

## ***Interactive comment on “Establishing the contribution of lawn mowing to atmospheric aerosol levels in American suburbs” by R. M. Harvey et al.***

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We are in agreement that the ozone concentrations used in this work are not representative of atmospherically relevant conditions and that these high ozone concentrations may in fact wound the grass clippings additionally, and may contribute to the elevated SOA yield. High ozone concentrations were used to induce pseudo-first order reaction kinetics and determine kinetic properties of the reactions. Nonetheless, additional description of these limitations will be included as follows.

Continuation of line 8, page 24455: “Ozone itself has also been shown to cause VOC

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emission in several plant species (Heiden et al., 2003; Woodbury et al., 1994; Kivimäenpää et al., 2013; Miresmailli et al., 2013). Depending on the reactivity of these VOCs, they may also undergo ozonolysis and contribute to additional SOA mass and could help explain the disparity between SOA yields in headspace vs. clipping experiments. We did not detect the emission of VOCs by grass clippings as a result of ozonolysis, which may be explained by their subsequent consumption by yet more ozone in the reaction chamber. Additional work is necessary to understand ozone-induced VOC emission by grasses and their subsequent reactivity with ozone.”

The focus of this work was to identify whether or not the two predominant GLVs emitted by grass clippings (HXL and CHA) or a mixture of the two could be used to model mow-induced SOA. 1-pentene-3-ol was also identified in the grass emissions but showed limited reactivity with ozone and very low yields (as shown in Supplemental Material S3), it was therefore not considered to contribute significantly to the total SOA mass. This discussion is also included in section 3.1.1 of the text. The emission profile of the grass clippings and headspace were the same, but the relative concentrations of the species were different between experiments (headspace vs. grass clipping), and between several days, as shown in Table 2. We will edit the caption in Figure 2 to clarify this point as follows (edits in italics).

“Fig. 2. Total ion chromatogram (TIC) of (a) VOCs emitted by grass clippings/headspace, and (b) as a result of the ozonolysis of grass clippings/headspace. 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 emitted VOCs by mowed grass include . . . .”

And include the continuation of line 16 on page 24445 “Both headspace and grass clipping experiments had the same VOC emission profile, though the relative amount of CHA and HXL differed between experiments, as shown in Table 2.”

One grass emission sample was collected during a mowing event using a portable

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autosampler and demonstrated the additional emission of VOCs by the lawn mower. Since AVOCs were not the focus of this work, they were not included in our chamber experiments or in this document, but may have an impact on the SOA produced as a function of lawn mowing. Our analytical method (TD-GC/MS) is sensitive to ppb-level concentrations of monoterpenes and sesquiterpenes, however they were not detected in this work.

Details on our calibration technique are given in section 2.2 starting on line 20. However, a discussion of detection limits was not given. This oversight will be corrected by including the following text:

Continuation of line 1 page 24442. "Detection limits were found by  $LOD = s_y \cdot t_{crit}/m$  where  $s_y$  and  $m$  are the error in the y-intercept and slope of the calibration curve, respectively and  $t_{crit}$  was taken at 95 % confidence level. The detection limits for CHA, HXL and propanal were  $0.096 \mu\text{g}$ ,  $0.058 \mu\text{g}$  and  $0.052 \mu\text{g}$ , respectively. Depending on the volume of air sampled, these masses correspond to ppb-level concentrations."

The chromatogram in Figure 2 is representative of all samples that were collected; with good peak shape and low baseline. Carryover and breakthrough studies were completed as part previous studies and their effects were found to be negligible. To clarify the experimental setup, additional descriptions will be included as follows:

Continuation of line 21, page 24441: "Rather than diluting with clean air to account for volume loss during sampling, the chamber was allowed to collapse slightly throughout an experiment."

Addition to line 2, page 24442: "Particle filters and ozone scrubbers were not used. . ."

It is very likely that OH is of importance in this work and we are currently performing experiments to understand its role. However, this work is not focused on a mechanistic study of the system, therefore we chose not to include it in this document.

We do not believe that differences in chamber studies between the work done here

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and that done by Hamilton et al., 2009 explain the disparity in the measured aerosol yields. Our starting GLV concentration (1.0 ppm) was only slightly lower than that used by Hamilton et al., 2009 (1.6 ppm), while our ozone concentration was about half that used by Hamilton et al., 2009 (0.8 ppm compared to 1.6 ppm). Ozone was, however, in excess of the GLV according to their molar equivalencies. To elaborate this discussion, we will include the following text:

Continuation of page 24449, line 4. "...monoterpenes; 9.5-24% for CHA and 8.6% for HXL. The chamber studies by Hamilton et al. (2009, 2009) were carried out at 1.6 ppm GLV and 1.6 ppm ozone while our yield experiments were carried out at 1.0 ppm GLV and 0.8 ppm ozone. In both studies, the absolute amount of SOA produced was limited by the GLV species. The aerosol yield, however, is representative of the total amount of GLV consumed as a function of total amount of SOA produced, so should be independent of starting conditions. The minor differences in reagent concentration do not explain the disparity between yield measurements here and by Hamilton et al. (2008, 2009). The ozonolysis of the endocyclic. . ."

The reactive uptake of aldehydes has been proposed as a mechanism for SOA growth and yet there remain uncertainties as to how this occurs. (Jang and Kamens, 2001;Mang et al., 2008) In accordance with the description presented by Hamilton et al. (2009), we present the possibility that propanal may undergo reactive uptake with 3-oxopropyl acetate to form less volatile species and contribute to particle-phase products. If the rate of uptake is high enough, this phenomenon may result in the peaked/valley behavior observed in propanal, which is both reproducible and significant (propanal signal well above our detection limit). To aid the reader and demonstrate significance in the signal, we will add error bars to the propanal signal in Figure 3a. Unfortunately, there is little known about the uptake rates of aldehydes; however, Esteve and Noziere (2005) proposed an uptake rate for acetaldehyde in acidic aerosol of  $3.3 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , which they conclude is not fast enough to contribute to aerosol, but that the uptake of larger aldehydes in the presence of acidic particles

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may favor partitioning to the condensed phase. Based on the mechanism proposed by Hamilton et al. (2009) and the uptake work done by Esteve and Noziere (2005), it is not far-reached to suggest that propanal may react with 3-oxopropyl acetate.

Additional discussion of the apparent disparity between SOA yield from single GLV component ozonolysis and GLV mix/headspace experiments will be included as follows:

Continuation of 24450, line 11. "The disparity in SOA yield between grass clippings and grass headspace ozonolysis experiments could be due to either the enhancement of SOA growth in clippings (i.e. chemical wounding by ozone, as discussed above) or the suppression of SOA growth in headspace and GLV mixture experiments. The presence of some volatile species (i.e. isoprene) have been shown to inhibit new particle formation (Kiendler-Scharr et al., 2009). Recently, Mentel et al. (2013) found that HXL suppressed SOA formation from the ozonolysis of  $\alpha$ -pinene. Mentel et al. (2013) determined that the SOA inhibition by HXL was a result of competing reactions with OH radicals, rather than ozone. The rate constant for  $\alpha$ -pinene ozonolysis ( $0.28 - 3.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ), is greater than that for HXL ( $7 \pm 3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ), while the OH rate constant for  $\alpha$ -pinene ( $1.2 - 6.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ) was seven order of magnitude smaller than that for HXL ( $1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ). (Zhang and Zhang, 2005; Kirstine and Galbally, 2004) The OH radical mechanism for SOA growth was not investigated in this study but given its potential reactivity with GLVs, warrants additional work. SOA growth in the grass headspace experiments could have been suppressed by the preferential oxidation of some low aerosol yield-volatile species that were not detectable using our methods. This rationalization, however, does not explain the low aerosol yield in the GLV mixture ozonolysis experiments."

We are in agreement that the only slightly smaller reaction rate constant for the ozonolysis of 1-penten-3-ol (as compared to CHA and HXL) reported by O'Dwyer et al. (2010) is not sufficient to explain why we observed it having limited reactivity with ozone. How-

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ever, we believe that this detail is not germane to the manuscript and therefore was not investigated fully.

Text describing grass clipping ozonolysis will be edited to describe figure 7a more accurately as follows: (edits in red)

"In grass clipping experiments, CHA and HXL 1-penten-ol were completely consumed within the first ~20 min of the reaction, while ozone concentration fell to background levels ~45 min post ozonolysis"

As mentioned above and by Referee #2, there are additional oxidation mechanisms (photooxidation/NOx/OH radical) not discussed/investigated in this work but that are believed to impact gas and particle phase results. A detailed mechanistic study, however, was not the focus of this work, as was mentioned in Section 3.1.1 and discussed on page 24455.

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