Answers to Reviewers for paper

Design of a new multi-phase experimental simulation chamber for atmospheric photosmog, aerosol and cloud chemistry research by J. *Wang, J.-F. Doussin, S. Perrier, E. Perraudin, Y. Katrib, E. Pangui, and B. Picquet-Varrault*

We would like to thank all the reviewers for the careful evaluation of the paper, for the quality of their comments and for their support. In order to improve the scientific quality of the manuscript, we have tried to consider all the comments: some data have been carefully reanalyzed, some additional model runs have been carried out and whenever possible some additional experiments or tests have been performed.

The reviewers have also expressed their interest in our instruments by suggesting a few dedicated studies, any of which could be the subject of a specific paper in itself. These suggestions are highly appreciated and we keep them as plan for future work.

Indeed, the full characterization of such a complex facility can not fit within the scope and the requirements of a single article. For the present article we want to focus our communication on the description and the choice of the design criteria of the new chamber as well as the first test and qualification studies.

The questions, comments and suggestions of the individual reviewers are addressed below. Answers are reported in *italic* characters.

Answers to Reviewer #1

P. Seakins (Referee)
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Received and published: 23 February 2011

General Comments

Atmospheric simulation chambers have a very important role to play in elucidating many aspects of atmospheric chemistry and in the validation of field equipment. A wide variety of types of chamber exist each with their own advantages and disadvantages. In addition to references cited in this paper, the referee has recently published a brief review of role of chambers in gas phase chemistry (Seakins 2010). This current paper describes the construction and validation of a new chamber which should provide novel information and fills an important 'gap in the market' of chambers.

The stainless steel construction allows for a wide variety of temperature and pressure variation which in combination with a focus on multiphase capability provides an important new resource to the community.

The paper provides a detailed description of the construction of the chamber, characterization of physical properties such as wall-loss rates and radiation fields and validation via studies of well characterized gas phase and multiphase systems.

Specific Comments

1) Temperature control – a major advantage in the construction of metal chambers is the potential for temperature control. This is mentioned in the description of the chamber construction (e.g. p 322), but there is no discussion about the performance of the temperature control in Section 4. Have temperature controlled experiments been carried out? I would be interested in seeing the performance in terms of the uniformity of the temperature within the chamber. A significant chiller unit would be required!

One possible concern is that the description implies that there is just one continuous volume – this could mean that the residence time of the thermofluid is quite long and there could be the potential for temperature gradients to be formed. Some temperature controlled chambers have multiple circuits to avoid this problem.

Indeed, the body of the chamber has been designed to allow the circulation of a cooling/warming thermofluid. In short, this means that it comprises a double wall. For each section of the chamber, this double wall is divided into two independent volumes which comprise internal walls to avoid short-tracks and reservoirs, and to force the thermofluid to meander around the reactor. Clearly this creates several possible pathways for the thermofluid. Fluid circulation modeling is currently being carried out, to determine the best pathway with respect to temperature homogeneity and specific experiments will be performed to verify the validity of these calculations.

The chiller unit we are acquiring is a 10 kW cooler which exhibit a flow rate in the range of 100 L/min. This should provide a residence time of 1 minute or better. Clearly tests are still on-going and this is why no additional information is provided in this paper. The description of the performance of the cooling/warming system will therefore be published at a later stage.

2) Wall loss rates – Wall loss rates for ozone at 3e-4 s-1 seem to be quite high, although the authors do note that this is dependent on the state of the walls. Extended treatment with 100 ppm ozone may of course cause damage to materials/instruments inside the chamber. Have wall loss rates been measured for other species?

Additional information concerning other chemicals such as VOC are now given in Table 5. In general wall losses for these species are quite small and can be determined – at least for the reactants – from the initial part of the experiments, i.e. before any irradiation or oxidant injection.

No damage on the material or instruments has been noticed so far with the ozone treatment while the Vaisala humidity gauge must be removed each time prior the treatment to prevent any reaction between the polymer fiber of the sensor and ozone which could lead to extended de-calibration.

3) FTIR analysis – FTIR is the primary technique for monitoring hydrocarbons. Is there any particular reason why there is no conventional GC capability? Possibly this is planned for the future. FTIR analysis of multi-component mixtures is relatively complex and a little information on the method of spectral deconvolution and analysis might be helpful.

FTIR in-situ analysis is clearly one of the basic tools to probe the reacting mixture in the chamber because

- *it does not induce any additional dilution of the mixture (no extractive sampling)*
- *it often provides non-ambiguous identification of the detected compounds thank to their IR fingerprints*
- *it is often very useful for the (inter-)calibration of other instruments*

Nevertheless it is true that its detection limit (commonly in the ppb range) is somewhat high especially when aerosol studies are forecasted (see Duplissy et al, 2008 for example). This is why a "classic GC-FID" system has been recently installed and an on-line mass spectrometer directly connected to the chamber is currently under development.

Additional information concerning the methods used for the spectra deconvolution are now given in section 3.2.2.

4) NOx-Propene Experiments – The role of incidental HONO in OH formation is an important one in chamber experiments and it is good to see that HONO measurement will be available for future experiments. It would be helpful to slightly expand the discussion on HONO/initiation times to give a feel of the sensitivity of the system to HONO and the role of HONO generated OH as opposed to other sources of OH (this should be available from the MCM simulation). Clearly the reader and authors want to have confidence that all important sources of OH are well characterized.

Additional runs have been set up with an initial concentration increased by 50% on one hand and decreased by 50%, on the other hand. The results are shown on the Figure 8. It shows that, in the case of the chosen experiment, the initial HONO load is the main parameter which *determines the propene oxidation rate. These observations support strongly the need for precise nitrous measurements.*

The use of numerical tracers inserted in the chemical mechanisms allowed to us to quantify the various OH source. The relative importance of these sources is now discussed in the text.

Technical Corrections

P317 – Worth referencing the most recent IPCC report in terms of role of O3 in climate change.

Correction has been made

P319 Except FOR the AIDA chamber....

Correction has been made

P321 Close bracket around reference to Eurochamp website.

Correction has been made

P322 ...double layers which allow circulating....

Correction has been made

P323 Re-word description of pumping set up (lines 9-13).

Correction has been made

P324 3 Basic analytical equipment

Correction has been made

P326 line 17 multi-pass cell. Do you have any protective coating on the mirrors? Another alternative is to have a sheath of inert gas blowing in front of the mirrors. Given that gas is always being taken from the chamber, it might be worth introducing the make-up gas in front of the mirrors.

The coating on the gold mirrors has been the subject of special thermal treatments to improve its resistance to chemical aggression and is defined as "hard gold protected". It is difficult to get information about this treatment as it is protected as a trade secret. Nonetheless, its efficiency with respect to oxidizing agent is remarkable. As an example, in the past fifteen years only two re-coatings have been necessary on the multiple pass cell installed in the other simulation chamber operated in our group to maintain it up to its initial performances (see Doussin et al, 1997).

Nevertheless, the possibility of introducing the make up gas in front of the mirror sound very interesting especially for systems where a very-high mirror reflectivity is required (such as cavity devices for example).

P327 What is the temporal resolution with which samples can be taken for subsequent HPLC analysis? A sample volume of 100 L is not insignificant in either the time taken or compared to the volume of the chamber if several samples are to be taken.

100 L can be collected in approximately 20 minutes (a higher flow rate would lower the collection efficiency). This can be useful for long experiments but indeed this time resolution must be improved for shorter experiments and/or to have the possibility to increase the number of samples during the same chamber run.

P332 (and elsewhere) superscripts in electronic states don't always work out.

Corrections have been made

P335 wiping

Correction has been made

P340 Remove HCOOH from the list of compounds for which there is good agreement.

Correction has been made

P343 ...using a SMPS, the data from which were cross checked....

Correction has been made

Table 2 – I understood Table 2 to be related to the mixing times at various fan speeds. However, fan speed is not mentioned in this table.

Fan speed is a parameter which is not really easy to determine. It would require the use of specific instrument and would not be really informative to any of the readers as the relation between the speed and the mixing rate is highly dependent on the fan design. Table 2 intends to give an idea of the relation between the various accessible mixing times and the average gas speed which can be of interest for future heterogeneous studies. Again, fluid dynamic calculations are planned in the near future but this represents a whole study in itself which we believe to be too specific to be given here.

Figure 5 – Would be helpful to label each disk with the actual distance from the lamps.

Correction has been made

Seakins, P. W. (2010). "A brief review of the use of environmental chambers for gas phase studies of kinetics, chemical mechanisms and characterization of field instruments." The European Physical Journal, Web of Conferences 9: 143-163.

This reference has now been added to the reference list.

Answers to Reviewer #2

Anonymous Referee #2
Received and published: 12 March 2011

General Comments

This paper describes a new chamber that has been developed for studies of atmospheric chemistry and clouds. The authors describe in detail the design of the chamber and the instruments available for physical and chemical measurements of gases and particles, and also the studies they have carried out to evaluate its performance. The evaluation includes the irradiation used for photolysis, mixing timescales, temperature, pressure, and RH range, flushing and filling behavior, cleaning procedures, particle wall loss, cloud formation, and comparisons of results obtained in this system with others for well-studied photochemical and SOA systems.

This is a wonderful system and the design and evaluation have been carefully and thoughtfully preformed. I am sure that much good and useful data will be obtained from future studies carried out here. The manuscript is very well written and it contains necessary and appropriate references and figures. I think is should be published in ACP, although I have a few comments for the authors to consider.

Specific Comments

1. Page 334, Section 4.3. Cleaning procedure: Is the rate of removal of wall contaminants by molecular diffusion under vacuum faster than by flushing with clean air? What about heating to increase evaporation from the walls?

It is difficult to answer this question because, to our best knowledge, such a comparison has not been reported so far in the literature and because the physics of the removal is clearly strongly different in both procedures. If one considers only the partial pressure of potential contaminants above the adsorbing surfaces, the vacuum reached in the chamber in less than one hour allows us to reduce it by a factor greater than 10^6*. Such a dilution factor is clearly difficult to obtain by flushing the chamber while this latter procedure may be further enhanced by matrix effect.*

Evacuation has also the great advantage to reduce the operating cost by minimizing the need of clean air supply. A key point is to increase the rate of evaporation from the wall. Heating the wall is, indeed, a solution which has been shown to be efficient (Akimoto et al, 1979). This is why the cooling system under development will also provide the possibility to heat the walls up to 60°C.

2. Page 342, Section 4.5.1. Aerosol particle background: I think an additional test of background that is probably more important than the one performed here would be to measure the amount of SOA formed when NOx is present and the lights are turned on, or OH radicals are formed by some other means, all in the presence of a seed such as ammonium sulfate. Of course the result can depend on chamber history, but this is what really matters for an SOA study.

Many other chemical systems which are considered as non-forming aerosol have already been studied in the chamber in the past months while the SMPS was also in use. They includes photolysis of NOx alone in various NO/NO_2 *ratio (some are reported in this paper), photolysis of light VOC such as propene of formaldehyde in the presence of NOx. In none of these cases, unexpected SOA formation was detected.*

Following the reviewer request, additional experiments involving the photolysis of NOx (ca. 200 ppbV) in the presence of ammonium sulphate seeds have been carried out. The initial aerosol loading has been kept low (ca. 3 $\mu g.m^{-3}$*) in order to have a sufficiently low relative uncertainties to detect a possible SOA production close to the detection limit values. No SOA production was detected for irradiation period in the range of five hours. Considering the uncertainties associated with the dilution rate measurements and the noise in the SMPS measurement, an upper limit for a background SOA production can be estimated in the range of* $<0.01\ \mu g.m^{-3}$.

These results are now mentioned in the revised version of the paper.

3. Page 346-347, Section 4.5.3. Particle lifetime: I suggest the authors read the papers by Crump & Seinfeld, J. Aerosol Sci. 12: 405-415 (1981); Crump, Flagan, & Seinfeld, Aerosol Sci. Technol. 2:303-309 (1983); and McMurry and Rader, Aerosol Sci. Technol. 4:249-268 (1985). They describe measurements and modeling of particle wall losses in chambers with and without electrostatic effects. Comparison of their results with those presented here would be useful.

We have carefully studied the papers indicated as references (as well as the relevant sections in Seinfeld and Pandis, 2006 and in Friedlander, 1977). This reading was highly informative and very relevant for a better determination of the aerosol wall losses in our chamber. Crump et al and McMurry et al have used a methodology which allows a precise determination of the wall losses in reactors as a function of the particles diameters by a continuous injection of monodisperse aerosols and by monitoring the steady-state number-concentration. This methodology is really efficient as it allows the user to deconvolute the dilution term and the loss term from the coagulation term by using appropriate monodisperse coagulation coefficients.

Considering the size of our chamber, the low level of wall losses and the flow rate limitation of the usual monodisperse aerosol production set-up, it is not really possible, in our case, to adopt this methodology due to the time needed to reach the steady state. We have considered the possibility to work in static condition, starting with a monodisperse aerosol and monitoring its loss. Again, the time needed to significantly seed the chamber was considered too long with respect to coagulation. Clearly, this must be improved in the near future and specific experiments should be organized.

Nevertheless, we have tried to apply the approach proposed by Crump, Flagan and Seinfeld, 1983 to polydisperse aerosol experiment.

For each bins of each size distribution acquired with time, we have considered the following kinetic equation

$$\frac{d(C(t))}{dt} = \left[\frac{Q}{V}\left(C_{\mathrm{inf\ low}} - C(t)\right)\right] - [\beta \cdot C(t)] - [K \cdot C(t) \cdot C_T(t)]$$

Where V is the chamber volume, Q the volumetric flow fed to the chamber, C_{inflow} *the aerosol concentration of the inflow (in our case this parameter is nil), C the aerosol number concentration of the considered bin,* β *the particle loss rate (in* s^{-1}*), K one half of the value of the monodisperse coagulation coefficient for an aerosol of the considered size (in* $cm^3.s^{-1}$*), and* C_T *the total aerosol number concentration.*

In this expression, the first bracket represents the seeding/dilution term, the second gives the wall loss while the third describes the coagulation term.

Practically, the differential was approximated by calculating the difference between two successive measurements. The time step between each measurement was 135 seconds.

The K values were taken from Seinfeld and Pandis, 2006 and interpolated from each bin mid-size value.

The total number concentration for each time step was then approximated with

$$C(t) = C(t - dt) + \frac{\Delta(C)}{\Delta t} \cdot \Delta t$$

The calculated number concentration versus time curve was then compared with the experimental. The calculus was initialized with the experimental size distribution taken after the end of the secondary aerosol production.

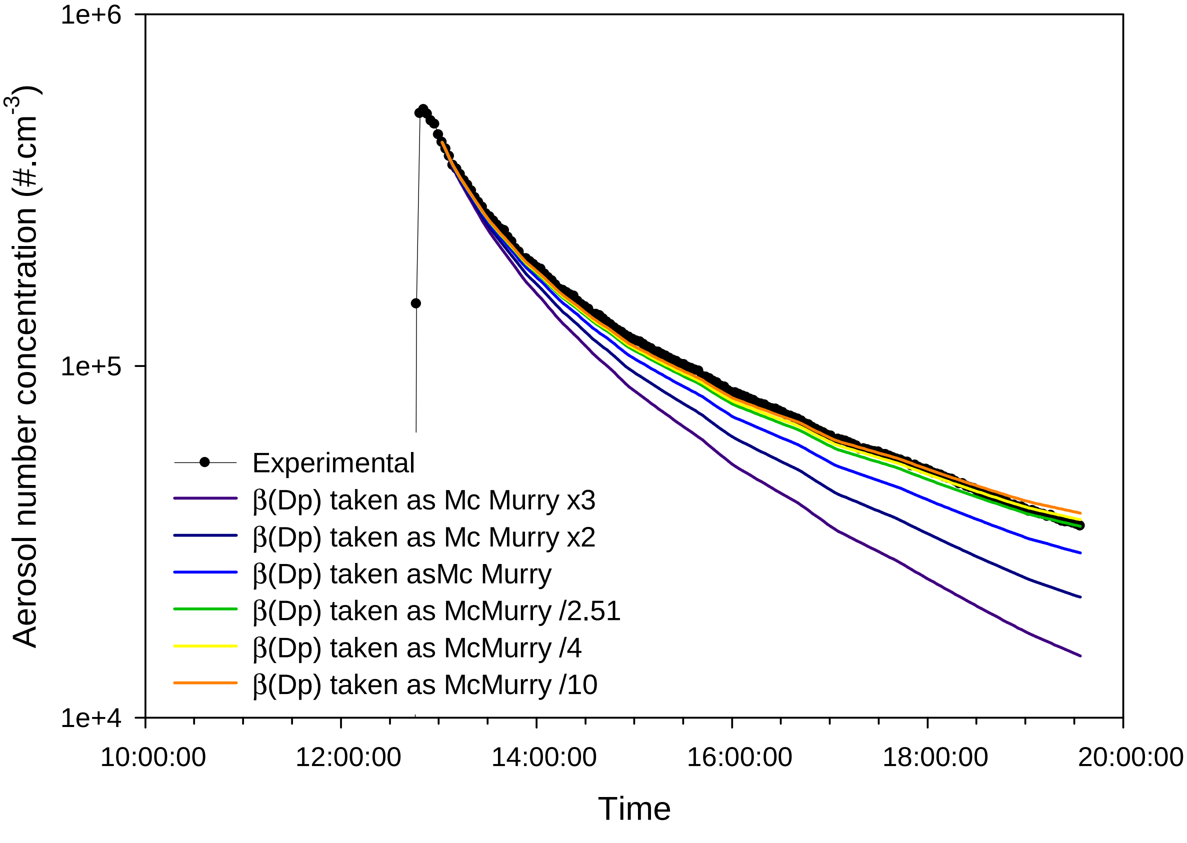

Figure 1 : Experimental and calculated number concentration. Various aerosol loss coefficient β ***were used. Reference*** β ***function was taken from Mc Murry and Rader, 1985 as calculated by these authors for a non charged aerosol, a reactor radius equal to 35 cm and a*** k_e ***value equal to*** $6.4x10^{-3}$ s^{-1}***.***

As it can be seen on Figure 1, experimental and calculated number concentrations are in good agreement when the β distribution calculated by McMurry and Rader (for a non charged aerosol, a reactor radius equal to 35 cm and a k_e value equal to 6.4×10^{-3} s^{-1}) is divided by 2.5 (see figure 2).

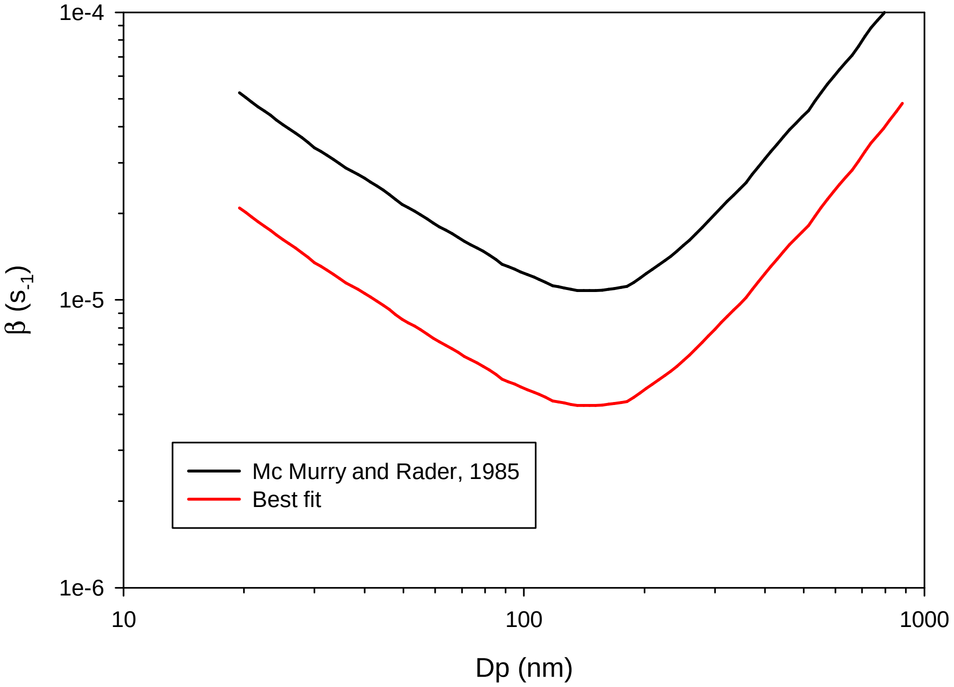

Figure 2 : β distribution as calculated by McMurry and Rader for a non charged aerosol, a k_e value equal to 6.4×10^{-3} s^{-1} and R=35 cm (black) and for R=88 cm .

This result sounds reasonable as the reactor considered by these authors has a radius 2.5 smaller than the CESAM chamber.

Nevertheless, in spite of this agreement, these calculations must be taken with great care as they may suffer from many approximations:

i) The first and probably the greatest approximation rely on the use of the monodisperse coagulation coefficient. As pointed out by Seinfeld and Pandis, 2006, monodisperse coagulation coefficients are the smallest values of the coagulation coefficient which tend to rise rapidly when cross-coagulations between particles of different size are considered. This increase could be up to two orders of magnitude. Any under-estimation of the coagulation would lead to an over-estimation of the wall loss. In consequence, the β values estimated here are probably upper limits.

ii) The second major uncertainty is the coefficient of eddy diffusivity k_e. Crump and Seinfeld have demonstrated that this key parameter could be estimated from the volumetric flow rate. In our case the flow rate which is due to the sampling by both gas monitor and SMPS is very small in comparison with the chamber volume. Furthermore, the CESAM chamber was continuously stirred with the help of an internal impeller. In consequence, in the absence of specific experimental involving some changes in the experimental device (e.g. to monitor fan speed and/or the fan electrical consumption), a precise evaluation of this parameter is not accessible.

In short, these calculations have brought to us a very interesting insight in the physics of the aerosol losses in the CESAM chamber. It has shown that aerosol loss parameter (β) falls in the range of few 10^{-6} s^{-1} or better. This observation helps in rationalizing the very low aerosol loss observed when mass concentration as a function of time are considered. This has been mentioned in the revised manuscript. Nevertheless, the above discussion has not been entirely reported in the paper as we believe that so far this important matter required more robust calculations and certainly dedicated experiments.

4. In my opinion the authors have missed an excellent opportunity to evaluate an important property of their chamber, which is the loss of semi-volatile organics to the chamber walls. It has recently been shown by Matsunaga & Ziemann, Aerosol Sci. Technol. 44: 881-892 (2010), that semi-volatile organics absorb into Teflon chamber walls and establish gas-particle partitioning equilibrium fairly rapidly. The fraction that absorbs can be substantial (>50%) and is likely to affect chamber measurements. It would be very interesting to determine the degree to which sorption occurs on the stainless steel walls of this chamber. If, for example, the walls can be passivated by the adsorption of a monolayer or so of organics, then it might be possible to operate this chamber in such a way that wall losses of semi-volatiles are much smaller than in Teflon chambers. This would be a great advantage.

The paper from Matsunaga and Ziemann, 2010 is indeed extremely interesting and highlights some potential artifacts arising from the use of simulation chamber to derive SOA yield. Clearly, it will be necessary to verify if these findings must be generalized to all type of chamber or not.

Nevertheless, we believe that investigating thoughtfully these phenomena requires a whole set of experiments and is a study in itself which can hardly be inserted in this paper which is already quite long.

Technical Corrections

1. Throughout the text: “dependant” should be “dependent”.

Corrections have been made

2. Table 7: “Pasadena” should probably be “Caltech”.

Correction has been made

Answers to Reviewer #3

Anonymous Referee #3
Received and published: 13 March 2011

Comments for the paper: Design of a new multi-phase experimental simulation chamber for atmospheric photosmog, aerosol and cloud chemistry research J. Wang, *J.-F. Doussin*, S. Perrier, E. Perraudin, Y. Katrib, E. Pangui, and B. Picquet-Varrault

This paper describes the setup and the features of a new simulation chamber for the investigation of atmospheric processes in the gas phase and aerosol / cloud phase.

The main feature, which distinguish this chamber from existing ones are the pressure and temperature variability together with an artificial light source.. The paper is well written and it describes first test measurements, which should show the versatile possible usage. I recommend this paper for publication in AMT after taking the following comments / questions into account:

1. As a simulation chamber of atmospheric processes it is important to be able to adjust the concentration of atmospheric trace constituents to their natural level, this is correctly pointed out in the paper) though the test experiments are carried out at very large concentrations given in table 5) which seem for most atmospheric situation unrealistic and some / most? of the analysis equipment seems to have not the necessary detection limit for real atmospheric concentration levels (like NO, NO_2, FTIR ..). Some explanation and adjustment of the purpose of the new chamber should be given.

It is only partially true to consider that most of the analytical equipment has not suitable detection limits for atmospheric level. For example, NOx monitor, ozone monitor, SMPS, OPC which are permanently installed on the CESAM chamber are exactly the same as those deployed on the field during research campaigns or by air quality monitoring networks.

Nonetheless, it is true that the equipment dedicated to VOCs measurement the detection limits are often too low to compare with real atmospheric levels.

The test experiments have been carried out at concentrations which are also higher than those found in the real atmosphere. Nevertheless, they must be compared with most of the chamber experiments carried out all around the world and they fall in the concentration range of most of simulation chamber runs. This can be easily explained by analytical difficulties due to detection limits or limited sampling possibilities. This can be also explained by the fact that experimental simulation does not consist in a close reproduction of reality but more in the implementation of experiments susceptible to produce results that can be extrapolated to atmospheric conditions. For example, the major part of the knowledge which is implemented in atmospheric models has been constructed on the basis of experiment conducted in the ppm range.

Nevertheless, the possibility for relevant extrapolation is now critically reduced with the growing importance of multiphase studies which involve the intrinsic non-linearity of phase changes. This has been recently illustrated by Duplissy et al, 2008.

This is why in the near future the improvement of the analytical environment of the CESAM chamber with respect to VOC measurements is planned.

2. It seems, but it is not clearly stated in the interpretation of the test experiments, is the mass balance during the NOx and the propene experiments obeyed or what are the processes which consume substances (for example NOx) and how reproducible those processes are. Because these are essential features for future investigations I would recommend to explain these features explicitly and in detail.

In the Propene/NOx/light experiments, after correction for dilution, C balance is obeyed within ±7%. No evidence of any systematic significant loss can be detected which is further confirmed by the good agreement with the simulated curves when no loss processes are added in the model for carbon-containing species. Among the non-monitored species, one count CO and CO_2 which are difficult to monitor with FTIR spectroscopy due to atmospheric interferences. This shows that at the considered reaction advancement, CO and CO_2 production is certainly small with respect to the initial propene load.

For the nitrogen balance, a clear loss can be detected as at the end of the shown experiment only 87±2% remains detected.

In simulation chamber experiment negative mass balance generally arise from two possible distinct causes: i) Insufficient capabilities of the analytical instruments which leave "invisible" a part of the products ii) Heterogeneous processes that draw the materials "out of sight" (generally to the wall)

Both reasons can be invoked to explain the N loss:

- *In such a chemical system one of the major loss process for nitrogen oxide is HNO_3 production (through OH + NO_2 reaction for example) and HNO_3 is well known as a "sticky" compound for surfaces. Hence most of the nitric acid produced escape from FTIR detection as it is scavenged from the gas phase by wall adsorption.*
- *Furthermore, reactions 7 and 8 which are heterogeneous are not equilibrated in nitrogen as neither $\alpha + \beta$ nor $\delta + \gamma$ are equal to unity. This means that the auxiliary mechanism which have been defined by the NOx/light experiment imply intrinsically an nitrogen oxide loss*

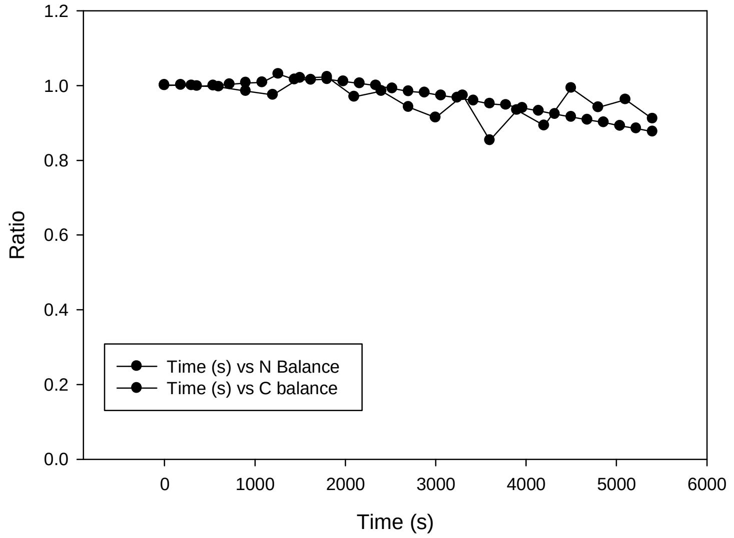

Figure 3 : Carbon and nitrogen balances as a function of time during propene/NOx/light experiment.

Answers to Reviewer #4

Anonymous Referee #4
Received and published: 14 March 2011
Design of a new multi-phase experimental simulation chamber.

The paper describes the design and initial characterization of a new stainless steel chamber at LISA that is designed to study gas phase, aerosol and cloud chemistry under carefully controlled conditions, with a wide range of analytical equipment for physical and aerosol characteristics, and gas phase and aerosol composition. The chamber provides a distinctive environment capable of covering a range of temperatures and pressures. It has the potential to become a major contributor the development of our understanding of atmospheric processes. The paper should be published, subject to a few minor changes. Some suggestions for such changes are made below:

1. A consequence of the choice of xenon arc lamps, which, when coupled with pyrex filters provide a good representation of the solar spectrum, is the inevitable variation in light intensity within the chamber. This problem is discussed in section 4.3, which states that there is a factor of 5 variation in intensity. Figure 5 seems to indicate a much larger variation, of more than a factor of 10. This problem is addressed by rapid mixing, but the discussion in section 4.3 is not very clear on the impact of the intensity variation on experiments (p334, l 14-18). It would be helpful if the Supplementary material contained results of simulations showing, for example, the variation in [OH] in the chamber for a range of accessible fan speeds and photolysis rates, using the model described in section 4.1, to help quantify the statement on p334 about the required photolysis rate for significant impact of the intensity variation.

Figure 5 has been built by horizontally interpolating the upward and downward measurements performed thank to a network of photodiodes. For each level, 18 points have be sampled which makes in total 162 measurements. Unfortunately, the closest measurements from the wall have been performed 15 cm away from it. The values near the wall have hence been largely extrapolated by the graphing software. Considering the difficulty of representing irradiances near a reflective surface (which can clearly not be linearly extrapolated) this region has been excluded from our analysis, this is why only a factor of 5 is stated in the article. The extrapolation area is now indicated on figure 5. Considering this approximation, this figure must be considered more as an illustration of the lighting inhomogeneity than a quantitative measurement.

In any case, for quantitative irradiation qualification, overall photolysis frequencies determination is always performed by mean of chemical analysis.

The statement which claim that "the impact of irradiation inhomogeneity can be considered negligible for a photochemical reaction whose photolysis frequency is smaller than 10^{-2} s^{-1}" is simply based on the comparison of characteristic times: considering the fact that the characteristic mixing time over the whole chamber is 60 s and that low irradiance area covers only a fraction of the overall volume, the effect of inhomogeneity on a photolytic process which exhibit a characteristic time approximately two time longer should be limited.

Nevertheless, even if in the atmosphere, there is not so many photolysis processes faster than this, we agree on the fact that this statement should be strengthen and that modeling could be one of the promising strategy to assess the impact of photolysis frequencies variation within the chamber volume. Unfortunately, coupling our mixing model with a chemical code is still a *work which overcomes our calculation capabilities due to the number of cells which needs to be defined to carefully describe the shape of the chamber. A computational fluid dynamics model (CFD) coupled with chemical transformation could also be a promising approach.*

Another approach could be the measurement of radicals themselves at various locations inside the chamber. Of course, this is directly dependant of radical measurement capabilities.

We agree that such assessment of the impact of light inhomogeneity will be necessary when fast radical chemistry kinetic studies will be carried out in the CESAM chamber and that it will have to be reported together with the related study as a validation test.

2. The investigation of wall reactions is quite limited. There is no systematic study of intensity or relative humidity dependence, which has been shown in the SAPHIR and EUPHORE chambers to be significant.

While a full analysis is beyond the scope of this paper, some indication of future plans to characterize these reactions more fully and of the planned protocol to investigate such reactions as a function of date and chamber condition – since they depend on the history of the chamber usage – would be reassuring.

Indeed the peculiarity of the behavior of NOx toward the chamber (its reductive nature) requires further investigation not only because it impact the dynamics of the photo-oxidant in the chamber but also because it is one of the feature which supports the complementarity of this new chamber with other existing devices (mostly oxidative chambers). It is hence planned to further characterize the wall reactions as a function of the relative humidity in the dark and under irradiation with a systematic monitoring of HONO concentration.

Before each experiment when data analysis requires modeling of the photo-oxidative chemistry, a NOx/light experiments is regularly conducted to determine the parameters of the auxiliary mechanism. Recent improvements in the pumping system allow now to leave permanently the chamber under secondary vacuum between all the experiments. This new capability seems to minimize the impact of chamber history on the wall reaction and leads to a lower variability of the related parameters.

3. The agreement between the measured and modeled concentrations in the propene experiment is very impressive. It would be even more convincing, though, if similar comparisons, over the range of conditions used, were shown in the Supplementary Material. It would also be helpful if more mechanistic information were provided: The paper states that OH and O_3 contribute to the propene decay. Presumably the former is the more important. It would be useful to know the [OH] calculated in the MCM simulations, and the reactions that lead to OH formation, throughout the experiments.

These calculations have been done and are presented in Figure 9.

Presumably $[HONO]_0$ is a major determinant in the initial OH formation and this is an adjusted parameter. How important is it throughout the experiments? It is implied that separate values were used for each experiment. What were they? A HONO instrument is now available – are the [HONO] required compatible with present observations? Given the established yields of HCHO and CH_3CHO from propene oxidation, what are the sensitive model parameters for the species shown in Fig 8. In demonstrating a satisfactory evaluation of the chamber chemistry, it is important to establish that the adjusted $[HONO]_0$ is not the pre-eminently sensitive parameter.

Additional runs have been set up with an initial concentration increased by 50% on one hand and decreased by 50%, on the other hand. The results are shown on the Figure 8. It shows that in the case of the chosen experiment, the initial HONO load is the main parameter which determines the propene oxidation rate. It must be noticed that combining its effect on the propene curves with those on NO, NO_2 *and ozone, this parameter is really sensitive and that there are little doubts on its value. These observations support strongly the need for precise nitrous measurements.*

There are a number of smaller suggested corrections:

P323, l6. ? Change to '..and prevents any low …pump from affecting the ..'

Correction has been made

P323,l10. Change 'adjunction' to 'use'

Correction has been made

P326 l17, should be 'globar'

Correction has been made

P327, l1 should be 'relatively'

Correction has been made

P331, l10. ? Change to ' that the dynamics are probably …'

Correction has been made

P331, l20. ? Change to 'due to changes in the zenith angle'

Correction has been made

P332 and subsequently. The atomic term symbols are wrongly formatted – should be O(3P) etc. J(O3) is ambiguous and should be J(O(1D)), or more conventionally J(O1D)

Correction has been made

P333, l2. Change isotropous to isotropic.

Correction has been made

P333, l10, 12. Should be Table 3.

Correction has been made

P333, l27. Change to 'greater than 70% …which overlaps…'

Correction has been made

P336, l25. Is the [HONO] increase really slower than the [NO_2] increase?

Clearly, it can be seen that from Figure 6 that NO_2 *decrease in the dark falls in the range of* $5x10^{11}$ *molecule.cm*$^{-3}$ *within one hour while in the same time the HONO increase is roughly* $2x10^{10}$ *molecule.cm*$^{-3}$*. This fact is also depicted by the value of the stoechiometric coefficient* β *factor in the reaction 7.*

P373, Fig 3. The axis units are not really compatible with the numbers – better to omit the 00:.

Correction has been made

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