

## ***Interactive comment on “Design and characterization of a smog chamber for studying gas-phase chemical mechanisms and aerosol chemistry” by X. Wang et al.***

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General comments: The authors attempt to describe the design and characterisation of a new smog chamber for studying gas-phase chemical mechanisms and aerosol chemistry. The manuscript suffers from a serious lack of details and discussion in several places. It can be considered for publication in AMT, if the authors address the following comments and concerns. Reply: Thanks for the comments. We really appreciate the hard work in reviewing this manuscript.

Main comments: Page 7737-7739: Generally, the introduction is too short and does

C3255

not provide a good enough overview of the range of existing chambers and their main features. This is not to ask for a literature review of existing chambers, but to provide an overview of the main design factors that the authors learnt from the literature and attempted to implement or avoid in their new design. Reply: Thanks. When we started to construct our chamber, we did review the literature for all the main design factors (indoor/outdoor? volume? wall material? light source? Temperature control?...). In the introduction, we have mentioned why we preferred an indoor one with a larger volume. In the revised manuscript, we have made these two factors more clearly stated. For the more detailed design factors like wall material, light sources and temperature control, we have added overviews of these design factors in the part of “2.1 Enclosure”, “2.2 Reactor” and “2.3 Light source”. In the revised manuscript we added “Although the aims of these smog chambers are similar, their designs and capacities vary widely, displaying big differences in factors like sizes, reactor wall materials and light sources.” (Page 7738 Line 8 in the AMTD version). We changed “The reactor material” (Page 7740 Line 10 in the AMTD version) to “Chamber reactor walls can be made of Teflon film (Cocker et al., 2001a; Carter et al., 2005), Pyrex (Doussin et al., 1997), quartz (Barnes et al., 1987), aluminum (Akimoto et al., 1979) or stainless steel (Wang et al., 2011). Except for the AIDA chamber (Saathoff et al., 2003), most bigger smog chambers of tens cubic meters were made of Teflon film for technical and economical reasons (Cocker et al., 2001a; Carter et al., 2005; Pandis et al., 1991; Johnson et al., 2004; Martin-Reviejo and Wirtz, 2005; Rollins et al., 2009). The reactor wall material of this chamber” and the related references (Page 7751 Line 26, Page 7753 Line 7 and Page 7755 Line 7 in the AMTD version). We also changed “The enclosure temperature” to “For indoor Teflon chambers, air conditioning systems are widely used to control the temperature within the troposphere temperature range which is roughly from -60 °C to 40 °C (Takekawa et al., 2003; Carter et al., 2005; Paulsen et al., 2005; Wu et al., 2007). The enclosure temperature of our chamber” (Page 7739 Line 23 in the AMTD version).

Page 7738, lines 9 – 20: this part of the introduction does not really explain the problem or the solutions and needs to be elaborated up on. Reply: Thanks. In the manuscript

C3256

we changed “Chamber wall effects are known to be an important source of uncertainties when evaluating the mechanisms or models (Carter et al., 1982; Carter and Lurmann, 1991; Dodge, 2000). Large volume reactors can minimize the wall loss of gas phase species and particles, therefore many studies of SOA formation have been carried out in large outdoor chambers (Leone et al., 1985; Stern et al., 1987; Pandis et al., 1991; Johnson et al., 2004; Martín-Reviejo and Wirtz, 2005; Rollins et al., 2009). But diurnal variations of the actinic flux and temperature make it difficult to model the experimental data and to reproduce the experiments.” to “Outdoor chambers are unique in the availability of natural sunlight. Many simulation experiments on SOA formation have been carried out in large outdoor chambers (Leone et al., 1985; Stern et al., 1987; Pandis et al., 1991; Johnson et al., 2004; Martín-Reviejo and Wirtz, 2005; Rollins et al., 2009). However, diurnal variations of the actinic flux and temperature make it difficult to model experimental data and to reproduce the experiments. Indoor chambers instead can provide precise control of temperature and humidity, but may suffer from the difference between the artificial light spectrum and solar spectrum, resulting in different rates of some photolysis reactions between the artificial and natural systems (Takekawa et al., 2003; Carter et al., 2005; Paulsen et al., 2005). Nonetheless, artificial light allows the experiments to be repeatable under same irradiation conditions. Smog chambers are not without any limitations or uncertainties in chamber wall effects when evaluating the mechanisms or models (Carter et al., 1982; Carter and Lurmann, 1991; Dodge, 2000). For example, off-gassing of NO<sub>x</sub> and other species from chamber walls may introduce contaminations to the background gas and affect the utility of the data. Similarly, chamber wall effects may lead to big uncertainties when evaluating experiments at low concentrations. Large volume reactors with small surface-to-volume ratios can minimize the wall effects and the wall loss of particles and gas phase species. Moreover, larger volume allows experiments of longer durations to be conducted and more instruments to be used.” (Page 7738 Line 9-16 in the AMTD version)

Page 7745: no discussion was provided at all for the implications of the data presented in Figure 2a for experiments at low/high temperatures? Does this mean that for experi-  
C3257

ments of this type, injection of chemicals has to be delayed until the target temperature is reached? If not, how would you deal with the data during the period of temperature stabilisation? Reply: Yes. We injected chemicals until the target temperature was reached.

Page 7745: the discussion of “dilution” is very abstract. Did the authors account for wall loss rate of the tracer compounds in your evaluation of the dilution effect? How would high volume sampling lead to dilution if you are not supplementing the chamber with any additional air? Reply: Concentrations of tracer compounds such as CH<sub>3</sub>CN or SF<sub>6</sub> may decrease during experiments due to wall loss, dilution or reactions with OH radical. Figure 1 shows the time series of CH<sub>3</sub>CN concentration during an experiment. CH<sub>3</sub>CN showed a stable concentration, which means no wall loss or dilution of this tracer compound. So in the manuscript we concluded that dilution was not detectable within the uncertainty of the instrument. For reactors that cannot easily collapse, high volume sampling may lead to dilution. As for our chamber, dilution due to sampling was expected to be very small because the flexible reaction bags can collapse to maintain a differential positive pressure between the inside of the reactor and the enclosure when air sample is withdrawn for analysis.

Page 7746: The discussion of the light spectrum and its suitability to the application of simulating atmospheric chemistry is currently absent from the manuscript. This needs to be included. The chosen lights account for part of the solar spectrum. What potential implication could this have on the gas phase and aerosol composition compared to the atmosphere? Reply: The drawback and the influence of the light spectrum were discussed in the section “2.3 light source” of the manuscript (Page 7741 Line 10-21 in the AMTD version).

Page 7747: Although the discussion mentions the size dependence of the particle wall loss, the characterisation was only provided using the total particle number ignoring the size dependence! No discussion was provided! Reply: Thanks. We did evaluate wall loss for particles with different sizes. In the revised manuscript we added “For aerosols

with  $d_p$  of 60, 100, 200, 300 and 400 nm, KN was determined to be 0.41, 0.23, 0.12, 0.08 and 0.10 h<sup>-1</sup>, respectively. Like the study by Takekawa et al. (2003), our results also suggested that smaller particles deposit more easily onto the reactor walls. For aerosols with  $d_p = 300$  nm, the wall loss rate of 0.08 h<sup>-1</sup> is near but lower than that of 0.10 h<sup>-1</sup> reported for the TCRDL chamber (Takekawa et al., 2003)" (Page 7747 Line 24 in the AMTD version) and the related reference before Line 23 Page 7755 in the AMTD version. "Values of KN... in our GIG-CAS chamber" was deleted. (Page 7747 Line 24-25 in the AMTD version).

Page 7749: No discussion is provided for the clear model over-estimation of NO<sub>2</sub>. This should be provided in the revised manuscript. Reply: The NO<sub>2</sub> concentrations were also over predicted at the beginning when Hynes et al. (2005) simulated the propene-NO<sub>x</sub> photolysis experiments with MCM v3.1. Similar phenomenon was also observed for ethene-NO<sub>x</sub> photolysis experiments (Bloss et al., 2005; Zádor et al., 2005). It seems that MCM v3.1 may under estimate the NO<sub>2</sub> sink at the beginning. Probably some unknown reactions involving NO<sub>2</sub> sinks need to be included in the mechanisms to better simulate the NO<sub>2</sub> concentration. Further studies are needed to improve the performance of the simulation. In the revised manuscript we added "The peak NO<sub>2</sub> concentration is over predicted and probably some unknown mechanisms involving NO<sub>2</sub> sinks need to be included for better simulation." (Page 7749 Line 4-5 in the AMTD version). References: Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, *Atmos. Chem. Phys.*, 5, 641-664, 10.5194/acp-5-641-2005, 2005. Hynes, R. G., Angove, D. E., Saunders, S. M., Haverd, V., and Azzi, M.: Evaluation of two MCM v3.1 alkene mechanisms using indoor environmental chamber data, *Atmos Environ*, 39, 7251-7262, 2005. Zádor, J., Wagner, V., Wirtz, K., and Pilling, M. J.: Quantitative assessment of uncertainties for a model of tropospheric ethene oxidation using the European Photoreactor (EUPHORE), *Atmos Environ*, 39, 2805-2817, <http://dx.doi.org/10.1016/j.atmosenv.2004.06.052>, 2005.

C3259

Page 7750: again the discussion of the results is very brief and does not provide enough information about the other datasets it is being compared to. Were they all also ozonolysis under dry conditions? did any of the studies involve photooxidation? did any of the studies use OH scavenger or use seed particles? Reply: Other datasets were all obtained at similar conditions. In the revised manuscript we added "Only the yields obtained for the dark ozonolysis of  $\alpha$ -pinene under dry conditions in the absence of OH scavenger and seed particles were considered." (Page 7750 Line 16 in the AMTD version).

Page 7750, line 12: SOA particle density is quite often assumed to be in the range of 1.2 to 1.4 g/cm<sup>3</sup>. A density of 1.3 g/cm<sup>3</sup> was determined for  $\alpha$ -pinene SOA in previous studies (e.g. Bahreini et al., 2005, Alfarra et al., 2006). In fact, the manuscript already states that the Saathoff et al., study applied a factor of 1.25 g/cm<sup>3</sup>. This has an effect on the yield calculations and should be included. Alternatively, the mass measured by the AMS (if available) should be used for the yield calculation. Reply: The density of  $\alpha$ -pinene SOA varied from different research groups. Wirtz and Martin-Reviejo (2003) and Wang et al. (2011) determined a density of 1.0 g cm<sup>-3</sup> for  $\alpha$ -pinene SOA. On the other hand, a unit density was still frequently used in the studies of  $\alpha$ -pinene SOA (Donahue et al., 2012; Henry et al., 2012). So we used the unit density for comparison with previous studies. In the revised manuscript we added "This assumed aerosol density is lower than that of 1.3 g cm<sup>-3</sup> by Bahreini et al. (2005) or Alfarra et al. (2006) for  $\alpha$ -pinene SOA. However, Wirtz and Martin-Reviejo (2003) and Wang et al. (2011) both adopted a value of 1.0 g cm<sup>-3</sup>. Here we used the unit density for all the experiments when comparing our results with those from previous studies." (Page 7750 Line 13 in the AMTD version) and the related references in Line 19-26 Page 7751. In the manuscript, we only used the SMPS data, similar to previous studies, to calculate the SOA yields. That way we can conveniently compare our results with theirs. References: Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., Tillmann, R., Wahner, A., Saathoff, H., Naumann, K.-H., Möhler, O., Leisner, T., Müller, L., Reinnig, M.-C., Hoff-

C3260

mann, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Praplan, A. P., DeCarlo, P. F., Dommen, J., Prévôt, A. S. H., and Baltensperger, U.: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, *Proceedings of the National Academy of Sciences*, 10.1073/pnas.1115186109, 2012. Henry, K. M., Lohaus, T., and Donahue, N. M.: Organic Aerosol Yields from  $\alpha$ -Pinene Oxidation: Bridging the gap between first-generation yields and aging chemistry, *Environ Sci Technol*, 10.1021/es302060y, 2012. Wang, J., Doussin, J. F., Perrier, S., Perraudin, E., Katrib, Y., Pangu, E., and Picquet-Varrault, B.: Design of a new multi-phase experimental simulation chamber for atmospheric photo smog, aerosol and cloud chemistry research, *Atmos. Meas. Tech.*, 4, 2465-2494, 10.5194/amt-4-2465-2011, 2011. Wirtz, K. and Martin-Reviejo, M.: Density of secondary organic aerosols, *J. Aerosol Sci.*, 34, S223–S224, 2003.

Page 7751, lines 4-5: The claim made here, and in other parts of the manuscript, that the facility can provide valuable data on aerosol chemistry has not been supported by any data in the current version of the manuscript. Only demonstration of gas phase chemistry and aerosol particle formation were illustrated. This has to either be supported by data or the text should be modified to reflect this fact. Reply: Thanks. Yes, aerosol chemistry is a very complicated topic. We only conducted the well-recognized “standardized tests” to see if our chamber performance was comparable with well-known chambers in other research groups. Multiple-phase aerosol chemistry is a challenging issue and we need to further check if smog chamber can help to deepen our understanding on this issue. In the revised manuscript we modified “gas-phase mechanisms and aerosol chemistry” to “gas-phase chemistry and secondary aerosol formation”. (Page 7737 lines 10-20 and Page 7751 lines 4-5 in the AMTD version)

Other comments and minor corrections: Page 7738, line 26: change “for long duration” to “for a long duration” or “for long durations”. Reply: As suggested we have revised it to “long durations”.

C3261

Page 7741: clean air at flow rates of 45 and 200 lpm is mentioned; a blower with flow rate of 1 m<sup>3</sup>/min is also mentioned. Please clarify these and how they are used! Reply: The flow rate of 45 lpm is used to provide ultra-pure matrix gas (Page 7741 Line 23-24 in the AMTD version). The flow rate of 200 lpm is used to provide matrix gas for high concentration precursors experiments (Page 7742 Line 3 in the AMTD version). We evacuate the reactor using a blower with a flow rate of 1 m<sup>3</sup>/min. To point out this, we added “to evacuate the reactor” in the manuscript (Page 7741 Line 4 in the AMTD version).

Page 7744, line 17: add Aiken et al., (2007, 2008) as the correct reference for elemental ratio measurements by HR-TOF-AMS Reply: Revised as suggested.

Page 7744, line 19: change “ammonia” to “ammonium” Reply: Revised as suggested.

Page 7747: why did propene was not lost to the walls, while NO, NO<sub>2</sub> and O<sub>3</sub> did?! Explain or discuss. Reply: Propene was supposed to be lost to the reactor walls, but its wall loss rate was relatively small. NO, NO<sub>2</sub> and O<sub>3</sub> instead may be lost to walls due to heterogeneous reactions. In the manuscript, we added “Unlike NO, NO<sub>2</sub> and O<sub>3</sub> that might be lost to the reactor walls due to heterogeneous reactions, wall loss rate of propene was relatively small and not detectable.” (Page 7747 Line 9 in the AMTD version).

Page 7747: How did the seed particles mode increase from 150nm to 200nm in the absence of condensation? Please provide an explanation or discuss. Reply: The increase of the median diameter from 150 nm to 200 nm was caused by coagulation of smaller particles and probably higher wall loss rate of smaller particles. In the manuscript we changed “grows up to 200 nm” to “increases to 200 nm due to coagulation of smaller particles and probably higher wall loss rate of smaller particles.”(Page 7747 Line 24 in the AMTD version).

Page 7747: did you mean “median” diameter or “mode”? not “medium”? Reply: We mean median diameter here. In the manuscript we changed “medium” to “median”.

C3262

(Page 7747 Line 23 and 24 in the AMTD version).

Page 7750, line 10: did you mean in the presence or absence of seed particles? Please clarify. If it was in the presence of seed, then the details should be included in Table 6. Reply: We mean absence of seed particles. In the manuscript we changed “without OH scavenger and seed particles added” to “in the absence of OH scavenger and seed particles”. (Page 7750 Line 10 in the AMTD version).

Page 7751, Line 2: Change “We have built an indoor smog chamber ever largest in China.” to “We have built the largest indoor smog chamber in China. . . .” Reply: Revised as suggested.

Table 1: DL for HR-TOF-AMS have been published and documented for the different chemical species that can be measured by this instrument (see DeCarlo et al., (2006) for details). I suggest that DL for organics is quoted here. Reply: Revised as suggested.

Table 3: The volume of the GIG-CAS chamber should be changed from “3” to “30” Reply: Revised as suggested. Thanks for careful check.

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Interactive comment on Atmos. Meas. Tech. Discuss., 6, 7735, 2013.

C3263

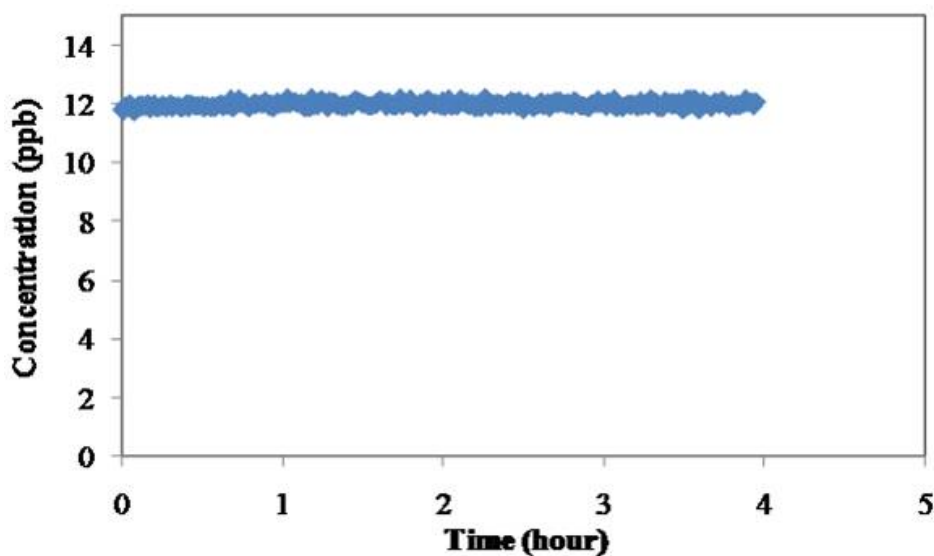


Fig. 1. Time series of CH<sub>3</sub>CN concentrations during an experiment

C3264