

Interactive comment on “Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber” by C. J. Hennigan et al.

Anonymous Referee #2

Received and published: 7 June 2011

General Comments:

Hennigan et al. present results from smog chamber experiments that aimed to characterize the modifications in the physical and chemical properties of biomass burning organic aerosols due to photochemical aging. In this work, biomass burning emissions were produced through the controlled burning of 12 biomass fuel types then were subsequently photochemically aged in a smog chamber over a few hours. The changes in OA mass as measured by Aerosol Mass Spectrometer resulting from photo-oxidation varied widely with fuel type, ranging from mass enhancement ratios of 0.7 to 2.9. In all

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cases, biomass burning OA particles became less volatile and more oxygenated with photochemical aging time as demonstrated by changes in volatility and m/z 44 mass fraction regardless of mass enhancement ratio. The authors showed that levoglucosan, used here as a tracer for the biomass burning POA, became rapidly depleted in the OA. From these observations, the authors suggested that a large fraction of the original POA was chemically transformed mostly due to oxidation of semi-volatile component of POA.

This work will improve our understanding of the atmospheric aging of biomass burning organic aerosol particles, which may alter their impact on climate. The paper was written in a clear and concise manner. It is recommended that this manuscript is published in ACP once the authors have addressed the issues brought up by the referees.

Specific Comments:

The paper highlights the wide range in mass enhancement ratios for the different biomass types, but there is very little discussion on the potential factors that may explain these differences. The authors state that another paper will focus on explaining these changes. Since these results are an important part of this work, a short discussion on possible factors that may be responsible for the variable mass enhancement ratios would be very useful. Some possible factors that might be considered include initial POA mass concentrations, particle phase, initial degree of oxidation of POA, NO_x/VOC ratios, predominance of specific SOA precursor types, VOC concentrations, oxidant:VOC ratios, temperature changes (this was considered in the paper) and the modified combustion efficiency. It would be useful to evaluate whether our current understanding of the SOA formation and aerosol aging mechanisms is sufficient to provide an explanation for both the mass enhancements and the changes in aerosol degree of oxidation.

The photochemical loss of levoglucosan was used to quantify the degree of processing of the initial POA. Could positive matrix factorization analysis be also used to confirm

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the that the photochemical loss rate of the overall POA mass is consistent with the loss of levoglucosan?

Page 12001, line 11: Did you perform any dark experiments (with and without addition of HONO) over 3-4 hrs to ensure that the chemical aging of the organic aerosols (i.e. AMS mass spectral changes) is solely due to photochemistry? A dark experiment would also allow for the quantification of levoglucosan:K⁺ ratios after dilution in the smog chamber (Figure 6).

Page 12002, line 3: What particle transmission efficiency was used here to calculate AMS organic masses? Can it be confirmed that this value is appropriate for OA from all biomass types used here and that the transmission efficiency hasn't changed during the aging experiment?

Page 12002, line 23: Why is there no mention of HR-AMS measurements? A discussion of O/C and H/C ratios would be very useful here. Will these measurements be presented in a future paper?

Page 12008, line 15: It is somewhat misleading to call these experiments "repeat experiments" as most of the experiments were repeated with the addition of HONO, and therefore not repeated under the same conditions as experiments they are being compared to (i.e. different NO_x/VOC ratios) using the same fuel. It should be emphasized that HONO was added to these experiments, therefore changing the conditions. It appears that the addition of HONO has reduced the mass enhancement ratio for the repeat experiments in all cases, some of which were statistically significant. Could this be an indication that the addition of NO_x enhances the fragmentation pathway of the VOC oxidation?

Page 12011, line 1: Figure 5a shows that f₄₄ does not appear to increase for the first hour of lights on, whereas f₄₄ increases from start of lights on in Figure 5d. Can these differences be explained?

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Page 12014, line 21: It would be more appropriate to call this gamma value an 'effective gamma' since the real uptake coefficient value cannot be greater than unity by definition.

Figure 3. Define error bars.

Figure 4. It may be helpful to show the standard deviations of the average R₂ values to show that the trends are statistically significant.

Figure 5. Why is there no expected range of f₆₀ in Fig 5b normalizing changes due to SOA formation and wall losses?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 11995, 2011.

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