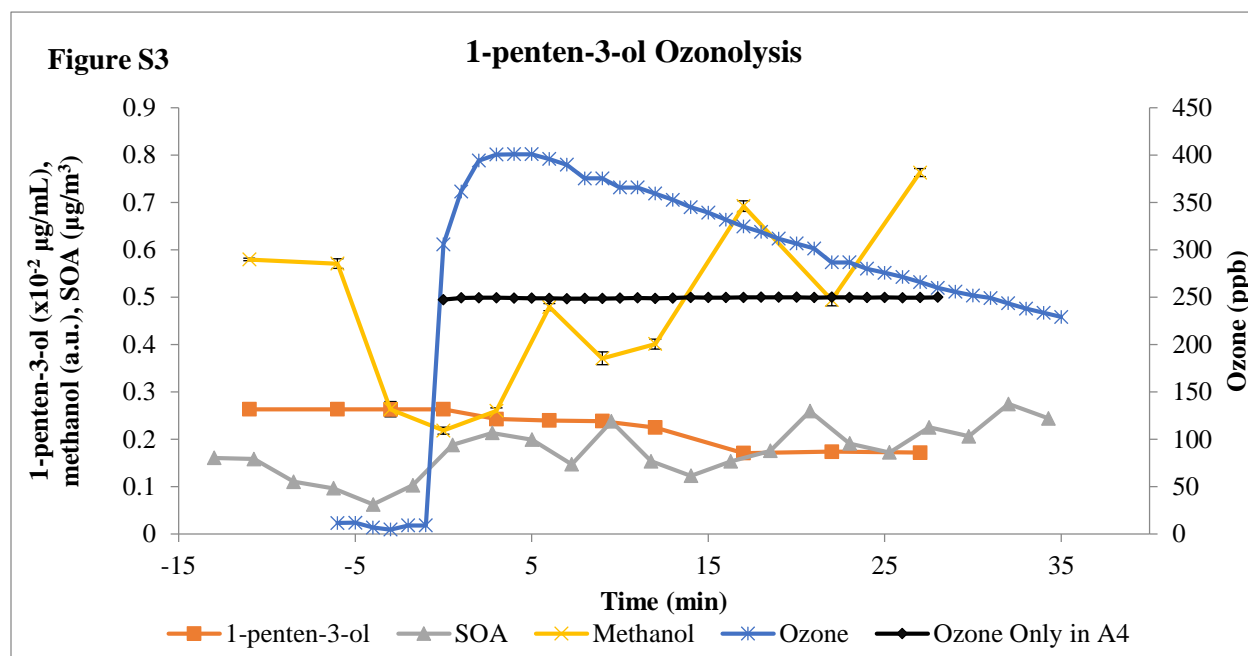
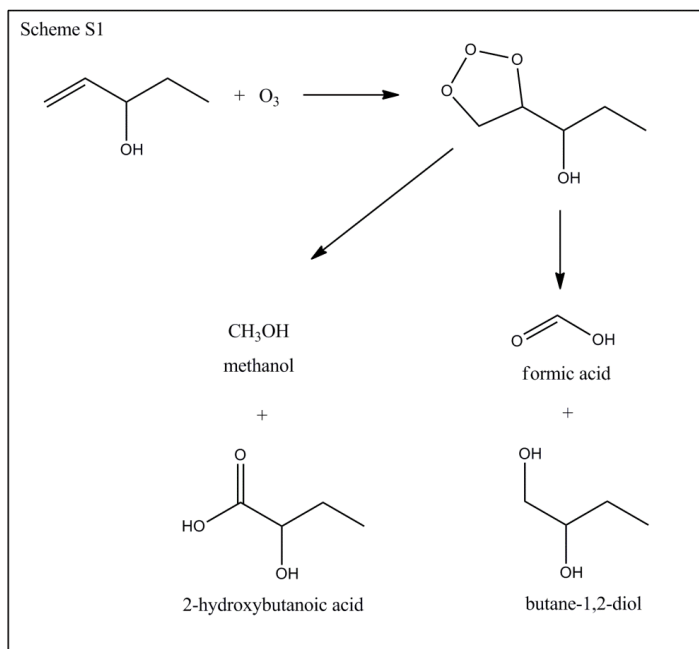


Figure S3 is the reaction profile for 1-penten-3-ol ozonolysis. Lines were drawn to aid the eye. 2.5 μL of 1-penten-3-ol was injected into the experimental chamber resulting in an initial concentration of $2.6 \times 10^{-3} \mu\text{g/mL}$. At time zero, 400 ppb ozone was injected.

Initial SOA concentration was about $0.15 \mu\text{g/m}^3$ and though it showed an increasing trend over the course of the experiment (final concentration of about $0.25 \mu\text{g/m}^3$), it never exceeded what we consider background levels; $<0.3 \mu\text{g/m}^3$.

At a 95% confidence level, the average 1-penten-3-ol concentration pre- and post-ozonolysis (2.6×10^{-3} and $2.2 \times 10^{-3} \mu\text{g/mL}$, respectively) are statistically different. However, upon injection of ozone, 1-penten-3-ol concentration did not show a dramatic drop in concentration, suggesting the decrease was not due to ozonolysis.

Ozone concentration (blue 'x') fell to about 225 ppb by the end of the experiment, but did not show the second order consumption (exponential decrease) that is indicative of the alkene-ozone reaction. However, in a separate experiment 250 ppb ozone was injected



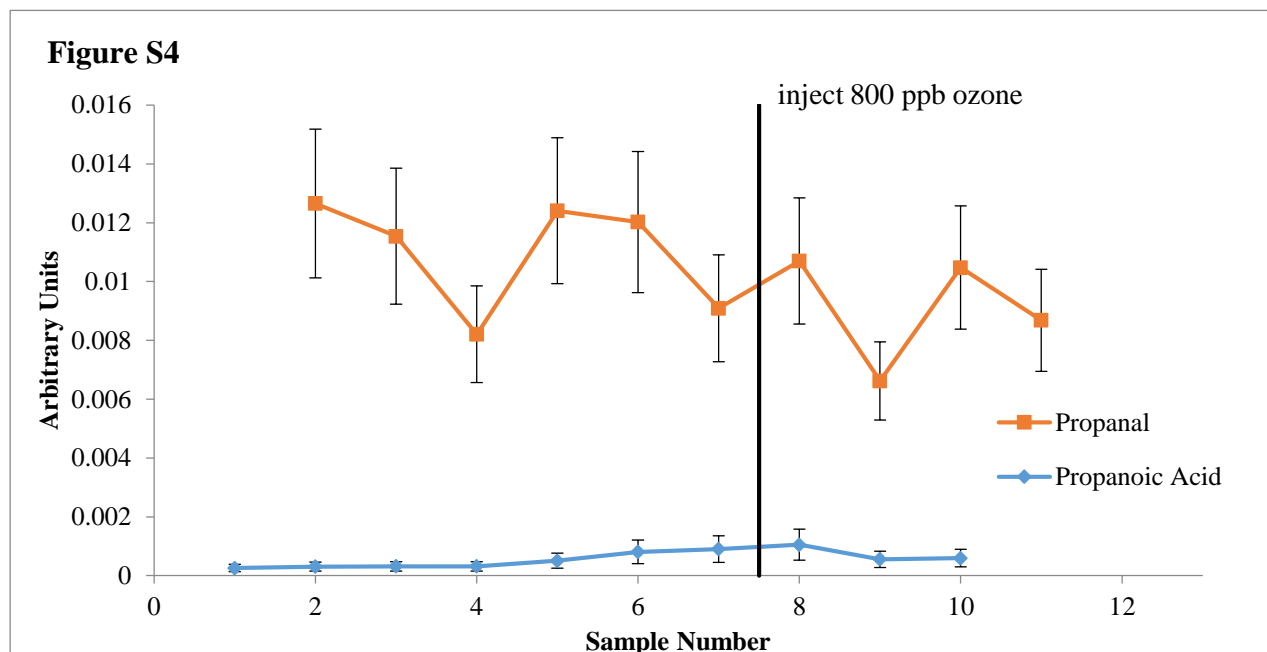
into the reaction chamber alone (black circle) and remained constant (251 +/-0.5% ppb) for over 5 hours.

According to Scheme S1, predominant products from the ozonolysis of 1-penten-3-ol include 1,2-butanediol, 2-hydroxybutanoic acid, methanol and formic acid. 1,2-butanediol and 2-hydroxybutanoic acid were not observed, but may need derivatization for analysis by GC/MS. Methanol was observed and does show an increasing trend in signal post ozonolysis, but the signal is sporadic.

The slight, sporadic increase in methanol signal and decrease in ozone concentration suggests that 1-penten-3-ol does have limited reactivity with ozone, but does not appear to produce significant SOA.

Lines in Figure S3 were drawn to aid the eye.

S4. Propanal Oxidation by Ozone

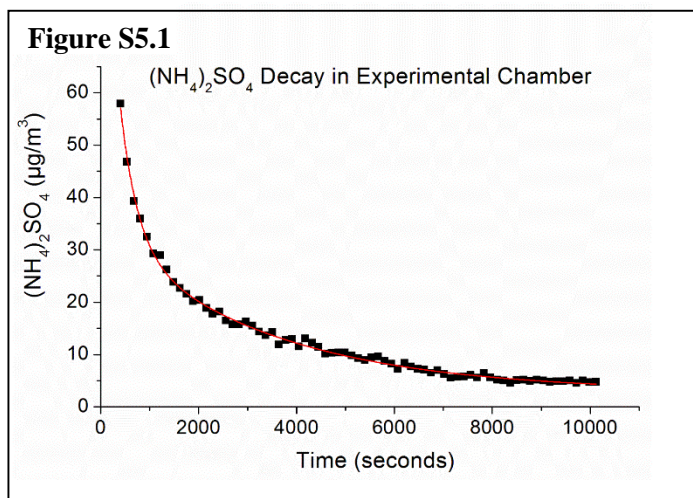


5 μL propanal was injected to the reaction chamber, resulting in a final concentration of $5.2 \times 10^{-3} \mu\text{g/mL}$. The signal from propanal remained relatively constant (within 20% as indicated by 20% error bars) throughout the experiment, at the 95% confidence level the average signal from propanal is not significantly different pre- and post-ozone injection. Suggesting it is not reactive with ozone.

Although its signal varied by 50% over the course of the experiment (50% error bars), at the 95% confidence level the average signal from propanoic acid is not significantly different pre- and post-ozone injection

Lines in Figure S4 were drawn to aid the eye.

S5. Aerosol wall loss in experimental chamber



Ammonium sulfate ((NH₄)₂SO₄) seed particles were injected into the reaction chamber and mass concentration was monitored for three hours. The decay in particle mass (µg/m³) was plotted against time (seconds) (Figure S5.1) and the data best fit a double exponential curve with the equation:

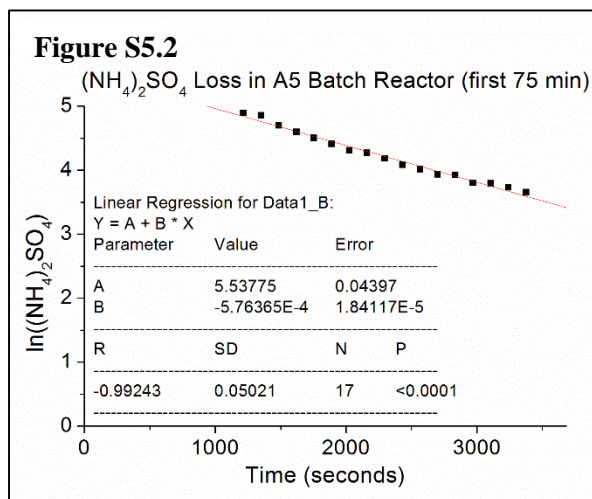
$$y = 2.86 + 27.45 * e^{\left(\frac{-x-404.7}{3332}\right)} + 26.81 * e^{\left(\frac{-x-404.7}{353.1}\right)}$$

However, since particle mass was usually monitored for 60-75 min in experiments, the first 75 minutes of data was used to correct for wall loss. A plot of the ln(particle mass concentration (µg/m³)) against time (seconds) (Figure S5.2) yields a straight line with equation:

$$y = -5.76 \times 10^{-4}x + 5.53$$

$$R^2 = 0.99$$

The absolute value of the slope of this line (5.76 x 10⁻⁴) can be used to correct for wall losses in experiments using equation S1 below, which was derived in accordance with Presto et al.²



$$\text{Wall Loss Corrected SOA}_{\text{max}} (\mu\text{g}/\text{m}^3) = \exp((t_{\text{max}}) \times (5.76 \times 10^{-4}) + \ln(\text{SOA})_{\text{max}}) \quad (\text{S1})$$

where SOA_{max} is the maximum SOA concentration measured (µg/m³) and t_{max} is the time at which this SOA max was measured (seconds post injection of ozone).

² Presto, A. A., et al. (2005). "Secondary Organic Aerosol Production from Terpene Ozonolysis. 1. Effect of UV Radiation." *Environmental Science & Technology* 39(18): 7036-7045.

A similar approach to determining particle loss can be made using SOA generated by the ozonolysis of GLV standards. For example, a HXL ozonolysis experiment gave the SOA profile in Figure S5.3. The HXL-derived SOA decay fits the exponential equation:

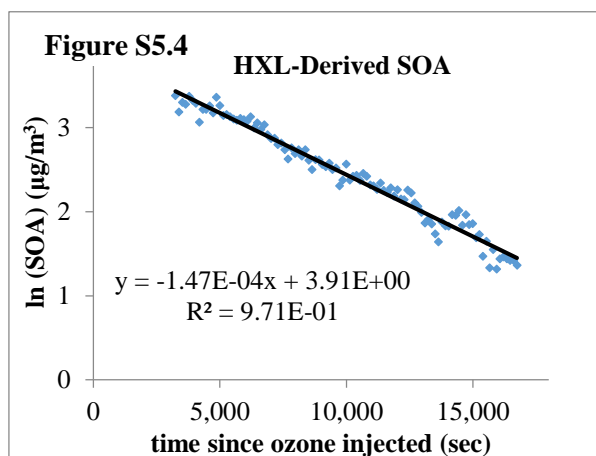
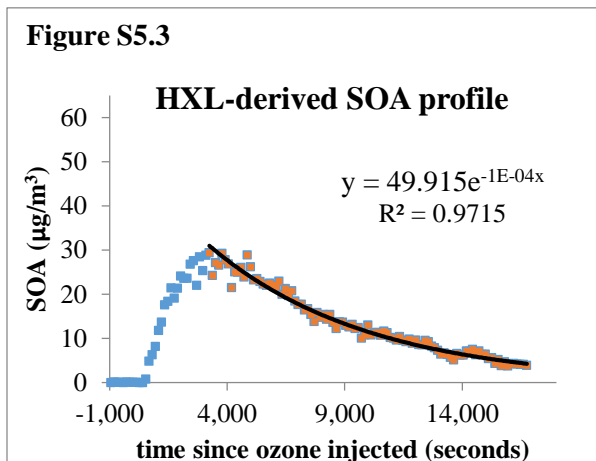
$$y = 49.915e^{-1E-04x}$$

Extrapolation to time zero (when ozone was injected) yields a SOA_{max} of 49.9 µg/m³, which represents the loss-corrected maximum SOA concentration, as compared to the maximum SOA measured; 29.4 µg/m³.

A plot of ln(SOA) against time (Figure S5.4) gives a straight line with y-intercept 3.91, which also corresponds to a maximum SOA concentration of 49.9 µg/m³.

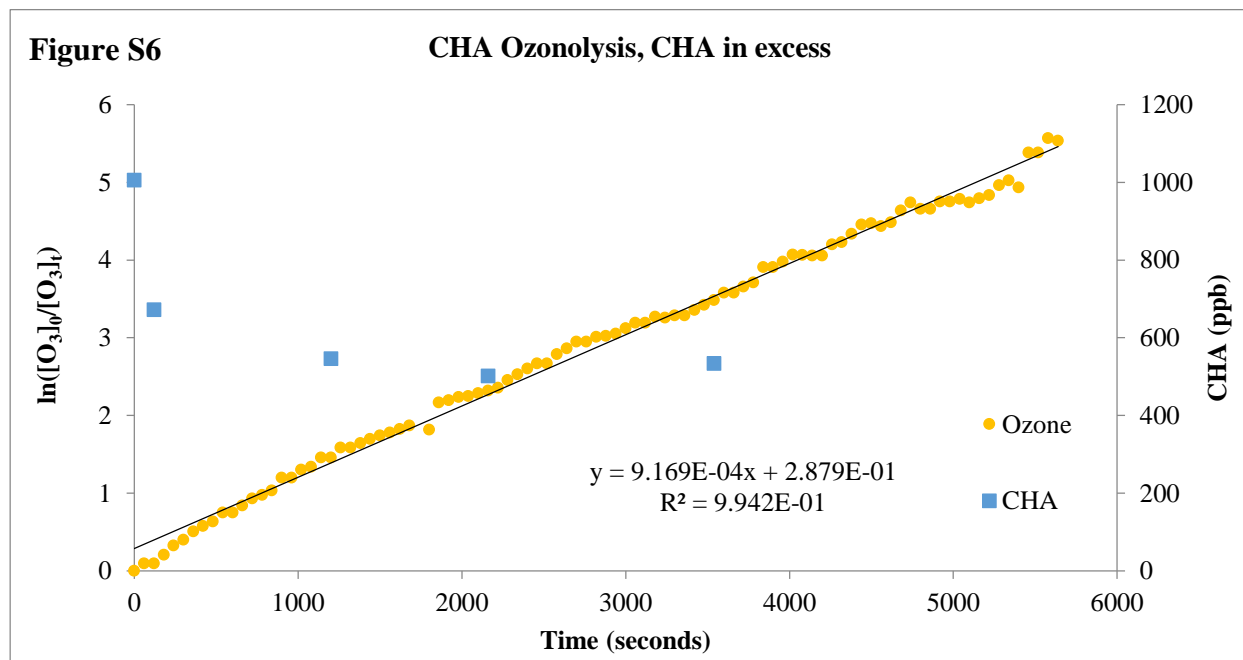
The (NH₄)₂SO₄ wall-loss correction gives a corrected maximum SOA concentration for the HXL-derived SOA of 190 µg/m³, a concentration even greater than the HXL-derived SOA wall loss term gives. Additionally, the slope of the HXL-derived SOA wall loss is -1.47x10⁻⁴ whereas the average slope of the (NH₄)₂SO₄ seed particles was -5.76 x10⁻⁴, almost four times that of the HXL-derived wall loss plot. Wall-loss is a function of both mass concentration and particle diameter. However, the mass concentration in the (NH₄)₂SO₄ wall-loss experiment and the HXL-derived SOA wall-loss experiment were on the same order of magnitude, and the average particle diameter was ~315 nm in both experiments.

The disparities in slope and corrected SOA_{max} between the two methods suggest that the processes leading to HXL-derived SOA decay are not fully modeled by (NH₄)₂SO₄ seed particles; there are likely other processes (phase partitioning, secondary reactions) leading to HXL-derived SOA loss. However, we chose to use the (NH₄)₂SO₄ seed particle wall loss correction term to remain in accordance with conventional practices, which use these inorganic seeds to determine SOA loss to experimental chambers.³



³ Carter, W. P. L., et al. (2005). "A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation." *Atmospheric Environment* **39**(40): 7768-7788., Cocker, D. R., et al. (2001). "State-of-the-Art Chamber Facility for Studying Atmospheric Aerosol Chemistry." *Environmental Science & Technology* **35**(12): 2594-2601.,

S6. Reaction Rate Constant Determination



In order to determine the rate expression for CHA and HXL ozonolysis, pseudo-first order reaction conditions were imposed by holding the GLV in excess and monitoring the consumption of ozone over the course of about one hour. GLV concentration was measured periodically throughout the reaction to ensure it remained in excess.

A plot of $\ln([O_3]_0/[O_3]_t)$, where $[O_3]_0$ is the initial ozone concentration and $[O_3]_t$ is the ozone concentration at time (t), against time (seconds) yielded a straight line with a slope of the observed rate constant (k_{obs})(sec^{-1}). (Figure S6)

The rate constant was then found using equation S2.

$$k_2 = \frac{k_{obs}}{[GLV]_0} \quad (\text{S2})$$

Where $[GLV]_0$ is the initial concentration of the GLV (molecules cm^{-3}).

This experiment was done twice for each GLV separately in the and the average rate constant was determined to be $3.6 (+/- 0.9) \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1} \text{ molecule}^{-1}$ and $7 (+/- 3) \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1} \text{ molecule}^{-1}$ for CHA and HXL respectively.

Date	k_2 ($\times 10^{-17} \text{ cm}^3 \text{ sec}^{-1} \text{ molecule}^{-1}$)	
	CHA	HXL
5/1/2013	4.57	5.79
5/3/2013	2.78	9.75
avg	3.58	6.6
stdev	0.90	2.7

S7. Contribution of Lawn Mowing to Atmospheric SOA

SOA concentration ($\mu\text{g}/\text{m}^3$) as a function grass dry weight (grams) (gdw) was determined for a series of grass clipping experiments throughout 2012. Assuming worst case scenario, the greatest SOA contribution was measured to be $82.0 \mu\text{g}/\text{m}^3$ SOA per 182 gdw grass for a particular mowing event. Normalization of this SOA concentration to our chamber volume (0.775 m^3) and application of wall-loss corrections, allowed us to estimate a SOA production rate of $0.70 \mu\text{g}/\text{gdw}$ SOA.

According to the New York State Department of Conservation, up to 6 tons of grass clippings (dry weight) can be produced per acre of lawn mowed, annually.⁴ Stevenson (2010) estimated that New England homeowners mow their lawns 20 times annually.⁵ These metrics correspond to a grass clipping production rate of $\sim 67 \text{ g}/\text{m}^2$ annually.

Using the SOA production rate above ($0.70 \mu\text{g}/\text{gdw}$) and the mass of grass clippings produced by an area of lawn mowed ($\sim 67 \text{ g}/\text{m}^2$ annually) yields an area-normalized SOA emission rate of $47 \mu\text{g}/\text{m}^2$ SOA per mowing or $936 \mu\text{g}/\text{m}^2$ SOA annually.

⁴ New York State Department of Conservation, Bureau of Waste Reduction and Recycling, "Leave it on the Lawn," 2013.

⁵ Stevenson, N. (2010). Encouraging Environmentally Responsible Lawn Care Behavior in New England: Utilizing Social Science to Develop Successful Outreach and Education. Environmental Science and Policy, Plymouth State University. M.S.: 172.