

Response to Reviews

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Inter-comparison of laboratory smog chamber and flow reactor systems on organic aerosol yield and composition

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We thank the Referees for the comments and we have incorporated the feedback to improve the manuscript. We have copied the remarks of each Referee in *black italics* and our responses are given in regular black font. Manuscript text including revisions is given in **regular blue font**.

Anonymous Referee #1

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General comments

The present study by Bruns et al. addresses the inter-comparison between laboratory smog chambers and flow reactors systems. The OH radical reaction of α -pinene as well as wood combustion emissions were used as model systems for the present study. The comparison was focused on the organic aerosol yield and the chemical composition. In general, the paper is very well written and the presented data set will be of huge relevance for the aerosol community.

Specific comments

A comparison of smog chamber (SC) and flow reactor systems (PAM and MSC) is so far missing in the literature. Nevertheless, it is not clear why different types of OH radical sources were selected for the comparison present in this study. Furthermore, it is a bit confusing which OH source was used for which experiment. This information should be clearly written in the experimental section and it should be included in Table 1. Furthermore, Table 1 should also contain information about NO_x and ozone concentrations as well as if the experiment was seeded or unseeded and which UV lamps (wavelength) were used for each experiment.

In both the PAM and MSC, OH radical was generated from the photolysis of O_3 in the presence of water vapor, whereas OH radical was formed in the SC through the photolysis of HONO. The photolysis of HONO was used as the OH source in the SC to reach sufficiently high OH exposure within the experimental time dictated by the chamber size and rate of sampling to overlap with the OH exposures obtained in the PAM and MSC. The presence of additional NO_x in the SC generated from the HONO photolysis is not expected to influence the yields in the wood combustion experiments as NO_x from the wood smoke is already present in the SC and flow reactors, however the yields may be influenced in the α -pinene oxidation, as discussed on page 319. As observed in previous studies (Chhabra et al., 2011; Lambe et al., 2015), no differences in the bulk composition are expected due to the presence/absence of NO_x . The OH sources have been added as a footnote to Table 1 (as well as UV lamp wavelengths for each device) and clarified in the text:

Table 1 footnote: “The OH radical source in the SC was the photolysis of HONO. The source of OH radical in the PAM and MSC was the photolysis of O₃ in the presence of H₂O_(g). The peak emission of UV light was at a wavelength of 368 nm in the SC (Platt et al., 2013) and at wavelengths of 185 nm and 254 nm in both the PAM and MSC.”

Page 315: “The MSC is described in detail by Keller and Burtscher (2012). Briefly, the MSC is composed of two 76 mL cylindrical quartz chambers (0.25 m length, 0.020 m diameter) in series. As in the PAM, OH radical is generated from the photolysis of O₃ in the presence of H₂O. Incoming sample was exposed to UVC light (5 total lamps at 4 W each; 185 nm and 254 nm emission lines; Heraeus, type GPH212T5VH/2) in the first chamber and to UVA light (Panacol-Elosol, type UV-H 255) in the second chamber... Unlike in the PAM and MSC, OH in the SC was formed from the photolysis of nitrous acid (HONO), as described below. Without the injection of HONO, similar OH exposures in the SC and flow reactors were not achieved within the experimental timeframe dictated by the chamber size.”

A figure showing the time evolution of NO_x in the SC during aging in the α-pinene experiments was added to the supplementary material (new Figure S1). For the wood combustion experiments, initial NO_x mixing ratios in the SC prior to aging are given in Table S1 in the supplementary material.

No O₃ data are presented as measurements were not made during the experiments.

A column has been added to Table 1 indicating that seed aerosol was used in the α-pinene experiments.

Even that the influence of NO_x is discussed at page 319 a discussion about side reactions is missing. Depending on the ozone concentration during the ozone photolysis, ozonolysis might take place changing the product distribution. It would be helpful for the discussion to provide a picture with the ozone concentration over the whole experiment duration. Besides this reaction, it can be also expected that the different types of UV lamps used for the experiments change the product distribution and aerosol yield due to photolysis of OVOCs (Presto et al., 2005).

Unfortunately, O₃ mixing ratios were not measured during the experiments. However, we have added a discussion on the possible effects of ozonolysis and different lamps in the SC and flow reactors. The following text was added (page 315): “The flow reactors use lower wavelength/more intense UV lamps than the SC and this could influence aerosol yields in both the α-pinene and wood burning experiments by altering the product volatility distribution. For example, Presto et al. (2005) found that yields from α-pinene oxidation were reduced by 20-40% in the presence of UV light compared to dark conditions (i.e., ozonolysis) due to the photolysis of species prior to partitioning to the aerosol phase. However, Hodzic et al. (2015) calculated that the gas-phase photolysis of species formed during the photo-oxidation of α-pinene (α-pinene/NO_x ratio of ~0.1) decreased the SOA yield by only ~15% and there was negligible effect on the bulk particulate oxygen-to-carbon ratio. Although O₃ was not measured in the current experiments and OH radical is expected to be the main oxidant in all systems, it is possible that the relative amount of ozonolysis relative to OH oxidation varied between the devices, which would also influence relative yields.”

Page 316, Line 12: The dilution might lead to a loss of VOCs/OVOCs. Is this considered?

Although the additional dilution of reactants in the PAM is small (~15%), this dilution could result in a loss of semi-volatile materials from the particle phase to the gas phase. However, we expect that any semi-volatile compounds lost from the particle phase due to dilution returns to the particle phase once oxidized in the PAM to form lower volatility products and thus, this dilution is unlikely to influence the yields/emission factors.

The text has been modified to include a discussion of this point (page 315): “When the reactants were sampled directly from the SC through the flow reactors, the dilution ratios were identical for the MSC and SC. The small additional flow of humidified air into the PAM resulted in a ~15% dilution of the reactants, which was accounted for when calculating yields and emission factors. The additional dilution step in the PAM may shift the partitioning of the incoming semi-volatile species towards the gas phase. However, once inside the PAM, these semi-volatile, gas-phase species are expected to repartition to the particle phase as they undergo oxidation to form lower volatility species and thus yields and emission factors were likely not affected.”

Page 318, Line 21: How was α -pinene oxidized in the PAM? According to Table 1 it was also oxidized in the PAM but in section 2.3 no information about these experiments is given.

α -Pinene was oxidized in the PAM in the same manner as the wood combustion emissions were oxidized during “SC sampling”. The text has been modified to include information about oxidization in the PAM during the α -pinene experiments (pages 318-319): “After the injection and mixing of α -pinene and seed aerosol in the SC, the mixture was sampled from the SC into the PAM or the MSC. Oxidation of the mixture in the flow reactors occurred in the same manner as oxidation of wood combustion emissions during SC sampling.”

Page 319, Line 16: Even that the NO_x concentration was zero at the beginning of the experiments a huge increase of NO_x concentration during three hours of experiment can be expected. It would be helpful for the discussion to provide a picture with the NO_x concentration over the whole experiment duration.

The time evolution of NO_x during the α -pinene experiments in the SC has been added as a Figure in the supplementary material (now Figure S1). The main text reads, “The injection of HONO into the SC resulted in NO formation upon irradiation, which was not present in the flow reactors, and may decrease the SOA yields in the SC (Ng et al., 2007). When maximum SOA yields were reached, NO_x mixing ratios in experiments 2 and 3 were ~100 and 120 ppbv, respectively (Figure S1). Ng et al. (2007) found that SOA yields from α -pinene photo-oxidation were decreased by ~40% in the presence of an initial NO_x mixing ratio of 198 ppbv. However, in our study, α -pinene/ NO_x ratios were 20-25 times higher than those used by Ng et al. (2007) and they started with high levels of NO_x whereas here initial NO_x concentrations were zero. Thus, the reduction in yields due to the presence of NO_x is expected to be lower than observed by Ng et al. (2007). The temporal evolution of NO_x and organic aerosol (OA) in the SC throughout aging is shown in Figure S1. As observed in previous studies (Chhabra et al., 2011;

Lambe et al., 2015), no differences in the bulk aerosol composition are expected due to the presence/absence of NO_x.”

Page 323, Line 15: Is it not clear why few of the experiments were conducted in the presence of seed particles and some not. It is known that the presence and type of seed particles can influence the partitioning of oxidation products (Spittler et al., 2006). In the absence of seed particles nucleation will occur forming a pure organic particle. This will change the partitioning behavior of the OVOCs and thus the aerosol yield. This might also explain the much lower aerosol yield obtained from the PAM.

In our study, all α -pinene experiments with the flow reactors and SC were conducted using seed aerosol. As the flow reactors sampled the α -pinene/seed aerosol reactant mixture directly from the SC, the reactants were the same in the SC and PAM. This is in contrast to previous literature studies comparing the PAM and SC (Chen et al., 2013 and Lambe et al., 2011a) where results obtained using the PAM without seed aerosol were compared to SC results obtained with seed aerosol. We agree with the Referee that this can influence partitioning and is one reason why our study improves the understanding of the PAM relative to smog chambers. The paragraph has been rewritten to clarify that in contrast to previous literature comparison, the PAM and SC experiments in this study were all conducted with seed aerosol: “Maximum OA yields determined using the PAM were within a factor of ~1.5 of those of the SC during the same experiments (Fig. 2, Table 1). Chen et al. (2013) and Lambe et al. (2011a) also compared OA yields from the PAM and an SC, however, the PAM and SC experiments were conducted under significantly different conditions. For example, in the studies by both Chen et al. (2013) and Lambe et al. (2011a), the SC experiments were conducted using seed aerosol, whereas the PAM experiments were not. This is in contrast to the experiments in the current study, where seed aerosol was present in both the SC and PAM.”

Technical corrections

Page 310, Line 25: The sentence (“For the wood combustion...”) should be rewritten.

This sentence has been revised as follows: “For the wood combustion system, emission factors measured from the MSC were typically lower than those measured from the SC. Lower emission factors in the MSC may have been due to considerable nucleation mode particles formed in the MSC which were not detected by the AMS or due to condensational loss of gases to the walls inside or after the MSC.”

Page 325, Line 26: “gas-phase” should be changed to gas phase.

“Gas-phase” has been changed to “gas phase.”

Page 344, Table 1: Please include a description for PAM/MSCL_{low, mid, high}. This is not given in the description of the Table or in the manuscript. Is it also not clear which numbers are given in parentheses.

A description of PAM/MSCL_{low, mid, high} has been added to the methods section as follows:

Page 314: “Hereafter, PAM_{high} corresponds to the maximum light intensity and PAM_{low} corresponds to a light intensity of ~70% of the maximum.”

Page 315: “The light intensity was varied during the experiments by adjusting the number of UVC lights used denoted as MSC_{low} (1 light on), MSC_{mid} (3 lights on) and MSC_{high} (5 lights on).”

The values in parentheses are two sample standard deviations and is denoted in a footnote in Table 1: “Two sample standard deviations are given in parentheses.”

Page 352, Figure 8: The figure caption should be rewritten. A short description for θ in the figure caption would improve the understanding of the figure.

The caption for Figure 8 has been rewritten to include a description of θ and now reads: “Comparison of PAM and MSC mass spectra to SC mass spectra for SOA generated during each wood combustion experiment when OH exposures were within 30% (Table 1). Theta (θ), the angle between two mass spectral vectors, describes the degree of similarity between the two mass spectra (Kostenidou et al., 2009). Dashed vertical lines indicate θ of 15° and 30°. Values of θ less than 15° indicate good agreement between the mass spectra, values between 15 to 30° indicate that there are similarities, but also important differences, and values greater than 30° indicate poor agreement (Bougiatioti et al., 2014).”

References

Presto, A. A., Hartz, K. E. H., and Donahue, N. M.: Secondary organic aerosol production from terpene ozonolysis. 1. Effect of UV radiation, *Environmental Science & Technology*, 39, 7036-7045, 2005.

Spittler, M., Barnes, I., Bejan, I., Brockmann, K. J., Benter, T., and Wirtz, K.: Reactions of NO_3 radicals with limonene and alpha-pinene: Product and SOA formation, *Atmospheric Environment*, 40, S116-S127, 2006.

Anonymous Referee #2

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General Comments:

In this paper the authors describe results of laboratory studies that compared the results of aerosol aging experiments conducted in a smog chamber, micro-smog chamber, and potential aerosol mass flow reactor. The latter device is often used to obtain high concentrations of OH radicals that allow more extensive oxidation of organic aerosol than can be obtained in a large smog chamber. The micro-smog chamber is a more recent device that is meant to serve a similar purpose. An important question is whether exposures of high OH concentrations for short periods of time is equivalent to exposure to low OH concentrations for long periods of time, which is expected to be more similar to the atmosphere. In this study the aerosol composition was measured with an aerosol mass spectrometer, aerosol mass with a scanning mobility particle sizer, organic gas phase species with a proton transfer reaction mass spectrometer, and other gases such as NO_x , O_3 , CO with other monitors. Oxidative aging was compared for aerosol formed from the reaction of alpha-pinene with ozone and for woodsmoke aerosol. The experiments appear to be technically sound and the data analysis and interpretation is

reasonable. The results will be useful for comparison with future studies conducted with these instruments. The manuscript is also clearly written. Overall, the manuscript represents a useful contribution to the literature and so I think should be published. I have a few suggestions.

Specific Comments:

1. The approach of the paper is to mostly note similarities and differences among the results obtained with the three aging apparatus and then provide reasonable speculations about the causes. Although the observations are interesting and may be useful, it seems that no new fundamental insights have been obtained. I come away from reading the paper with a feeling that I have learned relatively little other than sometimes results are similar and other times they are not. Are there no take-home messages? What do you conclude about the advantages and disadvantages of the different approaches? Are there conditions where one approach is likely to work better or worse than the others? How reliable is each approach? Is it worth doing other studies to try to investigate in more detail the various factors discussed as possible sources of differences? What specifically do you suggest? What is the likelihood that one or the other or any approach gives results that are representative of the atmosphere? Some effort should be made to give the reader something to take away.

We agree with the Referee that the manuscript is strengthened by adding a discussion on the broader outlook and take-home messages with regard to the use of these flow reactors. The general take-home message is that the PAM and SC agree well in terms of yields/emission factors and composition, whereas further investigation is needed to determine the representativeness of the MSC for simulating atmospheric aging. The agreement between the PAM and SC supports the continued use of the PAM to study atmospheric aging, which is encouraging as the PAM is logistically advantageous due to its portability and its ability to age on the time-scale of seconds to minutes. The PAM is also advantageous for simulating extended aging in the atmosphere, which is challenging in smog chambers due to difficulties in reaching high oxidant exposures without major losses to the chamber walls.

For the MSC, as well as the PAM, further work with more comprehensive coverage of the potential particle size range (i.e., include d_{va} range less than 100 nm and greater than 1 μm) would improve our understanding of the differences in yields when comparing to the SC. This is particularly important for the MSC, where it is not clear if the significant discrepancies in yields and emission factors were due to significant mass below the AMS detection range and/or the design of the MSC (i.e., higher oxidant concentrations leading to fragmentation and insufficient time for condensation of material onto particles inside the reactor).

For the wood smoke emissions with the highest aromatic content, the maximum emission factors measured in the MSC and PAM were largest relative to those measured in the SC, which may be due to the increased ability of aromatics to resist fragmentation to higher volatility products with multiple oxidation steps or higher VOC mixing ratios in these experiments. Further work comparing the yields from aging of aromatic species from the flow reactors and SC would clarify the applicability of flow reactors when analyzing reactants with high aromatic content.

In all cases, the OA loadings, although atmospherically-relevant for some parts of the world, were generally high. Complementary work is needed at lower concentrations (e.g., $<50 \mu\text{g m}^{-3}$)

to determine the representativeness of atmospheric flow reactor studies across a broader range of atmospheric concentrations.

We have expanded the conclusion section to address the points outlined by the Referee. The conclusion section now reads (page 333): “For the first time, the quantities and the chemical composition of organic aerosol generated from the oxidation of α -pinene and of wood combustion emissions with the same precursor mixture were determined using an SC, PAM and MSC. The PAM and SC agreed reasonably well in terms of quantity and composition for the systems and conditions studied here, considering the challenges associated with both approaches (e.g, wall losses of semi-volatile species). The agreement supports the continued use of the PAM to study atmospheric aging, which is encouraging as it is advantageous due to its portability and its ability to age on the time-scale of seconds to minutes. The PAM is also advantageous for simulating extended aging in the atmosphere, which is challenging in smog chambers due difficulties in reaching high oxidant exposures.

One concern with the ability of flow reactors to simulate atmospheric processes is that slower processes contributing to the evolution of the particle phase (e.g., condensed phase reactions) are not able to proceed during the relatively short residence time in these flow reactors. However, the similarity in terms of yields and composition shown here between the SC and PAM indicate that either these slow processes do not significantly alter bulk aerosol yields or composition or that these slow reactions are accelerated and/or compensated for by the fast oxidation in the PAM.

Discrepancies in yields and emission factors between the MSC and SC were larger than between the PAM and SC, possibly due to significant mass below the AMS detection range and/or the design of the MSC (i.e., higher oxidant concentrations leading to fragmentation and insufficient time for condensation of material onto particles inside the reactor). During α -pinene experiments, nucleation was observed in all three systems, higher OH concentrations increased the rate of nucleation and, depending on the residence time, similar OH exposures produced a range of OA sizes. The slowest system, the SC, produced OA in a size range corresponding to the seed, whereas the PAM and the MSC produced an OA mode smaller than the seed. In the case of the MSC, the fastest system, this mode was below the optimum transmission range of the AMS. For wood burning experiments, this size dependency was difficult to establish due to the presence of primary OA.

Further work with more comprehensive coverage of the potential particle size range (i.e., include d_{va} range less than 100 nm and greater than 1 μ m) would improve our understanding of the differences in yields and emissions factors when comparing the MSC to the SC. Determining the sources of discrepancy between the MSC and SC is critical for determining the applicability of the MSC for OA quantification.

For the wood smoke emissions with the highest aromatic content, the maximum emission factors measured in the MSC and PAM were largest relative to those measured in the SC, which may be due to the increased ability of aromatics to resist fragmentation to higher volatility products with multiple oxidation steps or higher VOC mixing ratios in these experiments. Further work comparing the yields from oxidation of aromatic species in the flow reactors and SC would clarify the applicability of flow reactors when analyzing reactants with high aromatic content.

In all cases, the OA loadings, although atmospherically-relevant for some parts of the world, were generally high. Complementary work is needed at lower concentrations (e.g., $<50 \mu\text{g m}^{-3}$) to determine the representativeness of atmospheric flow reactor studies across a broader range of atmospheric concentrations.”

Technical Comments:

None.