



Establishing the
contribution of lawn
mowing

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Establishing the contribution of lawn mowing to atmospheric aerosol levels in American suburbs

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Abstract

Green leaf volatiles (GLVs) are a class of wound-induced volatile organic compounds emitted by several plant species. Turfgrasses emit a complex profile of GLVs upon mowing, as evidenced by the “freshly cut grass” smell, some of which are readily oxidized in the atmosphere to contribute to secondary organic aerosol (SOA). The contribution of lawn mowing-induced SOA production may be especially impactful at the urban/suburban interface, where urban hubs provide a source of anthropogenic oxidants and SOA while suburban neighborhoods have the potential to emit large quantities of reactive, mow-induced GLVs. This interface provides a unique opportunity to study aerosol formation in a multi-component system and at a regionally relevant scale. Freshly cut grass was collected from a study site in Essex Junction, Vermont and was placed inside a 775 L Teflon experimental chamber. Thermal desorption gas chromatography mass spectrometry (TD-GC/MS) was used to characterize the emitted GLV profile. Ozone was introduced to the experimental chamber and TD-GC/MS was used to monitor the consumption of these GLVs and the subsequent evolution of gas phase products while a scanning mobility particle sizer was used to continuously measure aerosol size distributions and mass loadings as a result of grass clipping ozonolysis.

Freshly cut grass found to emit a complex mixture of GLVs, dominated by *cis*-3-hexenyl acetate and *cis*-3-hexenol, which were released at an initial rate of 1.8 (± 0.5) μg and 0.07 (± 0.03) μg per square meter of lawn mowed with each mowing. Chamber studies using pure standards of *cis*-3-hexenyl acetate (CHA) and *cis*-3-hexenol (HXL) were found to have aerosol yields of 1.2 (± 1.1)% and 3.3 (± 3.1)%, respectively. Using these aerosol yields and the emission rate of these CHA and HXL by grass, SOA evolution by ozonolysis of grass clippings was predicted. However, the measured SOA mass produced from the ozonolysis of grass clippings exceeded the predicted amount, by upwards of $\sim 150\%$. The ozonolysis of a mixture of CHA and

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HXL representative of environmental mixing ratios also failed to accurately model the SOA mass produced by grass clippings.

Aerial photographs and geospatial analysis were used to determine the turfgrass coverage in a suburban neighborhood, which was then used along with measured SOA production as a function of grass mowed to determine that lawn mowing has the potential to contribute $47 \mu\text{g m}^{-2}$ SOA to the atmosphere per mowing event by ozonolysis, which cannot be modeled solely by the ozonolysis of CHA, HXL or a representative mixture of the two.

1 Introduction

Volatile organic compounds (VOCs) are emitted by both biogenic (BVOCs) and anthropogenic (AVOCs) sources and play an important role in the chemistry of the atmosphere. The photooxidation of VOCs can lead to the formation of ozone, with which other VOCs can react (along with other atmospheric oxidants) to produce secondary organic aerosol (SOA) (Hallquist et al., 2009; Kroll and Seinfeld, 2008). Organic aerosols, including SOA are a major component of fine aerosols and influence climate through direct and indirect effects, although there is an expressed high degree of uncertainty about the magnitude of these effects (Kanakidou et al., 2005; Solomon et al., 2007). SOA also impacts local weather patterns and has been associated with deleterious impacts on human health (Miller-Schulze et al., 2011; Diaz et al., 2011). Currently, there remains significant uncertainty in our understanding of the environmental impact of SOA, owing to a still limited knowledge of its sources, composition, properties, and the mechanisms that lead to its formation and ageing (Hamilton et al., 2009; Carlton et al., 2009; Shilling et al., 2013). Identifying the sources, interactions and reactivity of VOCs is integral to understanding their impact on the formation of SOA and consequently on regional air quality and climate patterns.

Globally, biogenic SOA (BSOA) predominates over anthropogenic SOA (ASOA) (Hallquist et al., 2009). Though our understanding of the mechanisms that lead to SOA

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formation has improved, significant gaps exist in our understanding of SOA formation and ageing, namely our understanding of systems with competing reactive pathways. Several recent studies have stressed the potential importance of interactions between AVOCs, BVOCs and oxidants in SOA formation and ageing, and yet these interactions remain largely uncharacterized (Emanuelsson et al., 2013; Glasius et al., 2011; Spracklen et al., 2011; Hoyle et al., 2011; Shilling et al., 2013). Of special interest to our group is SOA production and ageing at the interface of urban and suburban/rural landscapes. This interface offers the unique opportunity to study atmospherically relevant mixtures of anthropogenic and biogenic VOCs and SOA, as will be discussed.

Characterized by a “freshly mowed lawn” smell, the cutting of turfgrass enhances emission of a complex mixture of C₅ and C₆ BVOCs, along with other low molecular weight oxygenated BVOCs (Kirstine et al., 1998; Brilli et al., 2011, 2012; Karl et al., 2005; Ormeno et al., 2010; Hatanaka, 1993; Kirstine and Galbally, 2004; Jardine et al., 2012; de Gouw et al., 1999). Together these BVOCs are termed green leaf volatiles (GLVs) (Karl et al., 2001). The most documented GLVs include the C₆ compounds *cis*-3-hexenal, *cis*-3-hexenol (HXL), *cis*-3-hexenyl acetate (CHA), and *trans*-2-hexenal. More recently, C₅ compounds (*cis*-2-penten-1-ol and 1-penten-3-ol) have also been identified in the wound-induced emissions of plants (Jardine et al., 2012; Karl et al., 2001; Orlando et al., 2001). Not only do these compounds have interesting roles in plant protection and plant-plant/plant-animal communication, GLVs also actively take part in atmospheric chemistry (Brilli et al., 2012; Pinto et al., 2007; Hartikainen et al., 2012).

Though individual VOCs differ greatly in their reactivity and consequently their SOA-forming potential, many grass-GLVs contain unsaturated double bonds, which are readily oxidized by ozone, hydroxyl radicals and nitrate radicals, providing important potential pathways to the generation of photochemical smog and SOA (Kirstine and Galbally, 2004; Aschmann et al., 1997; Orlando et al., 2001; Hamilton et al., 2009; O’Dwyer et al., 2010; Reisen et al., 2003; Joutsensaari et al., 2005). Brilli et al. (2012) estimate that grassland ecosystems emit up to 130 mg C m⁻² GLVs annually. Several other studies

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have reported GLV emission rates on the same order of magnitude for mowed grasses (de Gouw et al., 1999; Olofsson et al., 2003; Kirstine et al., 1998). Lawn coverage in the US is estimated at 10–16 million ha, which corresponds to a total of ~ 13 – 21 Gg C yr^{-1} of GLVs emitted by lawns in the US alone (Robbins and Birkenholtz, 2003). Omitting methanol and other low molecular weight GLVs, which account for $\sim 70\%$ of total GLV emissions and are not readily oxidized in the atmosphere, reactive lawn-GLV emissions can be estimated at between 3.9 and 6.3 GgC annually. Annual non-methane VOCs in North America are estimated at 84 TgC (Guenther et al., 2000; Brilli et al., 2012; Kirstine and Galbally, 2004; Kirstine, 2002).

The role reactive GLVs play in global SOA levels, however is not straightforward. Reports of GLV aerosol yields are varied. CHA is reported to have 8.5–24% aerosol yield from ozonolysis and less than 1% aerosol yield from photooxidation, while HXL has been reported to have 9.6% and 3.1% aerosol yield from ozonolysis and photooxidation, respectively (O'Dwyer et al., 2010; Hamilton et al., 2009; Hamilton et al., 2008). Based on GLV emission rates and SOA yield efficiencies, lawns in the US alone therefore have the potential to contribute $\sim 1.5 \text{ Gg C}$ of SOA to the atmosphere annually. Hamilton et al. (2009) estimated that photooxidation of the predominant C_6 GLVs HXL and CHA contribute as much as 1 – 5 Tg C yr^{-1} SOA to global emissions, which current models estimate to be between 25 – 300 Tg C yr^{-1} (Hamilton et al., 2009; Cahill et al., 2006; Hallquist et al., 2009; Solomon et al., 2007b). *Photooxidation* of these two GLVs alone could contribute a significant fraction of global SOA. The *ozonolysis* of GLVs, however, having greater aerosol yields than photooxidation, is likely to be an additional, significant SOA source to the atmosphere with important contributions to climate forcing and air quality at the airshed.

Hamilton et al. (2009) established the importance of GLV oxidation to global SOA using single-component systems, with one oxidant being introduced to each GLV separately. We extend this work by representing the multi-component system experienced in the environment, especially at the urban/suburban interface. At this interface, traffic and industry located in urban hubs provide a source of anthropogenic oxidants and

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ASOA, while suburban neighborhoods, with their sprawling monocultural lawns and recreational fields, have the potential to emit large quantities of mow-induced GLVs and BSOA. This scenario provides a unique opportunity to study aerosol formation in a multi-component system and at a regionally relevant scale (Nemitz et al., 2009; Karl et al., 2001; de Gouw et al., 1999; Gulden et al., 2007; Lefohn et al., 2010; Guenther et al., 2012; Steinbrecher et al., 2000). Since grass mowing typically occurs on hot sunny days in a regionally, seasonally and sometimes temporally coordinated fashion, emission of reactive GLVs is expected to occur in large-scale bursts. Simultaneously, tropospheric ozone is present at elevated concentrations on hot sunny days (Steinbrecher et al., 2000). In urban and suburban environments, GLV bursts into oxidizing atmospheric conditions therefore, provide an opportunity for concerted bursts of SOA into an airshed (Karl et al., 2001; Kirstine and Galbally, 2004). The interface between urban and suburban landscapes provides the opportunity to study SOA formation in a multi-component system at a small spatial and temporal scale, where ASOA can exceed BSOA and where processes leading to SOA formation could be different from those in largely forested regions (Emanuelsson et al., 2013; Fushimi et al., 2011; Steinbrecher et al., 2000; Starn et al., 1998; Aiken et al., 2009).

Although the GLV-emission profile of several grass and clover species has been characterized (Watkins et al., 2006; Olofsson et al., 2003; Kirstine et al., 1998; Karl et al., 2001; de Gouw et al., 1999; Brilli et al., 2012, 2011; Kirstine and Galbally, 2004; Kirstine, 2002) and the SOA yields of several individual GLVs have been estimated (Hamilton et al., 2009; Aschmann et al., 1997; O'Dwyer et al., 2010; Joutsensaari et al., 2005), to the best of our knowledge there is no reported work on GLV mixtures with respect to their aerosol yields. In this work, a holistic approach to understanding GLV oxidation and SOA evolution has been used to characterize the contribution of lawn mowing to local SOA levels. Thermal desorption gas chromatography mass spectrometry (TD-GC/MS) was used to characterize the VOC profile of mowed grass. TD-GC/MS was also used to monitor the consumption of GLVs upon ozonolysis and

the subsequent evolution of gas phase products, while aerosol size distributions and mass loadings were continuously measured using a scanning mobility particle sizer.

We show that the mow-induced GLV emission profile from turfgrass in a suburban neighborhood in Vermont, USA is dominated by CHA and HXL, which readily undergo oxidation by ozone to form SOA. Aerosol yields were determined for each GLV individually and used to predict SOA evolution for simple, atmospherically relevant mixtures of HXL and CHA and for grass clippings collected from the field. An apparent disparity between predicted and measured SOA production, along with the volatile product profile of each chemical system are discussed herein, highlighting the need to understand more fully the dynamic chemical interactions posed at the urban/suburban interface.

2 Experimental

Cis-3-hexenyl acetate (> 98 %) and *cis*-3-hexenol (99 %) were purchased from Sigma Aldrich and were used without further purification. Dry, zero air was produced by passing compressed air sequentially through silica, activated carbon and HEPA filters. This zero air was also used to generate ozone using a commercially available corona discharge ozone generator (OLSOA/DLS OzoneLab). Ozone concentrations were monitored with an American Ecotech Serinus O₃ Monitor (model E020010).

All experiments were performed in a calibrated Teflon chamber with a volume of 775 L at ambient temperature (~ 23 °C) and atmospheric pressure. Between experiments, the chamber was passivated with O₃ at high concentrations (1–2 ppm) and flushed with zero air to attain background aerosol mass loadings below 0.1 μg m⁻³.

Air samples were collected from the reaction chamber onto AirToxics glass sorption tubes (Perkin Elmer N9307008) that had been previously conditioned at 310 °C for 20 min and stored with Swagelok caps. Air was drawn through the sorption tubes using a personal sampler pump (SKC Airchek Sampler, model 224-44XR) at a constant rate of approximately 100 mL min⁻¹ (actual flow rate monitored by a F&J Specialty Products mini calibrator, model MC-500cc) for a known duration of time, allowing the total

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volume of air sampled to be determined. Typical sample volumes ranged between 0.6 and 3.6 L. Ozone scrubbers were not used because some have been shown to retain ozonolysis products (Uchiyama et al., 2012; Helmig, 1997).

Air samples were then transferred from the sorbent tubes by thermal two-step desorption (TurboMatrix TD 350, Perkin Elmer) to a gas chromatograph (Clarus 600, Perkin Elmer) equipped with a mass spectrometer (Clarus 600 T Perkin Elmer) detector. Prior to desorption, an internal standard of fluorobenzene (AirLiquide) was injected by the Turbomatrix TD directly onto the sorption tubes. During the first step of desorption, the sorbent tubes were heated to 330 °C for 8 min to desorb and cryo-focus GLVs onto a AirMonitoring trap held at -10 °C. The trap was then heated at a rate of 40 °C s⁻¹ to a final temperature of 310 °C, where it was held for 8 min. The GLVs were transferred to a GC analytical column (Stabilwax 30 m, 0.32 mm i.d., Restek) via a heated transfer line (250 °C). The GC oven was programmed as follows: held at 35 °C for 4 min, increasing 10 °C min⁻¹ to a final temperature of 220 °C. The total run time per sample was 22.5 min. The head pressure of the helium carrier gas was 1.8 psi, which resulted in a flow rate of 1.52 mL min⁻¹. Electron impact ionization (70 eV) was used and masses were scanned from 15 to 300 *m/z*. Chromatographic peaks were identified by comparison of retention times to those of known standards and by spectral matching with the NIST 2005 mass spectral library. Compounds were quantified on area basis using single ion monitoring.

Aerosol particle number and mass size distributions, as well as total aerosol mass loadings (assuming an average particle density of 1.2 g cm⁻³), were measured continuously with a scanning mobility particle sizer (SMPS, model SMPS 3080, TSI Inc., Shoreview, MN).

The vapor pressure of several organic ozonolysis products was estimated using structure based estimators courtesy of the Dortmund Data Bank found in the online database by Clegg et al. (2008). Estimates were made at 298K and are reported as an average of three estimates determined using methods described in references (Moller

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et al., 2008; Myrdal and Yalkowsky, 1997; Nannoolal et al., 2008, 2004; Stein and Brown, 1994).

2.1 Grass Experiments

The grass collection site chosen was located in a residential neighborhood in Essex Junction, VT (44.487653, -73.09365), approximately 10 miles east of Burlington, VT (Fig. 1). A geospatial analysis of the study site was performed using ArcGIS 9.0 software. Aerial photographs taken in 2004 were obtained from the Vermont Center for Geographic Information (Vermont Center for Geographic Information). The resolution of these photos was sufficient to visually identify residential turfgrass, ArcGIS software was used to quantify the area of turfgrass (36 acres) along with the total site area (131 acres).

A section of representative turfgrass comprised predominantly of genera *Festuca*, *Lolium* and *Poa* was mowed using a commercially available, residential lawn mower. Clippings were collected and transported in sealed paper bags to the University of Vermont, Burlington VT for analysis. Total time elapsed between mowing and sampling in Teflon chamber was between 60–90 min. Samples were collected from nine mowing events between September and November of 2012 and one event in May of 2013.

In grass “clipping” experiments, approximately 0.5 kg of grass clippings (wet weight) were placed directly inside the experimental chamber, which was then filled with zero air. Approximately 800 ppb ozone was injected directly into the chamber over the course of ~ 60 s. Grass clipping experiments were designed to represent environmentally relevant conditions, where ozone was allowed to interact with volatile species in the gas phase along with any reactive species contained within or on the blades of grass themselves. Whereas in “headspace” experiments, only volatile species within the headspace of grass clippings were flushed into the reaction chamber, to which ozone was then introduced. For the headspace experiments, approximately 150 grams of grass clippings (wet weight) were placed in a 0.4 L conical flask. Zero air was flushed through the conical flask for ~ 20 min into the reaction chamber, carrying the GLVs with

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it. Ozone was injected in the same manner as above. Headspace experiments represented a simplified version of the chemical system of interest, where only the volatile species emitted by cut grass were oxidized by ozone. In general, initial CHA and HXL concentrations were greater in headspace experiments than in clipping experiments.

This difference is likely due to experimental design; grass clippings were allowed to equilibrate in the experimental chamber for 20–30 min before ozone was injected while grass headspace was allowed to build up in the paper sampling bag for up to two hours before being flushed into the chamber. Grass clippings, however, continuously emitted GLVs (Supplement S1).

2.2 GLV standard experiments

GLV standards experiments were designed to further simplify headspace experiments and were used to determine whether SOA produced as the result of grass ozonolysis could be modeled by a single GLV or a two-component mixture of GLVs. Standards of CHA or HXL were introduced to the experimental chamber by evaporation via injection into a 3-neck flask over a warm water bath. A zero air carrier flow was flushed through the flask and into the reaction chamber for at least 15 min. Gaseous wall-loss of GLV standards was determined by monitoring GLV concentration within the reaction chamber for six hours. GLV concentration did not decrease over the course of this experiment, however and gaseous wall-loss was found to be insignificant (Supplement S2). Calibration was completed by collecting a known volume and thereby known mass of GLV standards from the experimental chamber onto TD tubes. Ozone was then injected as a brief burst and sampling continued. Standard experiments were carried out at a 1 : 1 and 1 : 2 GLV to O₃ molar ratio to determine aerosol yields and measure reaction products. High GLV mass loadings were used to ensure sufficient SOA mass and volatile product evolution for analysis.

Reaction rate constants (k) for the ozonolysis of CHA and HXL were determined using experimental protocol described elsewhere (Grosjean et al., 1993; Grosjean and Grosjean, 1994). Briefly, pseudo-first-order reaction conditions were induced, whereby

the GLV was present in excess of ozone, which was monitored throughout the reaction. A plot of $\ln([\text{Ozone}]_{t_0}/[\text{Ozone}]_t)$ vs time yields a straight line with slope k_{observed} . From the rate expression of the reaction, $k = k_{\text{observed}}/[\text{GLV}]_{t_0}$.

3 Results

3.1 GLV standard chamber experiments

3.1.1 Single GLV system

The total ion chromatogram (TIC) of GLVs emitted by cut grass (Fig. 2a) shows a relatively complex mixture of volatile organics, dominated by CHA, 1-penten-3-ol and 2-pentanone (peaks 5, 4 and 3, respectively). Also present is a significant amount of HXL (peak 6), which, along with CHA, is a SOA precursor when subjected to ozone (Scheme 1). This reactivity is clearly demonstrated by the TIC of the GLV mixture post-ozonolysis (Fig. 2b). 2-pentanone contains no chemical unsaturations and is therefore nonreactive with ozone, while 1-penten-3-ol, despite its unsaturations, does not appear to be highly reactive with ozone either, although chamber experiments with 1-penten-3-ol standards (Supplement S3) along with work done by Orlando et al. (2001) did indicate minimal reactivity with ozone.

A simplified scheme representing the ozonolysis of CHA is given in Scheme 1b. The ozonolysis of CHA is expected to form 3-oxopropyl acetate and propanal, along with two stabilized Criegee intermediates (CI-3 and CI-4) that produce propanoic acid and 3-acetoxy propanoic acid, respectively upon isomerization and hydration (Hamilton et al., 2008; Grosjean and Grosjean, 1997). Upon ozonolysis of CHA (Fig. 3a), we observed the evolution of propanal and propanoic acid using TD-GC/MS, but not 3-oxopropyl acetate or 3-acetoxy propanoic acid. The vapor pressure of 3-oxopropyl acetate (5×10^{-3} atm) is on the same order of magnitude as that of propanal and propanoic acid (0.4 atm and 4×10^{-3} atm, respectively), suggesting that it should be

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measured in the gas phase. However, it was not observed in this work and experimental identification of 3-oxopropyl acetate by others has been tentative at best (Grosjean and Grosjean, 1999; Li et al., 2013; Hamilton et al., 2008). The estimated vapor pressure of 3-acetoxy propanoic acid (4×10^{-5} atm) is relatively low, suggesting that it may partition to the particle phase and/or that the GC-based method used herein was insufficient to quantify this species.

According to Scheme 1a, propanal, propanoic acid, 3-hydroxypropanal and 3-hydroxypropanoic acid are expected products of the ozonolysis of HXL, of which we observed the evolution of both propanal and propanoic acid in the gas phase (Fig. 3b). 3-hydroxypropanal and 3-hydroxypropanoic were not observed. In accord with the estimated vapor pressures of these species (1×10^{-7} atm and 2×10^{-5} atm, respectively), we did not quantify 3-hydroxypropanal or 3-hydroxypropanoic.

In addition to the predicted ozonolysis products, we also observed the evolution of 2-propenal and propenoic acid from both CHA and HXL and the production of acetic acid from CHA and acetaldehyde from HXL. Considerable work has been done by Hamilton et al. (2009) to identify the oxidation products of CHA and HXL, and though they identify acetic acid, it is attributed to fragmentation of other species during their mass spectrometry ionization process. To our knowledge, this is the first known observation of these species as CHA and/or HXL ozonolysis products, however a full understanding of the mechanism leading to their formation is not clear and warrants additional work. As stated above, Scheme 1 is a simple representation of the ozonolysis via the Criegee mechanism and does not take into account the many competing reaction pathways likely occurring simultaneously. These alternative reaction pathways are not within the scope of this work and are discussed elsewhere, yet still do not account for these products (Hamilton et al., 2009; Li et al., 2013).

The evolution of volatile ozonolysis products occurred as a concerted burst in both GLV systems, after which the signal for most products remained steady. In the ozonolysis of CHA, however, the propanal signal decreased over the course of ~ 25 min before peaking again 30 min post ozonolysis (Fig. 3a). This valley/peaked response sug-

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gests the presence of secondary reactions resulting in the consumption/production of propanal in the CHA system. While propanal was also measured as a product of HXL ozonolysis, the valley/peaked response was not observed for that system (Fig. 3b). Hamilton et al. (2009) propose a mechanism for the uptake of propanal by 3-hydroxypropanal, (product of HXL ozonolysis). Although we did not see evidence to support the uptake of propanal by HXL, the mechanism proposed by Hamilton et al. (2009) could apply to the CHA system, where the valley/peak response in propanal provides evidence for its reactive uptake. Based on a mechanism for oligomer formation proposed by Hamilton et al. (2009), hydrated 3-oxopropyl acetate (CHA- ozonolysis system) could react with propanal to produce 2-(1,3-dioxan-2-yl)ethyl acetate (Scheme 2). Based on this oligomer's estimated vapor pressure (5×10^{-7} atm), it would likely partition between both the particle and gaseous phase, however we did not observe this species using our GC-based methods (Reisen et al., 2003). This secondary reaction may also explain why 3-oxopropyl acetate was not observed in CHA ozonolysis experiments.

In the general mechanism shown in Scheme 1b, propanoic acid is produced by ozonolysis of CHA. According to Li et al. (2013), the evolution of propanoic acid is a result of the α -addition of water to CI-3 to form 1-hydroperoxypropan-1-ol, which further decomposes to produce propanoic acid. Li et al. (2013) also performed a kinetic investigation of the mechanism for CHA ozonolysis that confirmed that formation of 1-hydroperoxypropan-1-ol is the favored reaction pathway for CI-3 (Li et al., 2013). However, they found that the subsequent decomposition of 1-hydroperoxypropan-1-ol to propanoic acid and water has an energy barrier of $45.57 \text{ kcal mol}^{-1}$ and is therefore not likely (Li et al., 2013). Nevertheless, we observed propanoic acid as a product of CHA ozonolysis (Fig. 3a) and this is the only proposed pathway leading to its formation. The oxidizing environment in which these reactions were performed could lead to further oxidation of propanal, which was observed as a major ozonolysis product of both GLVs, to produce propanoic acid. However, we saw no evidence of the consumption of propanal coinciding with the production of propanoic acid in the reaction profile

of CHA or HXL. Additionally, separate experiments showed that propanal standard did not oxidize to form propanoic acid when injected into the experimental chamber in the presence of high ozone (Supplement S4). The decomposition pathway leading to the formation of propanoic acid, therefore, appears relevant, despite being energetically disfavored.

In the ozonolysis of each GLV, SOA evolution began immediately upon introduction of ozone into the reaction chamber and reached a maximum concentration in ~60–90 min before decreasing slowly, likely due in part to particle loss to the chamber walls. Aerosol yields, Y , for CHA and HXL were calculated according to Eq. (1) where $\Delta[\text{SOA}]$ is the maximum SOA concentration ($\mu\text{g m}^{-3}$, assuming a particle density of 1.2 g cm^{-3}) and $\Delta[\text{GLV}]$ is the total amount of GLV consumed ($\mu\text{g m}^{-3}$) at that SOA maximum (Odum et al., 1996).

$$Y = \frac{\Delta[\text{SOA}]}{\Delta[\text{GLV}]} \times 100\% \quad (1)$$

Ozonolysis of CHA and HXL individually resulted in a measured aerosol yield of 0.24 (± 0.08)% and 0.26 (± 0.1)% respectively (Table 1). Particle loss to chamber walls was estimated according to Presto et al. (2005) and proved to be significant (Supplement S5), with an average wall deposition rate of $5.76 \times 10^{-4} \mu\text{g m}^{-3} \text{ s}^{-1}$, which is greater than experimental chambers used by others (2.5×10^{-5} and $1.0 \times 10^{-4} \mu\text{g m}^{-3} \text{ s}^{-1}$) (Presto et al., 2005; Cocker et al., 2001; Carter et al., 2005; Wu et al., 2007). Given the large surface-to-volume ratio of our chamber, however (5.3 m^{-1}), compared to that of others (2.12 to 2.8 m^{-1}), a greater deposition rate is expected (Presto et al., 2005; Wu and Bauer, 2012). Unless otherwise noted, all subsequent reports of “measured” or “observed” SOA concentrations account for these wall-losses.

Our wall-loss coefficient (Supplement S5) was used to correct aerosol yield from GLV standard experiments. The corrected aerosol yields from ozonolysis of CHA and HXL were 1.2 (± 1.1)% and 3.3 (± 3.1)% respectively (Table 1). The error associated

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with these yields is due to the variability in the amount SOA formed in experiments. Our aerosol yield values are lower than the wall-loss-corrected aerosol yields reported by Hamilton et al. (2008, 2009), which were on the order of magnitude of prevalent monoterpenes; 9.5–24 % for CHA and 8.6 % for HXL. The ozonolysis of the endocyclic double bond of monoterpenes, as is the case in α -pinene, terpinolene and limonene however, results in the formation of oxygenated species with higher molecular weight than the parent hydrocarbon that likely partition into the particle phase and contribute to SOA, resulting in relatively high aerosol yields. Alternatively, CHA and HXL are linear alkenes that, upon oxidative cleavage via ozonolysis, produce species with relatively low molecular weight and thereby high volatility, likely contributing to the gaseous phase and subsequently should result in a lower aerosol yield than their cyclic counterparts.

3.1.2 Two GLV component mixtures

As stated above, we measured several different, potentially reactive compounds in the complex mixture of GLVs emitted by grass clippings. Recent work by Shilling et al. (2013) in the CARES campaign indicates that VOC mixtures have a significant impact on SOA formation. With the goal of better understanding SOA formation and yield under environmentally relevant conditions (where VOCs exist as a mixture), we performed two-component ozonolysis experiments with CHA and HXL. In one experiment, ozone was introduced to a GLV mixture containing a 1 : 1 (mole ratio) mix of the two components, while a second experiment was designed to represent the ozonolysis of environmentally relevant GLV mixtures, containing a 1:5 mole ratio of HXL to CHA, analogous to that measured from real grass clippings.

The reaction profile for the ozonolysis of the 1 : 1 GLV mixture (Fig. 4) shows that the majority of both CHA and HXL is consumed within the first five minutes of the reaction. SOA and volatile product evolution occurred immediately, reaching maxima less than 20 min into the reaction. SOA and volatile product concentrations remained relatively constant post-maxima and propanal did not exhibit the peak/valley trend observed in the CHA-only ozonolysis experiments. Qualitatively, the 1 : 1 GLV

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5 mix reaction profile bears a strong semblance to that of the HXL-only ozonolysis profile (Fig. 3b), suggesting HXL in an equimolar concentration, is more reactive to ozonolysis than CHA. The reaction rate constants we calculated also indicate that HXL ($k = 6.7 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) is more reactive to ozone than CHA ($3.6 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) (Supplement S6). These reaction rates agree well with those found by Kirstine and Galbally (2004) ($5.4 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ for CHA and $6.4 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ for HXL), who used the relative reaction rate method and also found that HXL was more reactive to ozonolysis. Using the aerosol yields measured in this work and the initial mass of GLVs injected into the chamber, total SOA production for the 1 : 1 mix was expected to reach $125 (\pm 85) \mu\text{g m}^{-3}$. However, the maximum wall-loss corrected SOA concentration measured was $9.8 \mu\text{g m}^{-3}$.

10 The ozonolysis of 1 : 5 GLV mix also resulted in the rapid consumption of GLVs and the immediate evolution of SOA and volatile products (Fig. 5). This reaction profile more closely approximates the CHA-only reaction profile (Fig. 3b), with both propanal and acetic acid exhibiting the valley/peak trend, which suggests the occurrence of the same secondary reactions observed in the CHA-only system. Aerosol yields predicted the formation of $50 (\pm 17) \mu\text{g m}^{-3}$ SOA, much more than the maximum wall-loss corrected SOA concentration observed; $5.3 \mu\text{g m}^{-3}$.

20 The disparity between the measured and predicted SOA concentrations in mixture experiments could suggest the presence of secondary chemistry that resulted in the consumption of GLVs without the production of SOA, which may have also been the case in grass clipping experiments. Figure 6a and 6b show reaction profiles for the ozonolysis of grass headspace. In this experiment, HXL and CHA are present in a 1 : 7 mole ratio and are subjected to 470 ppb ozone. SOA evolution begins immediately and reaches a wall-loss corrected maximum of $15.7 \mu\text{g m}^{-3}$ within 20 min before beginning to decrease, which coincides with the complete consumption of HXL, supporting our hypothesis that HXL has an important role in SOA formation in the mixture. CHA also decreases throughout the reaction but is never completely consumed and there is no corresponding SOA growth even with continued consumption of the CHA, suggesting

that CHA plays a minor role in the evolution of SOA in the mixture, as compared to HXL, but is being consumed via some other mechanism.

3.2 Grass ozonolysis reaction profile

As stated above, although grass clippings emitted several volatile species, the GLV profile was dominated by CHA, HXL and 1-penten-3-ol (Fig. 2a), all of which are unsaturated and thereby have the potential to undergo oxidation by ozone as predicted by Scheme 1. Despite its unsaturation, however, 1-penten-3-ol showed limited reactivity with ozone (Supplement S3). Initial CHA, HXL, and ozone concentrations for several experiments are listed in Table 2 and are on the same order of magnitude and mole ratio as the “1 : 5 standard mixture” experiment above. In the ozonolysis of both grass headspace and grass clippings, these three GLVs decreased in signal (albeit to a much smaller extent for the 1-penten-3-ol), while that of their corresponding gas-phase oxidation products, propanal, propanoic acid, and acetic acid increased. As in the GLV standard reactions, we also observed the evolution of propenal, propenoic acid, acetic acid and acetaldehyde, which have not previously been observed as products of grass ozonolysis.

A typical reaction profile for the ozonolysis of grass clippings is shown in Fig. 7a and b. The injection of 800 ppb ozone (at time 0) resulted in an initial burst of SOA. High ozone loadings were used to ensure a complete oxidation of all GLVs and to model GLV standard ozonolysis experiments (Table 1), but do not represent atmospherically relevant conditions, as discussed below. In several headspace and grass clipping experiments, the resultant SOA concentration increased to its maximum (up to $\sim 50 \mu\text{g m}^{-3}$ or $\sim 215 \mu\text{g m}^{-3}$ in headspace and clipping experiments, respectively) approximately 20–30 min post-ozonolysis before decreasing rapidly to background levels. We also observed a SOA concentration drop in grass headspace experiments (i.e., no grass clippings in the reaction chamber), suggesting that the rapid decrease in SOA concentration in clipping experiments is not due to sorption to the grass clippings and cannot be explained entirely by wall loss mechanisms. The mechanism for SOA loss in grass

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clipping and headspace experiments is not understood but may involve secondary reactions that increase the volatility of SOA as it ages. Understanding SOA reactivity and loss warrants additional work.

In both headspace and clipping experiments, volatile products increased as a concerted burst within the first 10 min of ozone injection. In the first 40 min of headspace experiments, 50 % of CHA, HXL and 1-penten-ol was consumed, while more than 90 % of the ozone was consumed. CHA concentration decreased then remained constant once ozone had been depleted. Propenal and acetaldehyde increased steadily post ozonolysis. Propanal increased, but exhibited a peak-valley behavior similar to that in GLV standards experiments. All other VOC products decreased post ozonolysis.

In grass clipping experiments, CHA, HXL and 1-penten-ol were completely consumed within the first 10 min of the reaction, while ozone concentration fell to background levels 35 min post ozonolysis. GLV concentrations were lower in grass clipping experiments than in headspace experiments, but this may have been a result of experimental design, as grass clippings were not allowed to equilibrate in the reaction chamber for more than a ~ 20 min before ozone was injected. Acetic acid, propanoic acid and propenoic acid signal fell after an initial burst, while propanal remained steady after its post-ozonolysis increase (similar to HXL standard experiments).

Applying the calculated (wall-loss corrected) aerosol yields above (Eq. 1) to the measured GLV emission rates in both headspace and clipping experiments, theoretical SOA production could be estimated (Table 2). The observed, wall-loss corrected SOA concentration in grass headspace experiments was less than predicted by aerosol yields with a -120 % difference. This difference was similar to the degree of disparity in the 1 : 1 mix ozonolysis experiment (-115 % difference), suggesting the 1 : 1 mix may model SOA production from grass headspace to some degree.

The observed, wall-loss corrected SOA production in grass clipping experiments was much *greater* than aerosol yields predicted ($+170$ %). The ozonolysis of neither the 1 : 1 mix nor the 1 : 5 mix resulted in the over production of SOA, as was seen in grass clippings, suggesting that neither mix accurately models grass clippings. Based on the

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corrected SOA yields, when summed, HXL and CHA account for only a small fraction of observed SOA (15 (\pm 13) %). Because GLVs are continuously emitted by grass clippings, they likely represent a continuous source of SOA, rather than a one-time burst, which may contribute to the observed disparity between predicted and measured SOA.

This disparity may also suggest that other, potentially important processes are contributing to SOA evolution by the mowing and subsequent oxidation of grass, as will be discussed below.

As demonstrated by the disparity between predicted and actual SOA production, the ozonolysis of HXL or CHA alone does not accurately represent SOA from the ozonolysis of grass clippings or grass headspace. Mixtures of the two dominant reactive GLVs are more representative of the grass headspace system than the grass clippings, and produce similar *trends* in SOA growth and volatile product evolution. Therefore, predictions of atmospheric SOA mass loading using even these two predominant GLVs underestimate actual SOA loading resulting from lawn mowing.

4 Contribution of lawn mowing to atmospheric SOA

The site area chosen for this study was a residential, suburban neighborhood in close proximity to an industrial, urban landscape. A geospatial analysis of the 131 acre area around the study site showed that lawns and turfgrass comprise 27.5 % of the total landcover in this suburban neighborhood (36 acres). Remaining landcover was comprised of wooded lots, scrub-brush and impervious surfaces such as roads, driveways and rooftops. Lawn mowing has been estimated to produce $\sim 1.3 \times 10^3$ g dw m^{-2} yr^{-1} of clippings (where g dw is grams dry weight) (Supplement S7). Stevenson (2010) estimated that New England homeowners mow their lawn 20 times annually, and so we predict that approximately 66 g dw m^{-2} mowing $^{-1}$ of grass clippings are produced by New England lawns. We estimate that lawns in this typical suburban neighborhood have the capacity to emit 8.66 (\pm 0.08) μ g m^{-2} CHA and 1.21 (\pm 0.06) μ g m^{-2} HXL as a concerted burst upon mowing. Based on our corrected aerosol yields, these GLVs

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have the capacity, therefore, to contribute 177 mg SOA to the neighborhood airshed, annually.

However, as shown above, the **actual** SOA measured due to the ozonolysis of grass clippings is much greater than predicted by our yields, so the estimate above is not truly representative of the potential contribution of lawn mowing to SOA levels. Taking a “top-down” approach to this estimate predicts that $0.9 \mu\text{g g dw}^{-1}$ SOA could be produced upon mowing, where $\mu\text{g g dw}^{-1}$ represents the mass of SOA produced (μg) as a function of grass dry weight in grams (g dw). For our study site, this SOA production rate corresponds to $47 \mu\text{g SOA per square meter mowed}$ or $940 \mu\text{g m}^{-2}$ SOA annually (Supplement S7). Based on reported emissions from forested landscapes and the fraction of forested landscape in the region of the study area, isoprene and monoterpenes are estimated to contribute 2500 and 2000 $\mu\text{g m}^{-2}$ annually, respectively (Guenther et al., 1994; Zheng et al., 2013). Lawn mowing, therefore, has the potential to emit a significant amount of SOA, comparable to the two predominant SOA sources, as a concerted burst to the local airshed.

As stated above, ozone was introduced to the experimental chamber as a one-time burst that resulted in concentrations of about 800 ppb, which is much greater than average ozone levels in Chittenden County, VT (~ 60 ppb) (US Environmental Protection Agency, 2013). 800 ppb ozone was used in preliminary grass clipping experiments to ensure a sufficient concentration to result in SOA growth and was used in subsequent GLV standard and grass experiments for the sake of consistency. Though ambient ozone concentrations are lower than the experimental ones used herein, they *are* expected to be elevated on warm, sunny days, the same time lawn mowing is expected to occur. Additionally, ozone plumes can be transported several hundred kilometers from industrial or urban sources to rural sites where they can interact with BVOCs (Mao et al., 2006; Bertschi and Jaffe, 2005; Wang et al., 2006). For example, plumes originating in New York City, NY can extend 600 km and contain up to 160 ppb ozone (Lee et al., 2011). The prevailing winds in Essex Junction, VT are from the west, putting the study site five miles downwind from the City of Burlington, VT and many industrial areas,

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which may introduce an additional source of ozone. Therefore, it is possible that local ozone levels in rural landscapes could be elevated during mowing events. Additionally, in the field any consumed ozone is expected to be replenished by other sources that are prevalent in the atmosphere, whereas in our experiments ozone was injected as a single burst (Steinbrecher et al., 2000). Exposure to a concerted burst of 800 ppb ozone is admittedly different than an exposure to 100 ppb over the course of 8 h, which would be a more representative exposure scenario, but such exposures will require use of a continuous flow reaction chamber.

Despite our efforts to model real world conditions in our experiments, the atmosphere offers complexities that may lead to additional SOA evolution as a result of lawn mowing. Work done by Kirstine and Galbally (2004) Orlando et al. (2001) and Papagani et al. (2001) have shown that grass GLVs have considerable reactivity with nitrate and hydroxyl radicals, on the same order of magnitude as common anthropogenic VOCs. Hamilton et al. (2009) predicted a 3.1 and 0.9% aerosol yield from the photooxidation of HXL and CHA respectively. Given the established reactivity of GLVs with other atmospheric oxidants, additional work should be done to characterize the volatile products and SOA produced from the photooxidation of GLVs.

This work focused on the interaction of two predominant GLVs and their roles in SOA formation, however there is also growing evidence to indicate that the presence of anthropogenic organic aerosol and AVOC in conjunction with BVOC synergistically enhances the production of SOA (Shilling et al., 2013; Emanuelsson et al., 2013; Hildebrandt et al., 2011). The relatively large ratio of landcover encompassed by lawns in suburban neighborhoods represent a source of BVOCs, which, by definition are in close proximity to urban and industrial sources of BVOCs and BSOA, as well as elevated concentrations of oxidants. There are several sources of A/BVOCs and A/BSOA at the urban/suburban interface that provide ample opportunity for interaction. For example, the emissions of lawn mowers themselves have been found to contribute $4 \mu\text{g m}^{-3}$ aerosol during a mowing event, likely from unspent fuel emissions and agitated plant debris and soil (Drewnick et al., 2008). Additional work is needed to determine whether an

anthropogenic enhancement effect drives additional SOA production from the ozonolysis of grass clippings, not seen in headspace or GLV standard experiments. These experiments should include the ozonolysis of GLVs in the presence of seed aerosols, which would serve as a proxy to ambient atmospheric particulate matter or primary organic aerosols and should also involve GLV oxidation in the presence of AVOCs and oxidants.

5 Conclusions

Though many volatile species are emitted by grass clippings, the profile is dominated by CHA and HXL, which are easily oxidized by ozone to produce significant amounts of SOA, in addition to a suite of oxygenated volatile products. Herein we report the first known observation of propenal and propenoic acid as ozonolysis products of both CHA and HXL, as well as support other products previously reported in the literature (Hamilton et al., 2009; Li et al., 2013; Reisen et al., 2003; O'Dwyer et al., 2010; Aschmann et al., 1997). We found that the mowing of lawns has the potential to contribute up to $47 \mu\text{g m}^{-2}$ SOA to the atmosphere, which cannot be modeled solely by the ozonolysis of CHA or HXL. While these two GLVs were found to produce SOA upon ozonolysis, they each largely under predict SOA mass loading from ozonolysis of grass clippings or simple binary mixtures of the two. The disparity between measured and predicted SOA mass loading may be rectified by incorporating additional oxidation sources, BVOCs, AVOCs and ASOA, which may contribute to an anthropogenic enhancement effect in grass clipping oxidation.

The ozonolysis of two-component mixtures of CHA and HXL begins to suggest that the chemical processes leading to SOA formation could be better modeled by mixtures, than by single-component systems. However, the chemical processes involved are not well understood and warrant additional work.

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Supplementary material related to this article is available online at
[http://www.atmos-chem-phys-discuss.net/13/24435/2013/
acpd-13-24435-2013-supplement.pdf](http://www.atmos-chem-phys-discuss.net/13/24435/2013/acpd-13-24435-2013-supplement.pdf).

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Table 1. Experimental conditions and SOA for several GLV standard ozonolysis experiments, used to determine average aerosol yield for GLVs. Corrected SOA accounts for aerosol wall loss (Eq. E1, Supplement S5) and was used to determine the corrected SOA yield for CHA and HXL, **1.22 (± 1.1) %** and **3.28 (± 3.1) %**, respectively.

Date	CHA consumed ($\times 10^3 \mu\text{g m}^{-3}$)	HXL consumed ($\times 10^3 \mu\text{g m}^{-3}$)	Ozone Injected (ppb)	Measured SOA ($\mu\text{g m}^{-3}$)	Corrected SOA ($\mu\text{g m}^{-3}$)	Measured Aerosol Yield	Corrected Aerosol Yield	
10 Oct 2012		2.08	800	6.3	60.1	0.30 %	2.88 %	HXL
18 Feb 2012		5.47	1000	11.8	22.8	0.22 %	0.42 %	
23 Apr 2013		2.72	950	27.5	178.0	1.01 %	6.54 %	
					average standard deviation	0.26 % 0.1 %	3.28 % 3.1 %	
10 Apr 2013	5.61		500	7.1	25.4	0.13 %	0.45 %	CHA
10 Apr 2013	5.86		3400	15.3	33.4	0.26 %	0.57 %	
12 Apr 2013	5.76		950	18.7	67.2	0.32 %	1.17 %	
18 Apr 2013	2.97		1500	7.4	21.0	0.25 %	0.70 %	
26 Apr 2013	2.86		1100	17.8	91.1	0.62 %	3.19 %	
					average standard deviation	0.24 % 0.08 %	1.22 % 1.1 %	

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Table 2. Experimental conditions, SOA and GLV results for several grass clipping and headspace experiments. Ozone concentration was ~ 800 ppb for each experiment. Predicted SOA concentration determined using initial GLV emissions and wall-loss corrected aerosol yields. RSD is the relative standard deviation in the value to the left. RSD of predicted SOA is driven by the high uncertainty in the aerosol yield calculation (Table 1). RSD in HXL and CHA concentrations and masses determined using each GLV calibration.

	Date	SOA (# cm ⁻³)	SOA (μm ⁻³)	Wall Loss Corrected SOA (μg m ⁻³)	Predicted SOA (μg m ⁻³)	RSD	HXL (μg m ⁻³)	RSD	HXL per m ² lawn (μg m ⁻²)	RSD	CHA (μg m ⁻³)	RSD	CHA per m ² lawn (μg m ⁻²)	RSD
Clippings	23 Oct 2012	11 835	39	55	9.55	2.51	137	0.09	0.14	0.04	2100	0.04	2.29	0.04
	27 Oct 2012	6077	16	27	1.21	1.12	31.4	0.49	0.022	0.19	75.7	0.87	0.05	0.87
	6 Nov 2012	46 102	82	113	10.05	4.12	39.2	0.39	0.033	0.18	3650	0.04	3.10	0.04
	28 May 2013	73 630	120	153	3.74	2.41	56.6	0.30	0.0079	0.03	785	0.04	0.11	0.04
Headspace	23 Oct 2012	1190	5.9	8.8	43.56	1.58	885	0.03	1.7	0.02	6060	0.04	11.36	0.42
	27 Oct 2012	348.42	2.9	3.8	13.34	3.34	120	0.13	0.19	0.12	3920	0.04	6.35	0.49
	6 Nov 2012	1422	5.2	16	9.66	1.44	205	0.22	0.089	0.16	1220	0.04	0.53	0.39
	8 May 2013	793.657	6.8	12	5.59	1.60	113	0.11	0.23	0.11	788	0.03	1.60	0.35

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Fig. 1. Turfgrass (light green) in a suburban neighborhood in Essex, VT comprises 28% of the total landcover (131 acres), the mowing of which releases a complex profile of unsaturated GLVs, which upon ozonolysis have the potential to contribute to atmospheric SOA. Study site (44.487653, -73.09365) denoted by yellow circle.

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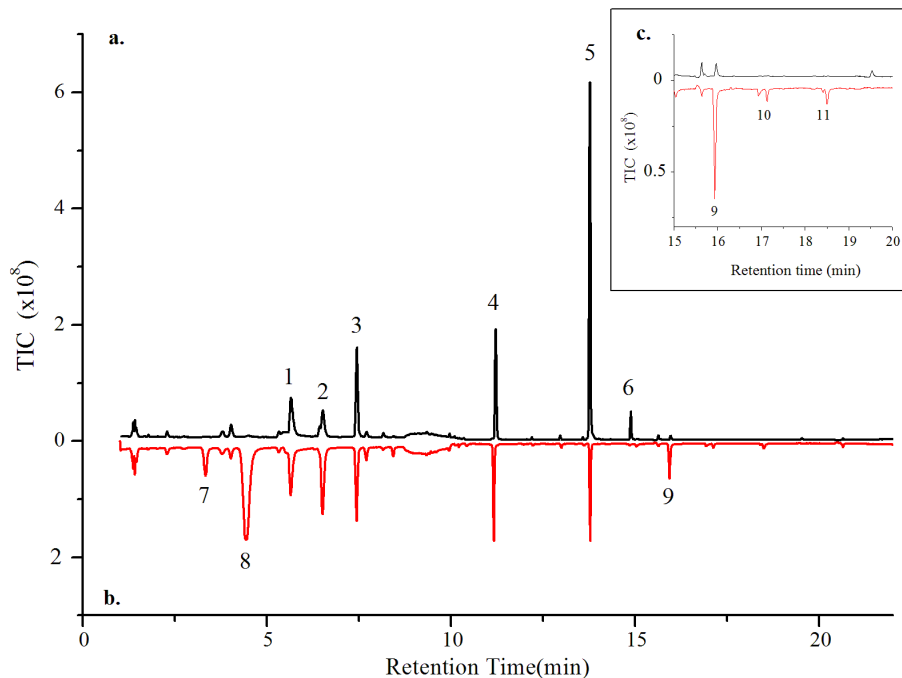


Fig. 2. Total ion chromatogram (TIC) of **(a)** VOCs emitted by grass clippings and **(b)** as a result of the ozonolysis of grass clippings. **(a)** GLVs emitted by cut grass (black trace) show a complex mixture of volatile compounds with (3) 2-pentanone, (4) 1-penten-3-ol, (5) *cis*-3-hexenyl acetate and (6) *cis*-3-hexenol predominating. Other VOCs emitted by mowed grass include (1) methanol and (2) ethanol. Immediately post ozonolysis **(b)** (red trace, 800 ppb ozone), (5) *cis*-hexenyl acetate and (6) *cis*-hexenol signal dropped significantly indicating their reactivity with ozone, while chromatographic peaks from (7) propanal, (8) propenal, (9) acetic acid, (10) propanoic acid and (11) propenoic acid appeared, apparent products of *cis*-3-hexenyl acetate and/or *cis*-3-hexenol ozonolysis. Propanoic acid (10) and propenoic acid (11) are more clearly seen above the base line in the enlarged **(c)**.

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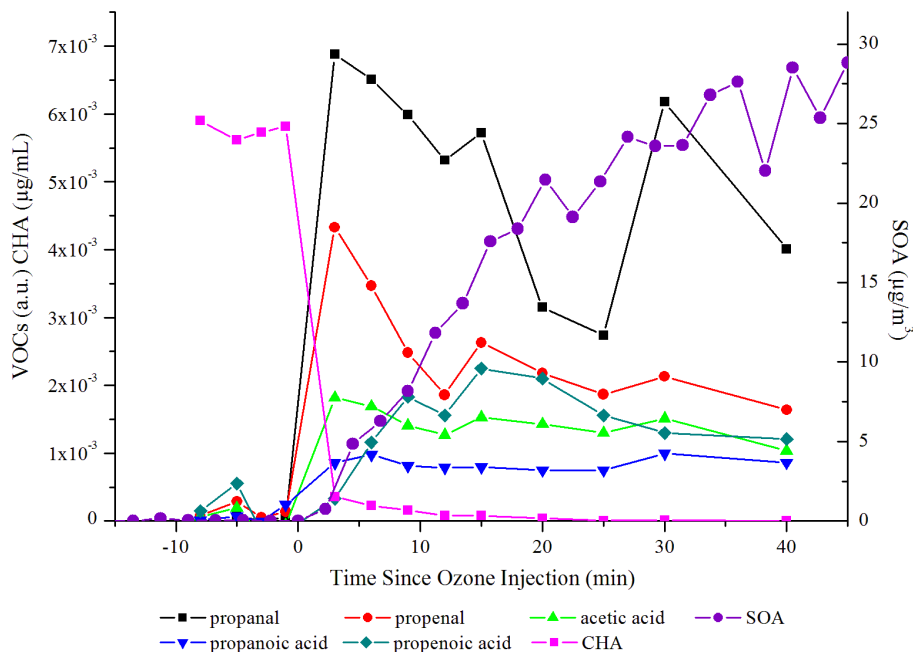


Fig. 3a. Reaction profile for the ozonolysis of predominant grass GLVs. At time zero, 800 ppb ozone was introduced to $5.7 (\pm 0.1) \times 10^{-3} \mu\text{g mL}^{-1}$ of CHA, which resulted in SOA growth and the evolution of volatile products; propanal, propenal, propenoic acid, acetic acid and propanoic acid.

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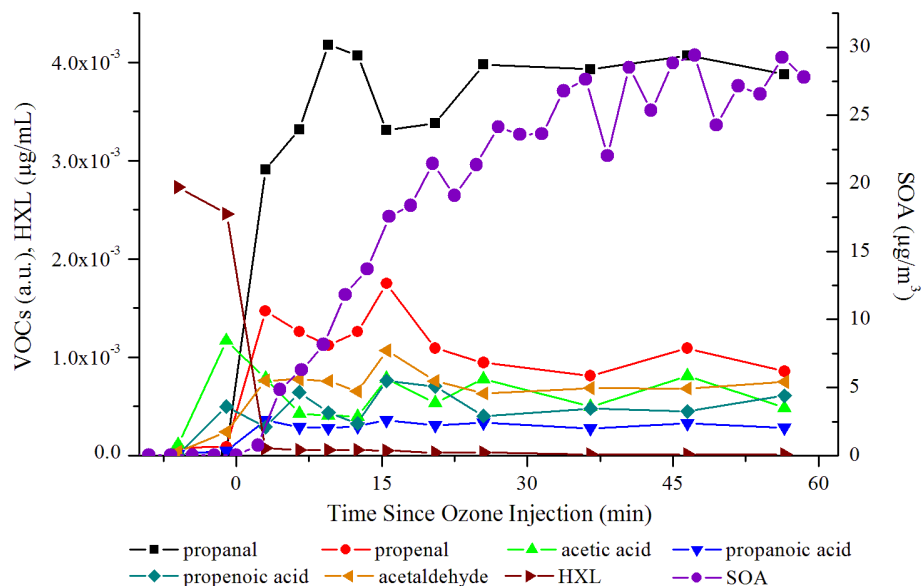


Fig. 3b. At time zero, 900 ppb ozone was introduced to $2.6 (\pm 0.2) \times 10^{-3} \mu\text{g mL}^{-1}$ HXL, resulting in the evolution of SOA and the same volatile products as in (a), with the addition of acetaldehyde. Lines between data points drawn to aid the eye.

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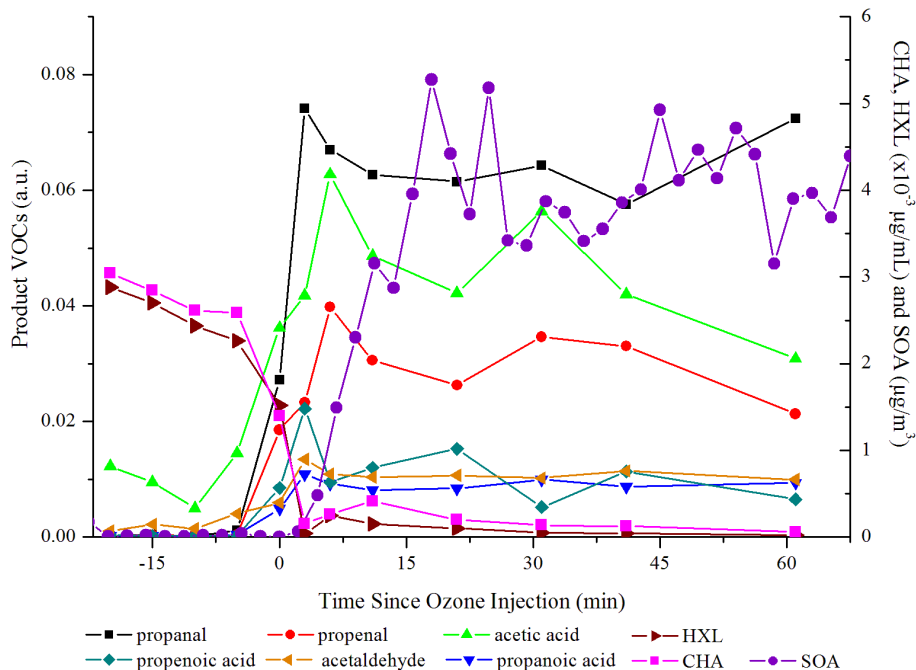


Fig. 4. Reaction profile of the ozonolysis of a 1 : 1 mix of CHA and HXL (initial concentration $2.8 (\pm 0.2) \times 10^{-3} \mu\text{g mL}^{-1}$ each). 900 ppb ozone was injected at time zero, after which SOA and volatile products (propanal, propenal, propenoic acid, acetic acid, propanoic acid, acetaldehyde) increased in signal. Lines between data points drawn to aid the eye.

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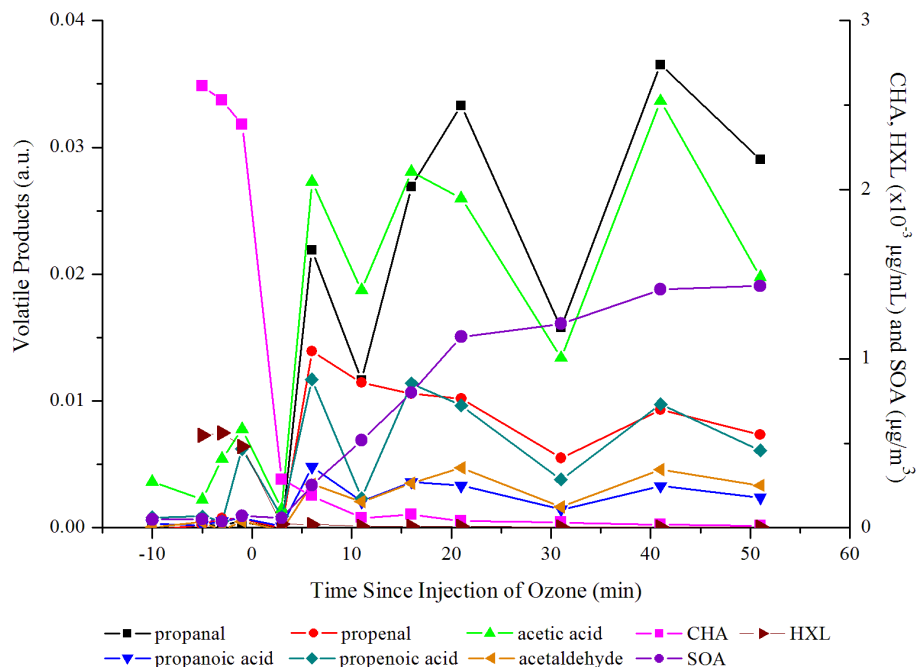


Fig. 5. Reaction profile of the ozonolysis of a 5 : 1 mix of CHA and HXL (initial concentration $2.5 (\pm 0.1) \times 10^{-3} \mu\text{g mL}^{-1}$, and $0.5 (\pm 0.04) \times 10^{-3} \mu\text{g mL}^{-1}$ respectively. 800 ppb ozone was injected at time zero, after which SOA and volatile products (propanal, propenal, propenoic acid, acetic acid, propanoic acid, acetaldehyde) increased in signal. Lines between data points drawn to aid the eye.

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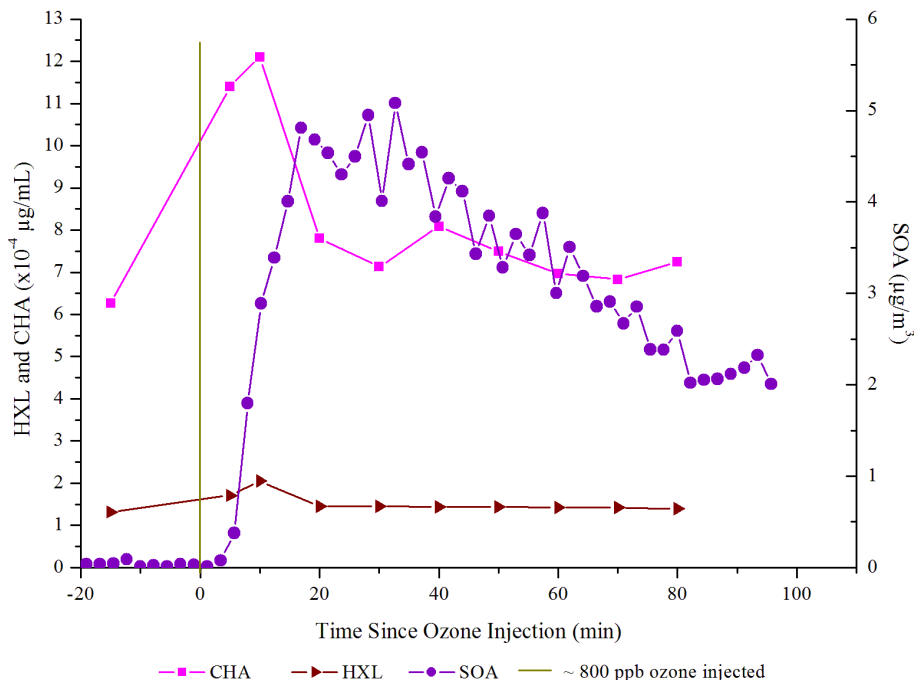


Fig. 6a. Zero air was flushed through grass clippings and into the experimental chamber, carrying with it GVLs contained in the grass headspace. Maximum concentrations of CHA and HXL ($12 (\pm 1) \times 10^{-4} \mu\text{g mL}^{-1}$ and $2.05 (\pm 0.01) \times 10^{-4} \mu\text{g mL}^{-1}$ respectively) were measured post ozonolysis, which we believe was due to incomplete mixing within the experimental chamber before ozone injection. Ozone data was not available, but at time zero ~ 800 ppb ozone was injected (indicated by vertical line) and within 20 min HXL concentration dropped below the instrument detection limit while SOA reached its maximum wall-loss corrected concentration ($15.7 \mu\text{g m}^{-3}$). CHA remained relatively constant after the first 20 min of the reaction ($0.74 (\pm 0.05) \times 10^{-3} \mu\text{g mL}^{-1}$) and was never completely consumed. Lines between data points drawn to aid the eye

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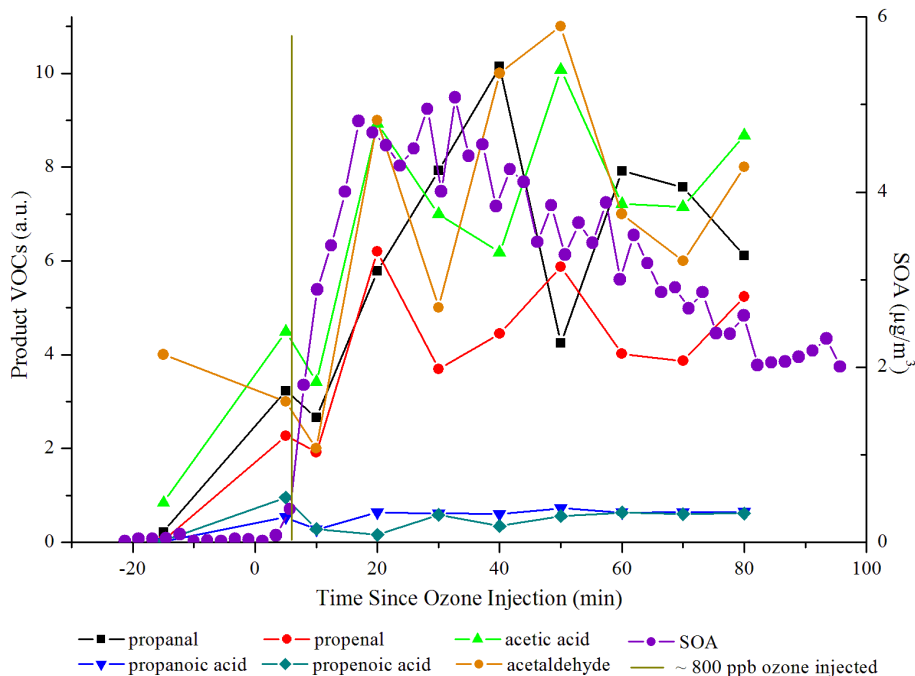


Fig. 6b. In addition to the evolution of SOA, the ozonolysis of grass headspace resulted in the evolution of several volatile products, including propanal, propenal, propenoic acid, acetic acid, propanoic acid, acetaldehyde, several of which have not previously been reported as products of CHA or HXL ozonolysis. Lines between data points drawn to aid the eye.

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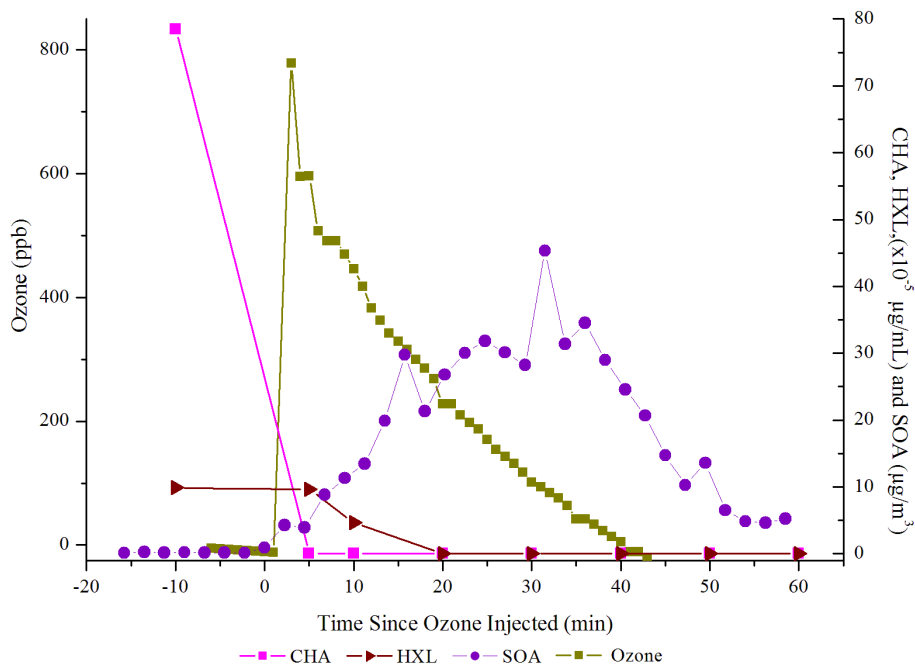


Fig. 7a. Approximately 0.5 kg of grass clippings were placed in the experimental chamber, which was then filled with zero air. Initial concentrations of CHA and HXL were $80 (\pm 20) \times 10^{-5} \mu\text{g mL}^{-1}$ and $10 (\pm 8) \times 10^{-5} \mu\text{g mL}^{-1}$, respectively. At time zero ~ 800 ppb ozone was injected and both CHA and HXL concentrations dropped below the instrument detection limit within the first five minutes of the reaction, while SOA concentration increased for about 30 min before reaching a maximum of $\sim 91 \mu\text{g m}^{-3}$ (wall-loss corrected). Lines between data points drawn to aid the eye.

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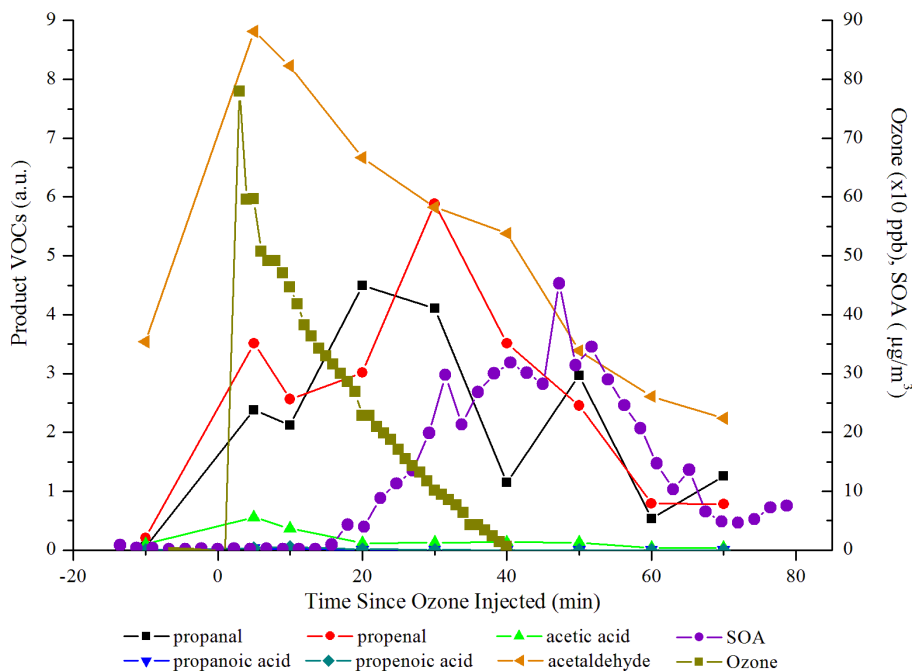
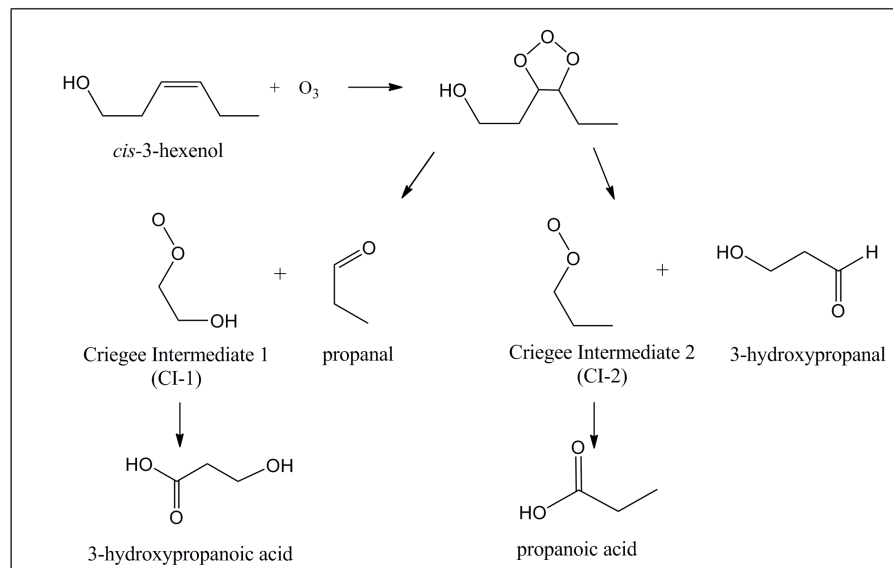


Fig. 7b. In addition to the evolution of SOA, the ozonolysis of grass clippings also resulted in the evolution of several volatile products, including propanal, propenal, acetaldehyde and acetic acid. Trace amounts of propenoic acid, and propanoic acid, were measured. Several of these volatiles products have not previously been reported as products of CHA or HXL ozonolysis. Lines between data points drawn to aid the eye.

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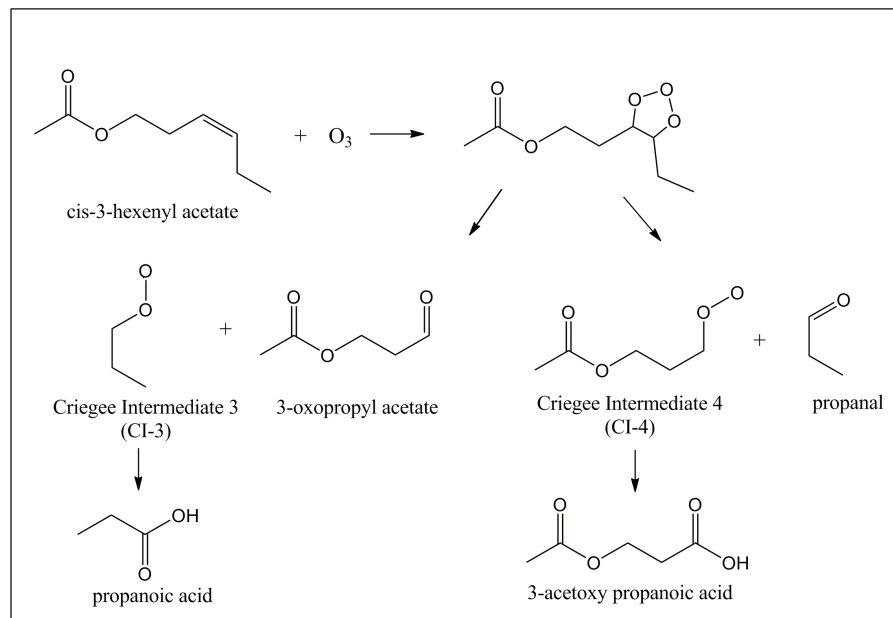


Scheme 1a The ozonolysis of HXL is predicted to produce 3-hydroxypropanal and propanal along with the stabilized Creigee intermediates CI-1 and CI-2, which produce 3-hydroxy propanoic acid and propanoic acid respectively upon isomerization and hydration.

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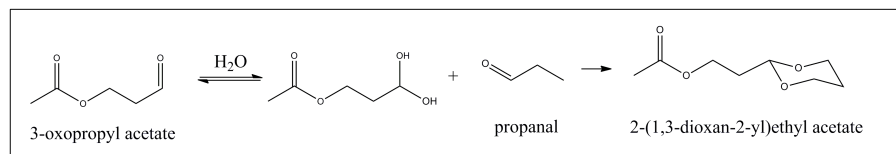


Scheme 1b The ozonolysis of CHA is predicted to produce 3-oxopropyl acetate and propanal, along with two stabilized Criegee intermediates (CI-3 and CI-4) that produce propanoic acid and 3-acetoxy propanoic acid, respectively.

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Scheme 2 Upon hydration, aldehyde functionality of 3-oxopropyl acetate could react with propanal, both predicted products of CHA ozonolysis (Scheme 1b), to produce 2-(1,3-dioxan-2-yl) ethyl acetate (VP 5×10^{-7} atm).

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