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Atmospheric Measurement Techniques Discussions

Interactive comment on "COMPASS – COMparative Particle formation in the Atmosphere using Simulation chamber Study techniques" *by* B. Bonn et al.

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General

We appreciate both reviewers' comments, thank both for their time spent and expertise used to improve the current stage. Each of the comments will be discussed in the following. In order to allow a better comparison to the individual remarks the comments are splitted into major and minor comments with the corresponding reviewers' number (#1 and #2) above the individual aspects named.

Major comments

Reviewer #1 only

1. Language issue: *Response: Thanks for the comment made. There is certainly no native English speaker among the authors and we will act as suggested for a better understanding of the content and the points made.*

2. Context of work and its relation to laboratory based simulation or smog chambers, further input on simulation chambers, emphasizing the portability of the novel approach and title: *Response: This pack of comments include quite valuable suggestions that will be followed where possible: (I+II) We will include an extra subsection on previous and current approaches performed using simulation chambers to make the reasoning for an alternative set-up more evident. Therefore the different current approaches such as static and flow chambers will be named, the atmospheric chambers using ambient sunlight summarized and the PAM chamber approach using ambient air within the laboratory shortly explained. This will be followed by a new Table 1 comparing the different chambers and listing every chamber benefits and challenges (here: Table 1, revised article: new Table 1).*
   Please note in this context: We called this portable twin chamber "simulation chamber" because of the aim to allow box modelling. This requires a certain well defined state including flows and wall losses excluding significant contributions of turbulence and dilution. However, in the historical sense a simulation chamber with a high amount of applied instruments especially optics on gas-phase measurements is certainly not meant. Otherwise a move in space would be impossible. This highly equipped state is hard to achieve for a portable system so that the approach and the instrumentation depend on the focus of the individual study. Since the twin chambers are essentially flow tubes they can be characterized as a common simulation chamber, but not with respect to well defined temperature and radiation conditions as in the laboratory using lamps. It's an intermediate

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state between the large atmospheric simulations chambers such as EUPHORE (Valencia, Spain) or Caltech chamber (Pasadena, US) or SAPHIR (Juelich, Germany) and the ambient measurements. We will clarify those aspects in the text.
(III) *The portability will be stated clearly adjoined with the reason for that.*
(IV) *By forcing the system into a certain state (high ozone, no radiation, high VOCs) the set-up can provide answers about the progress of ambient processes in a kinetic sense and about limiting parameters. This forcing into a certain condition by the modification led to the naming of simulation chamber studies as the process then can be simulated. I am aware of a large set of static chambers such as at Valencia (EUPHORE (Becker, 1996)), at the Paul-Scherer-Institut (PSI-SCAC (Paulsen et al., 2005)), at Juelich (SAPHIRE (Karl et al., 2004)), at Caltech (Catech chamber (Kroll and Seinfeld, 2007)), Penn State University (PAM (Kang et al., 2007)), at Créteil (CESAR (Wang et al., 2011)) and at the University of Toronto (TPOT (Slowik et al., 2012)) in order to investigate ambient air mixtures and their processes at well or partially well-defined conditions. The benefit of well-defined laboratory particles is at the same time its largest deficit, since they hardly meet conditions in the ambient. Reaction pathways, atmospheric chemistry mixtures and aerosol formation as well as ageing can be investigated in detail. Moreover this approach allows to observed the daily and seasonal change as aerosol composition is highly diverse and of notable change throughout the year.*
In order to prevent misunderstand the title shall be changed to
"COMPASS - COMparative Particle formation in the Atmosphere using ***portable*** *Simulation chamber Study techniques"*

3. Chamber characteristics such as light transmission and leak rate: *Response: Thanks for this comment. The light transmission is indeed important information and will be added in a further table (here: Table 2, revised article: new Table 2, former table no's will be shifted by +2) in the study for different light spectra regions (UV, visible, sunlight) as provided by the company. The leak rate is actually included in the dry deposition rate as CO_2 was chosen as reference gas and the deposition rate was obtained from*

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*initial and final mixing ratio measurements. The aspect of dry deposition rate constant will therefore be corrected to "**loss rate consisting of leak rate and dry deposition**".*

4. Concerns about the particle loss rates: *Response:*

   (i) *The high level of loss rate was certainly a point of intensive discussion among the ones using the set-up. It is worth to note that a laminar flow profile (flow tube) is being applied on the contrary to a standard experimental chamber. Therefore different residence times and process stages are to be considered in the axial direction of the flow towards the wall. Particles at the outer ranges of the chamber experience a notably closer wall contact and longer residence time than particles in the centre of the flow. As a consequence particles will diffuse to the outer regions of the flow and will experience a higher loss rate. For common time scales of flow chamber experiments of seconds up to two minutes this hardly changes the conditions in the central part. But for longer residence times required for notable effects of additions in the atmospheric range of compounds this result in an increased loss rate for particles. The second aspect is the stickiness of particles with respect to carbon dioxide used for gases. Thus, the gas loss rates maybe assumed as leak rate while the extrapolated particle loss rate to both i.e. the leak and the deposition loss. We will include the revised particle loss rate (here: Figure 1, revised article: Figure 5) and state the extrapolated loss rate for gases at a size of 1 nm in molecular diameter.*
   *In the text we will include the extrapolated sticking loss rate **kloss,stick, gas** as "**As the gas loss rate was determined for a non-sticking gas, we extrapolate the particle based loss rate including sticking to the wall surface to** $k_{loss,stick,gas}$ **= (1.84±0.01)×10^{-3} s^{-1}.Therefore sticking gases will get lost on the chamber walls 100 times faster providing a lifetime in the gas-phase of about 9 min.**"*

   (ii) Long term effects: *Response: The long term effects are certainly a key aspect for any chamber including wall losses and resuspension. In the present approach however, both chambers will be affected in a similar way and comparative studies will only be affected in case one chamber displays an extreme increase in particles,*

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resulting in enhanced particle mass losses in one of both chambers. This was not observed in our testing experiments in notable amounts. Nevertheless, before any new experiment the chambers are run for a day under excess oxidative conditions to prevent chemical interactions.

(iii) The distinct loss rates of particles: *See response to comment (i) above.*

5. Concerns about the pen-ray applied for ozone production: *Response:*

(i) Place of pen ray installation: *Response: Certainly this aspect will be clarified. The pen-ray was located in the uppermost part, where the ambient air flows out of the aluminium tube protecting the chamber from rainfall. It was placed basically in the uppermost 10 cm of the widening inlet section.*

(ii) Effects of pen-ray lamp on gases and particles in the chamber air as well as on particles already deposited to the wall: *Response: The authors are aware of the cleaning aspect of lamps regarding chamber walls. The lamps used had a distinct spectrum at 253.7 nm, where the ozone absorption band is located. Most of the ambient gases absorb at a different wavelength. But a notable impact may be present. However, the PTR-MS data of both chambers didn't show significant effects on organic gas mixing ratios with and without additional ozone at Frankfurt, and only to a moderate extend on gases at Taunus Observatory between with and without sunlight. But that is of course a point to be investigated in future studies.*

(iii) Mode change in the presence of ozone: *Response: Yes, the mode clearly changes. Please find the mode fitted data in Figure 2 of this response. The ozone was increased in COMPASS 1 on DOY 287 at noon and returned back to normal conditions on DOY 289 shortly after sunrise after the ozone lamp was turned off.*

(iv) High ozone values chosen at Frankfurt: *Response: The basic goal of that first testing period was to figure out if there is any effect on the particle size distribution at all. The lamp chosen was of high intensity. This was corrected at the second study at the spruce field site, where much more reasonable values have been adjusted.*

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(v) Erratic ozone structure in Figs.11 and 12: *Response: There are several possible reasons for this behaviour: One is the high relative humidity at night-time for the first ozone period, while during the second with reduced light the modified chamber was covered and thus isolated by an aluminium foil. Second, a potential attraction to moths at night-time with intensive light. Insects have been seen at one early check to be present in the chamber with the ozone pen-ray possible attracted by the light. A third potential reason may be different airmasses arriving at the site of interest and its impact on the ozone production intensity. Depending on the prevailing wind direction there is substantial impact from the anthropogenically influenced Rhine-Main-area or there is primarily biogenic impact from the opposite directions. Therefore the NO_x and VOC impacts changes notably on the short scale. As the modified chamber was covered by aluminium in the second phase especially aspects one and two may be influenced: No attraction of insects due to missing light and better isolation from temperature drop. Further details require more studies to elucidate the exact cause for this behaviour.*

6. Temperature inside the chambers: *Response: Yes, but the sensor was not protected from sunlight! Thus the temperature can be seen partially as solar radiation measurement the chamber temperature within the sunlight. No the particles and gases have not been measured twice. For this very good purpose either the time resolution would have to be reduced or more instrumentation would have been required. The latter was not available during those particular studies.*

7. Small reference number to literature: *Response: This study provides the first measurement with the novel set-up therefore the results and discussion sections rely on the new measurements only. Regarding the general discussion and comparison with former studies, which aimed to investigate similar aspects we will add the corresponding references listed above (comment 2. (IV)). However, this approach is hardly comparable to lab studies.*

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Minor comments

Comments of reviewer #1:

1. P. 5959. Title to be changed: *Response: As stated at major comment no. 1 we will change the title and include the word 'portable' to make this aspect clearer.*

2. Abstract modification: *Response: Deleting the first three sentences will be made. The deposition rate summary will be changed to loss rate for gases and particles separately, respectively. The reference to the individual testing periods, i.e. ozone, solar radiation and VOC addition, will be extended. The entire abstract will therefore be changed as follows:* ***"In this study we report the set-up of a novel twin chamber technique that uses the comparative method and establishes an appropriate connection of atmospheric and laboratory methods to broaden the tools for investigations. It is designed to study the impact of certain parameters and gases on ambient processes such as particle formation online and can be applied in a large variety of conditions. The characterisation of both chambers proved that both chambers operate identically with a residence time*** x_τ ***(COMPASS 1)=26.5±0.3 min and*** x_τ ***(COMPASS 2)=26.6±0.4 min at a typical flow rate of 15 L min*** $^{-1}$ ***and a gas leak rate of*** $(1.6 \pm 0.8) \times 10^{-5}$ ***s*** $^{-1}$***. Particle loss rates were found larger due to their stickiness to the chamber walls with an extrapolated maximum of*** 1.8×10^{-3} ***s*** $^{-1}$ ***at 1 nm, i.e. a hundredfold of the gas leak rate. Comparison measurement showed no significant differences. Therefore operation under atmospheric conditions is trustworthy. To indicate the applicability and the benefit of the system a set of experiments was conducted at different conditions, i.e. urban and remote, enhancing ozone and terpenes as well as reducing sunlight in separate experiments. In order to do so, an ozone lamp was applied to enhance ozone in one of both chambers; the measurement chamber was protected from radiation by a first aid cover and VOCs were added using a small additional flow and***

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a temperature controlled oven. During the elevated ozone period ambient particle number and volume increased substantially at urban as well as at remote conditions by a different intensity. Protection of solar radiation displayed a clear negative effect on particle number, while terpene addition did cause a distinct daily pattern. E.g. adding β-pinene particle number concentration rose by 13% at noontime, while no significant effect was visible during darkness. Therefore the system was found to be a useful tool to investigate local precursors, the details of ambient particle formation at surface locations as well as potential future feedback processes."

3. p. 5961, reference to IPCC: *Response: Will be provided. Thanks.*
4. p. 5962, reference to other attempts in that area so far: *Response: Will be made.*
5. p. 5965, reference Bourtsoukidis et al. (2012): *Response: Will be inserted. Thanks.*
6. p. 5966-5977, residence time determination: *Response: The goal was to establish a reasonable time for gas-phase reactions with reasonable concentrations while keeping the losses at a moderate level. Therefore different flow rates applicable to the instrumentation used are applied to allow a future change of the flow depending on the specific aim of the study and the required sampling flow.*
7. p. 5967, reference to Seinfeld and Pandis (2006): *Response: Will be added. Thanks.*
8. Comment: Section on particle deposition and the fitting procedure. *Response: Will be explained in a better way. The revised Figure 5 (see major comment #4) will be introduced and the process of acquisition explained in detail.*
9. *Response: No, only ambient aerosol was used.*
10. p. 5970: *Response: Correct. Year **2012** was meant. Will be changed.*
11. p. 5070, particle formation: *Response: Those measurements are made in an area affected by traffic. Because of the huge emissions particle growth rates are much more*

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enhanced compared to the ones commonly observed at remote sites. Nevertheless a clear growth can be seen and be analysed when using a mode fitting tool. Indeed, PAK is PAH and was a failed translation from German into English. Will be corrected.

12. p. 5972, reference to Fig. 8: *Response: Will be added to section 4.1.1.*

13. p. 5972, scatterplot of ozone vs. N: *Response: Will be added.*

14. p. 5974, reference to possible role of OH: *Response: Radicals such as OH and NO_3 were meant. This will be corrected in the text.*

15. p. 5974, l.4-5: *Response: See response to major comment 5 (v) and the impact of moths.*

16. p. 5974, l. 23-25. Erroneous statement: *Response: Particle number increase above 10^5 cm^{-3}, but the upper detection limit of the counter was 105. Therefore the values of 9.99e+4 were removed.*

17. pgs. 5975 and 5976: *Response: The section titled "Phase II" is somewhat hard to follow and should be made clearer: Will be made the following way: "Phase II – **tests at remote conditions**".*

18. p. 5979, lines 23-25: *Response: Correct. This was meant different. As two chambers are used in parallel the loss rate (and not deposition rate as the reviewer remarked above) is identical in both chambers. Except for newly formed mass and number the loss rate is identical and can be neglected in the ratio. The actual correction of the additional reduction/production in the experimental (modified) chamber then depends on the size distribution present and the time of being formed. That is one of the essential reasons of using two chambers. This point will be made obvious in the new subsection including Table on benefits of the novel approach.*

19. p. 5980, lines 9-11: *Response: OK. We will reformulate this sentence to make the hypothetical character more evident: "Therefore this **indicates** a potential rise in particle mass **during elevated** ozone **episodes as expected** in future climate **projections**.".*

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20. p. 5987, Table 3: *Response: The significant changes that are highlighted in bold are somewhat selective. E.g., why is acetaldehyde highlighted, but methyl salicylate is not? Author response: Evident, because the uncertainty range is larger than the baseline. The change in methyl salicylate is statistically not significant. Only those with significant changes are marked bold.*

21. p. 5988, Table 4: *Response: The significant changes that are highlighted in bold are somewhat selective. E.g., why is formaldehyde highlighted, but methyl salicylate is not? Author response: See comment above.*

Comments of reviewer #2:

1. Studies of revealing the need to have a second chamber: *Response: The second chamber was set up in order to manage two basic challenges of a chamber approach, i.e. (1) Any modifications due to the presence of the chamber walls such as losses as well as (2) To establish a direct way of intercomparison at atmospheric level with ambient conditions. Direct intercomparison was only made in order to quantify the gaseous and particulate loss rates. While those where found insignificant for non-sticking gases such as carbon dioxide ($k_{loss,gas,non-sticky} = (1.3 \pm 0.6) \times 10^{-5}\ s^{-1}$), the losses found for particles were quantified substantial. Extrapolated to the molecular size range this was found for sticky gases as $k_{loss,stick,gas} = (1.84 \pm 0.01) \times 10^{-3}\ s^{-1}$ and therefore about 150 times per second more severe. If we take into account the residence time at for instance a flow rate of 15 L/min (mean: 2142 s) 92% is to be expected. We would conclude this result as a need for a second chamber. This will be stated clearer in the revised text at the end of the deposition section 3.2: "**As the extrapolated loss rate of particles to molecular sizes results in a total loss of about 92% for sticky gases we conclude that***

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the usage of two chambers is highly preferable for our kind of comparable effect studies."

2. Complexity of the system, when changing only a single variable at once: *Response: Thanks for naming this important aspect. Since the atmospheric system is essentially complex and modifying a single parameter or variable may result in a change of a large sum of variables, we quantify as much parameters as possible and apply a box model for interpretation of our observations. In order to understand at least parts of the entire system a start with changing a single parameter only is recommended. To prove for instance the effect of changing two parameters at once we have changed the light and oxidative conditions to see which one is more important (section 4.2.1). But certainly this important aspect should always considered when performing such kind of experiments.*

References

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Karl, M., Brauers, T., Dorn, H. P., Holland, F., Komenda, M., Poppe, D., Rohrer, F., Rupp, L., Schaub, A., Wahner, A. (2007). Kinetic Study of the OH-isoprene and O_3-isoprene reaction in the atmosphere simulation chamber, SAPHIR. *Geophys. Res. Lett.*, 31:L05117.

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Aspect	Simulation chambers	COMPASS	Ambient meas.
Controlled conditions (gases, T, rH, particles and composition)	Yes (benefit)	Partly yes (modified parameter(s), basic conditions, benefit), partly no (several unknowns, disavantage)	No (disadvantage)
Atmospheric mixing (transport, dilution)	No (disadvantage)	Before the inlet. Not after entering the tubes	Yes (benefit)
Acquisition of knowledge (formation processes, interaction, heterogeneous chemistry	Condition specific, but difficulties in extrapolating to ambient conditions (benefit and disadvantage)	conditions variable but can be fixed to a certain range	Interdisciplinary approach needed, huge data analysis, difficulties in separation of effects
Applicability to atmospheric conditions	Usually not directly, extrapolation needed (disadvantage)	Yes, chosen condition specific (benefit)	Certainly (benefit)
Particle loss Sampling flow limitations	Yes (disadvantage), the longer the worse chambers Yes (disadvantage)	Yes, but unimportant because of using two Yes (disadvantage)	No (benefit) No (benefit)
Comparable to similar conditions for effect studies	Yes (benefit)	Yes (benefit)	Hardly because of several unknowns (disadvantage)
Box model studies	Possible (benefit)	Possible (benefit)	Hardly poss. (disad.)

Table 1. List of benefits and disadvantages for the present set-up (COMPASS) compared to simulation chamber studies and atmospheric measurements.

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Spectral range	Percentage of light passing
300-380 nm (UV)	90.5%
380-780 nm (visible)	83.5%
300-2100 nm (sunlight)	91.9%

Table 2. Transparency measurements concerning the chamber wall material of ETFE foil obtained for a thickness of 200 μm.

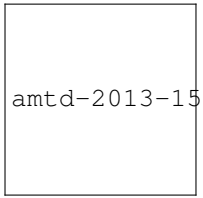

Fig. 1. Dry particle *loss* rate kloss,part inside *both* chambers *as* a function of the particle size. The uncertainty ranges is displayed by the shaded areas. The fit for the average values between diameters of *30* and *370* nm is shown in red *and extended to molecular sizes.*

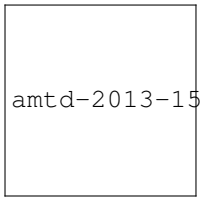

Fig. 2. Aerosol particle modes fitted with a maximum of 3 modes between 9.6 and 422 nm in diameter. Red represents the case of enhanced ozone, black the reference case. Note: The smallest number of modes with best fit was used, which can result in a different number of modes for both chambers at the same time!

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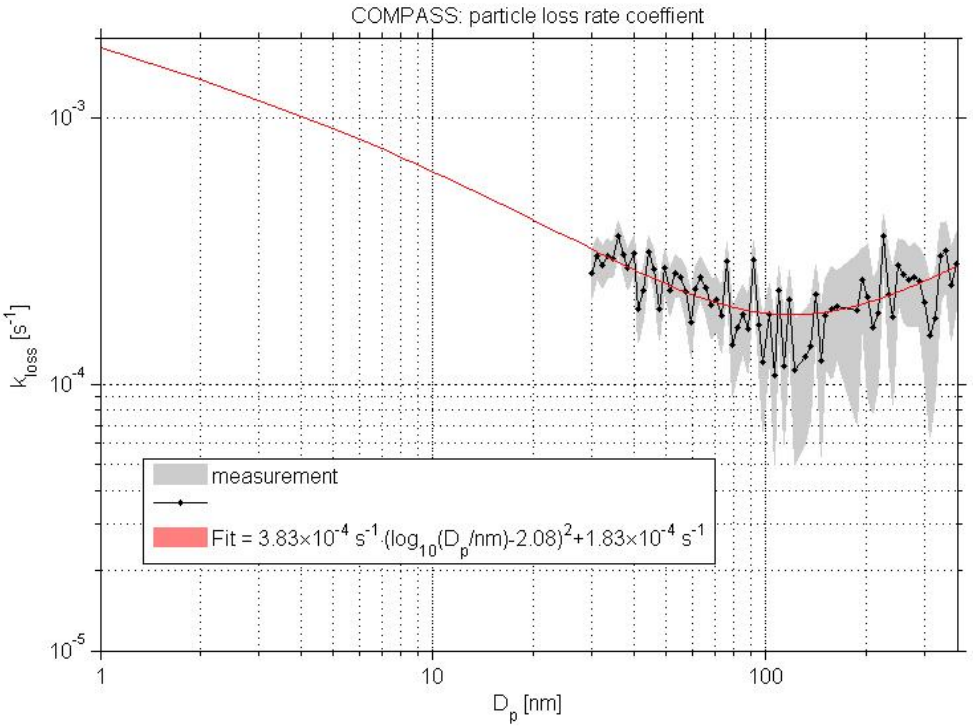

Fig. 3.

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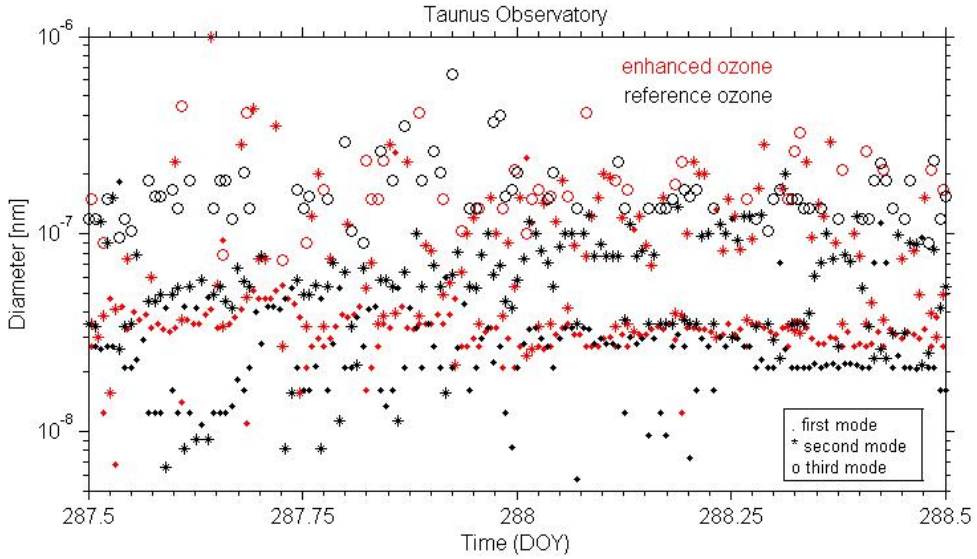

Fig. 4.

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