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> Interactive Comment

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

## Anonymous Referee #2

Received and published: 9 December 2013

### **General Comments**

This paper describes a series of chamber experiments investigating the secondary organic aerosol formation and gas phase oxidation products produced from green leaf volatile ozonolysis. The yields obtained were then used to extrapolate to atmospheric impact of grass mowing in a suburban area. This is an interesting paper and makes the first attempt to use chamber generated SOA yields to determine if grass mowing is an important aerosol precursor, albeit in a rather simplistic bottom up way. There are some very interesting components to this paper, particularly using the headspace of real grass clippings as the VOC source, being more representative of the actual





emissions. However, the view that GLV are probably the only compounds responsible for SOA formation is clearly not sufficient to model this source. I would recommend publication of this paper in ACP after minor corrections.

The ozonolysis of grass clippings experiments really should have been done at much lower ozone concentrations. There is no way to compare a short burst of 800 ppb to 8 hours of 100 ppb (which the authors acknowledge). The ozone is obviously leading to much higher levels of reactive VOCs that lead to a massive increase in SOA formation in comparison to the headspace example. I would have thought that 800 ppb of ozone would start to attack the surface of the plant. It is well known that ozone stress leads to an increase of reactive VOC emissions (such as monoterpenes and sesquiterpenes) in live plants and it would seem plausible that this is also the case on the cuttings. It would certainly account for the large increase in SOA, particularly as both mono- and sesquiterpenes have large aerosol yields. More is needed on the limitations of this approach.

At points in the manuscript it is difficult to follow what experiment is being discussed. I think a table showing the grass headspace and grass clipping VOC profile would be useful. A chromatogram is given but this gives the reader no idea about what other BVOC species were identified. Were any mono- or sesqui-terpenes or isoprene seen as low level components? This may be an important contributor to SOA due to the higher aerosol yield of these compounds.

### Specific comments

Page 24441, line 11: There are not enough details on the chamber included here. What was the relative humidity in the chamber? Do you dilute the chamber with clean air or does it collapse during the experiment? There is little said here about the TD methodology for GLV. These compounds and their oxidation products are very sticky and it is often difficult to get a clean background signal from the TD tubes. How was quantification performed – gas standard, denuders, liquid injections? Also, was there

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a water removal step or were the experiments carried out under dry conditions. These compounds, especially the acids are very difficult to analyse well in GC without derivatization. I would have expected poor peak shapes and incomplete desorption from the tubes. What was the recovery of the analysis? Did you have a filter on the sample line to ensure you don't sample the SOA? Page 2443, section 2.1: Do you think that you will get significant losses or a different VOC profile between mowing and sampling? Did you try to increase VOC emissions by wounding the grass again before putting in the chamber? You mention the [VOC] is different between headspace and clippings but this data is not presented apart from in the graphs.

Page 24445, line 20: There is no discussion here or at other places in the manuscript about OH chemistry. Ozonolysis of alkenes leads to the formation of OH radicals and thus this chemistry could account for many of the additional oxidation products that continue to rise even when the ozone and VOC have been removed. The acetic acid formed could be heterogeneous chemistry followed by re-volatilisation to the gas phase or OH chemistry. It is strange however, that acetic acid in figure 3b actually increases before the ozone is added?

Page 24447, line 1: I am really not convinced by this argument for the changing concentration of propanal. How close is the peak area to the limit of detection? Is this phenomenon reproducible? Line 15: The vapour pressures of the monomer is not so low. What would its gas to particle ratio be? It would have to be very fast chemistry to stop you seeing the monomer in the gas phase. Line 25: Again no discussion of heterogeneous or OH chemistry as sources.

Page 24449, line 4: No discussion of the differences in chamber studies. In Hamilton et al., 2009, the [VOC] and [O3] are much higher (1.6ppm) and the RH is 6%. It would be better to at least give some thoughts on why your values are so different.

Page 24450, line 11: The formation of much lower than expected SOA is strange. Is your VOC:O3 ratio the same in both the single and mixed cases?

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Page 24451, line 7: The rate constant for 1-penten-3-ol was measured by O'Dwyer et al as  $1.64 \times 10-17$  cm<sup>3</sup> molecules-1 s-1. This is only around half the CHA value you obtained. There seems to be an inconsistency there. A drop in rate by a factor of 2 would not make it so slow that you would not observed a drop during your experiment.

Page 24452, line 11: here it states that within 10 minutes of ozone being added, the HXL and CHA are completely consumed. This is not what is shown in figure 7a, where it takes over 20 minutes for the HXL to be lost and this is slower than the CHA?

Technical corrections Page 24436, line 19: Insert "freshly cut grass WAS found" Page 24437, line 3: The meaning of this sentence is unclear. Page 24440, line 9: I think you should insert "ozone is OFTEN present" Page 2442, line 17: should be "m/z 15 to 300"

Supplemetary Info Figure S3: can you really call this SOA? Surely it is just aerosol mass? Scheme S1: This reaction should primarily form formaldehyde and 2-hydroxybutanal as the first generation products + the associated criegee intermediates.

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