

Interactive comment on “Mass yields of secondary organic aerosols from the oxidation of α -pinene and real plant emissions” by L. Q. Hao et al.

L. Q. Hao et al.

hao.liqing@uef.fi

Received and published: 1 February 2011

Response to Referee #2:

The authors thank the reviewer for his/her constructive and helpful comments:

P. 28793, l. 9 and P. 28801, l. 9 Definition of volume growth factor is ambiguous. Do you refer by size to the diameter or to the volume? Please, define V-GF precisely. Moreover, calling the quantity which describes the shrinking a growth factor is somewhat confusing, it is correct though. I suggest to reconsider the terminology.

Answer: We assume that the reviewer is referring here to the “volatility growth factor” and not to “volume growth factor,” the latter of which is not used in the manuscript. While admittedly using the term “growth” to refer to aerosol volatility seems counter-

C13141

intuitive, this is actually the accepted term in the aerosol community. Volatility growth factor, like hygroscopic growth factor, is derived from diameter. We have provided a precise definition in the revised manuscript (Section 2): “Aerosol volatility is presented, expressed as the volatility growth factor (VGF), the ratio of diameter of particle size after evaporation (Deva) to the original sampled diameter (Dori)”

P.28794, l. 3ff This approach to determine the loss rates is applicable only after the aerosol mass production stopped. You did not specify a criterion when you assumed/know that this was indeed the case. This criterion maybe easy for the reaction O₃ with α -pinene, since α -pinene ozonolysis products do hardly react further with O₃. However Ng et al.(2006) demonstrated that particles grow significantly even when the primary precursors are totally consumed.

How do you determine that the aerosol mass production really stopped when OH was in the system? How did you determine that no further reaction of multiple unsaturated terpenes took place after the primary precursors were consumed? I suggest to explain this a little more in the manuscript.

Answer: The procedure for determining aerosol wall loss coefficients is presented in Sec. 2.1. As this and the other reviewer have noted, we did not supply sufficient information in the original manuscript. In fact, we estimated the time-evolution of OH concentrations during each experiment using a kinetic model that is described in detail in Hao et al. (2009). An example of our model result for P1023 is shown in Fig. 6. One measure of the success of our wall loss model, and the validity of the implicit assumptions, is that the experimental data fit to Eq. 3 was excellent, with R² > 0.95.

In response to the reviewer’s comments we have added the following text in Section 2.1:

“The value of k was estimated using the measurements after the oxidation reactivity had completely stopped in the OH-dominated chemistry or the reactivity fraction contributed less than 10% of total reactivity in the O₃-initiated chemistry. To establish this

C13142

we used model estimates of OH concentrations that are described in greater detail in Hao et al. (2009). The experimental data fit to Eq. 3 was excellent ($R^2 > 0.95$), which gives us confidence that the model assumptions of diameter-independent volume loss and negligible gas-particle partitioning during the analysis period were valid."

P.28795, l. 5f I don't understand how can you have an inlet flow of 40 l/min and an out flow of only 15 l/min? Do you inflate the chamber? But then the volume is not 6 m3 all the time. Please, explain.

Answer: As described in the manuscript (Sec. 2, Line 10), '... In both sets of experiments, ozone enriched air (50-800 ppb) was introduced into the chamber at a flow 40 L min⁻¹ following of VOC precursor additions. Ozone injection marked the start of each experiment. After addition of BVOCs and oxidants, the inlet flow was turned off and the chamber was operated in batch-mode; i.e., the chamber was gradually emptied by sample flows to the instruments.' This addition of ozone occurred in the beginning of experiment for approximately two hours following the addition of BVOCs/TME. After this two-hour period, the chamber was fully inflated and thus we turned off inlet flows and operated the chamber in batch mode (that is, only drawing air out of the chamber and into our instruments).

P. 28800, l. 9 Fig. 10 of Mentel et al. 2009 does not show the mass yields, but the mass as a function of consumed VOC. Let's call this type of plot for the moment a growth curve. Since these linear growth curves have positive x-intercepts (nucleation thresholds), the mass yields as a function of VOC or the formed aerosol mass, will also have curvature (like in your Figure 2a). Consider the following equation (m : aerosol mass, y_{inc} : incremental yield, b : y-intercept of the growth curves):

$$m = y_{\text{inc}} \times \text{VOC} - b$$

$$m/\text{VOC} = Y = y_{\text{inc}} - b/\text{VOC}$$

Y is increasing with increasing VOC , thus with increasing m because b/VOC is de-

C13143

creasing and y_{inc} approaches Y for large VOC . The slopes of the linear growth curves ($= y_{\text{inc}}$) give the maximum yield (in the case of linear growth curves). If you compare Mentel et al. 2009 Figure 10 with Ng et al. 2006 Figures 3 and 4 and consider the VOC you will recognize that for that small turnovers, below 100 $\mu\text{g}/\text{m}^3$ Ng's curves are also quasi-linear. Mentel et al.'s dynamic range of VOC is small, thus they may have underestimated the maximum yield. Considering this there seems to be no difference within the errors for the different type of studies.

Answer: We thank the reviewer for these thoughtful insights; we realized that we misunderstood the meaning of Fig. 10 in Mentel et al. (2009) even before the reviewers' comments were received. We failed to understand the existence of the nucleation threshold (parameter b in the reviewer's equation). In Mentel et al. (2009) the SOA mass yield is also aerosol mass dependent (M_0), which has also been shown in similar studies (e.g., Figs. 3, 4 and 5 in Coeur-Tourneur et al. (2009, 2010). This is consistent with our observations.

For a better comparison of our results with Mentel et al. (2009), we have rephrased the paragraph (Line 9-21, 28800) to:

"Few mass yields have been reported from chamber studies of real plant BVOC oxidation. Mentel et al. (2009) reported incremental mass yields of SOA from OH/O₃ initiated pine/spruce emissions. They used a flow reaction chamber with VOC residence time of about 65 mins and ozone level ≤ 80 ppb. For better comparison of these results with our observations, we consider mass yields from only the monoterpene precursors, observed to be $5.2 \pm 0.5\%$, $5.3 \pm 0.6\%$ and $3.5 \pm 0.6\%$ for α -pinene, pine and spruce SOAs, respectively. Based on the maximum organic absorption concentrations in Mentel et al. (2009) for α -pinene (around $4.1 \mu\text{g m}^{-3}$), pine ($2.8 \mu\text{g m}^{-3}$) and spruce ($1.1 \mu\text{g m}^{-3}$) SOA (see Fig. 10, Mentel et al, 2009), the mass yields in this study were interpolated to be 9%, 8% and 4% for α -pinene, pine and spruce SOA, respectively. Their reported values are slightly lower than ours. This difference in mass yields may be due to differences in experimental conditions, e.g., residence times that

C13144

are greater and aerosols slightly more aged in our batch-mode chamber experiments in contrast to the flow chamber used in Mentel et al."

Question: how did your growth curves look like compared to Mentel et al. (2009) and Ng et al. (2006)? Are they straight or slightly upward bent? Can you estimate your nucleation thresholds? Is your mass dependent yield really mass dependent or does it reflect essentially the fact that you also observe a nucleation threshold.

Answer: The growth curves in this study are shown in Fig. S1, in which we observe that aerosol mass loadings are quasi-linear with respect to the reacted VOCs. Though the chemical composition of real plant emissions consists of compounds with more than one double carbon bond in their molecular structure, the absence of oxidants (specifically OH) at end of experiments is likely the reason why we did not observe a sharp upward bend in the growth curve such as that reported in Ng et al. (2006).

Figs. S1 and Fig. S2 are provided in a form of supplement.

The nucleation threshold for pine SOA is 3.0 ppb, for spruce is 4.0 ppb and for α -pinene SOA is 5.4 ppb, as shown in Fig. S2. The mass yields are aerosol mass dependent specially under mass loading 5 $\mu\text{g}/\text{m}^3$ for the real plant SOA as shown in Fig. 4 in the manuscript. Mass yields show a less stronger Mo dependent when Mo is larger than 5 $\mu\text{g}/\text{m}^3$.

P.28802 I.23 P.28804, I.26 Do you have an idea about the driving force of this aging in the absence of oxidants?

Answer: The driving force for the aging in the absence of oxidants might be from cross-reactions among gas- and/or particle-phase products. Examples include accretion reactions such as amide formation and esterification.

P. 28803, I.24 Could it be that the particles were in an amorphous state - liquid or glassy - and started to crystallize?

Answer: The particle phase derived in our plant chamber experiments might be an
C13145

amorphous solid, most probably a glassy-state (Virtanen et al, 2010). As Fig. 5 demonstrates, aerosols become less volatile via an aging process even after the complete consumption of oxidants. This cannot rule out the possibility that the particles are initially in a liquid state, but become more glass-like and less volatile with the aging. We have no evidence that particles were crystalline. Transmission electron microscope (TEM) images and electron diffraction analyses of SOA particles from previous experiments did not show any indications of crystalline particle.

P. 28805, I. 1 The fact that the observations can be described by one set of parameters for the two product model suggests that the SOA formation is independent on the precursor mix. This seems to be in contrast to the previous statement that SOA formation depends on the precursor mix?

Answer: We agree with the reviewer that the volatility and AMS data (Fig. 5) suggest differences in aerosol composition while the presentation of a single set of two-product model parameters (Fig. 4) suggests that the particles are in fact similar. In presenting the model parameters it was not our intention to suggest that the particles are chemically identical, only that a single set of parameters can be fit to the data. In addition, Fig. 4 shows that some scatter that is no doubt caused by compositional differences.

Corrections:

P. 28970, I.15 Must read Saathoff et al. 2009

P. 28791, I. 1 Capitel S in name of reference Kiendler-Scharr et al. 2009. The reference Kiendler-Scharr et al. 2009b does not appear throughout the body of the manuscript. Please check.

P. 28793, I. 6 9 Typos: evapourate evaporation evaporate evaporation

P. 28797, I. 18 You refer to Fig. 2a

Answer: All the corrections have been made in the revised manuscript.

Reference:

Coeur-Tourneur, C., Tomas, A., Guilloteau, A., Heyry, F., Ledoux, F., Visez, N., Riffault, V., Wenger, J.C. and Bedjanian, Y., Aerosol formation yields from the reaction of catechol with ozone, *Atmos. Environ.*, 43, 2360-2365, 2009.

Coeur-Tourneur, C., Foulon, V., and Larázžal, M., Determination of aerosol yields from 3-methycatechol and 4-methylcatechol ozonolysis in a simulation chamber, *Atmos. Environ.*, 44, 852-857, 2010.

Hao, L. Q., Yli-Pirilä, P., Tiitta, P., Romakkaniemi, S., Vaattovaara, P., Kajos, M. K., Rinne, J., Heijari, J., Kortelainen, A., Miettinen, P., Kroll, J. H., Holopainen, J. K., Smith, J. N., Joutsensaari, J., Kulmala, M., Worsnop, D. R., and Laaksonen, A.: New particle formation from the oxidation of direct emissions of pine seedlings, *Atmos. Chem. Phys.*, 9, 8121-8137, doi:10.5194/acp-9-8121-2009, 2009.

Mentel, Th. F., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Dal Maso, M., Fisseha, R., Hohaus, Th., Spahn, H., Uerlings, R., Wegener, R., Griffiths, P. T., Dinar, E., Rudich, Y., and Wahner, A.: Photochemical production of aerosols from real plant emissions, *Atmos. Chem. Phys.*, 9, 4387-4406, doi:10.5194/acp-9-4387-2009, 2009.

Ng, N.L., Kroll, J.H., Keywood, M.D., Bahreini, R., Varutbangkul, V., Flagan, R.C., and Seinfeld, J.H.: Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, *Environ. Sci. Technol.*, 40, 2283-2297, 2006.

Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirilä, P., Leskinen, J., Mäkelä, J.M., Holopainen, J.K., Pöschl, U., Kulmala, M., Worsnop, D.R., and Laaksonen, A.: An amorphous solid state of biogenic secondary organic aerosol particles, *Nature*, 467, 824-827, 2010.

Please also note the supplement to this comment:

C13147

<http://www.atmos-chem-phys-discuss.net/10/C13141/2011/acpd-10-C13141-2011-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 28787, 2010.