Interactive comment on “Characterization and testing of a new environmental chamber designed for emission aging studies” by A. Leskinen et al.

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General Comments:

This paper describes the design and initial testing of a new environmental chamber for studies of atmospheric particle formation and transformation. Although it does not present any new scientific results, it may be appropriate for this journal because a chamber can be considered an important measurement tool, and its characteristics can affect all measurements made from experiments in the chamber. Therefore, if the paper described a chamber that is well designed for its intended purpose and provided all (or at least most) needed characterization data, then I think its publication in this journal would be appropriate.

This paper is clearly written and gives a good description of how the chamber is designed and some of its characterization data. I have two main problems with this paper; one concerning the nature of the light source employed (i.e., the design of the chamber), and the other concerning the lack of important characterization data. These and other problems are discussed below.

> `We thank Professor William Carter for reviewing the manuscript carefully and for his critical and very valuable comments. Our answers to the comments are addressed below and the text will be corrected accordingly in the revised manuscript.`

Specific Comments:

This chamber is similar in many design characteristics as that described by Carter et al (2005). Although that reference is cited in the "methods" section, it should also be cited in the introduction when they list environmental chambers with different designs. It is now extensively being used by Cocker and co-workers for SOA studies, some of which are cited in this manuscript. My comments on this paper are based in part on my experience with design and use of the chamber described by Carter et al (2005).

> `Instead of referring to “Hallquist et al., 2009, and references therein” we cite Carter et al. (2005), Paulsen et al. (2005), and Cocker et al. (2001) in the introduction, as these chambers are discussed later in the manuscript.`

The spectrum of the light source in this chamber is given in Figure 4 of the manuscript. It shows no intensity in the UV region from 300 to about 340 nm. Although this spectrum is sufficient for photolyzing NO_2, it will result in abnormally low photolysis rates relative to atmospheric for other photolyses that are potentially important radical sources, such as photolysis of O_3 forming O^1D (which might be important in their "cleaning" process) and photolysis of aldehydes and other photoreactive compounds whose action spectra decrease rapidly near the 300 nm cutoff for ground-level sunlight. Although light sources should not have significant intensity below the 300 nm cutoff, it is important that they have a spectrum similar to sunlight in the important 300-400 nm region.

Figure 2 in Carter et al (2005) shows the spectrum of the type of blacklights usually used in environmental chambers with blacklight light sources. This is the type they should have used in this chamber. If this is not feasible because of safety regulations, they need to include a discussion of the problems with these lights with regard to some potentially important photolysis process, and a justification as to why it is sufficient to consider only NO_2 or HONO photolysis for their purposes. People reading this paper to study how to design their own chambers need to know the limitations of this type of light source.

> `We are aware that the blacklights we used do not cover all`

ground-level atmospheric reactions. The installation of these types of lamps (denoted hereafter as "365 nm lamps") were a compromise between the costs, safety, and desired NO_x reactions (NO_2 photolysis, HONO photolysis), at the time we equipped the chamber facilities.

Later, we have installed blacklight lamps that produce UV irradiation in the wavelength range of 310-400 nm (denoted hereafter as "350 nm lamps"). The relative irradiance spectra of both types of lamps are illustrated in Fig. R1.

We included discussion about the difference between the irradiation from the 350 nm and 365 nm lamps in the manuscript pointing out that, in addition to NO_2 and HONO photolysis, the 350 nm lamps initiate also other atmospherically relevant reactions, such as the O_3 photolysis to O^1D and its further forming of OH radicals, and photolysis of aldehydes and ketones. Photolysis of these simple carbonyls can directly produce alkoxy radicals that react quickly with O_2 to form more HO_2 radicals. In high NO_x experiments this can increase important OH radical production by converting HO_2 to OH when HO_2 reacts with NO. By using the 365 nm lamps this OH recycling would be dramatically reduced.

For the characterization of the chamber, our purpose was to perform high NO_x experiments, because the combustion aerosol experiments always come with high concentrations of NO_x. Thus, we chose to produce the OH radicals via the HONO photodissociation, which also produces NO_x.

Since a major objective of use of this chamber is to study PM formation in the chamber, they need to provide information on background PM formation. As discussed by Carter et al (2005), conducting pure air or propene - NO_x irradiations and measuring particle formation provides a very useful and sensitive test of background particle formation. These experiments should involve no particle formation, and if particles are observed they are likely due to contamination. They found that particles formed in such irradiations with new reactors were very high but declined over time, but that the results are variable and relatively high levels are observed from time to time, presumably due to wall offgasing of contaminants whose reactions form particles. It is not due to offgasing of particles themselves, at least in the chamber of Carter et al (2005), because there is no PM formation in the lack of added SOA precursors in experiments where added NO_x or CO suppress OH radicals.

Because of the importance of background PM and the results of the characterization of the Carter et al (2005) chamber, this paper is not acceptable for publication until at least pure air and/or propene - irradiations are carried out and the results described. (Simply because other groups have published papers on PM formation in chamber experiments without conducting or reporting these important background characterization tests, it does not mean it is scientifically acceptable.) If particle formation is observed, they should conduct CO - air or CO - NO_x experiments to see if it is due to particle or particle precursor contamination. Carter et al (2005) also describe characterization of NO_x or HONO offgasing or other background effects, though they not be as important as background PM for the types of experiments to be conducted in this chamber. Nevertheless, it would be good if they could report these types of characterization results as well, or at least mention that NO_x or HONO offgasing is also observed in chambers and should be characterized if experiments are to be conducted that would be affected by this.

We performed four blank experiments with purified air ('Air 1-4' in Fig. R2). After four hours of irradiation the wall loss corrected background mass concentration was 0.4-1.9 $\mu g/m^3$ (assuming density of 1 g/cm^3), which is at the same level as in Carter et al. (2005).

Consequently, we carried out two experiments with purified air + carbon monoxide ('CO + Air 1-2 in Fig. R2). In these experiments the wall loss corrected mass concentration after four hours of irradiation was 0.2 µg/m^3. This observation is also in accordance with the results of Carter et al. (2005). Based on these results, we can conclude that no - or very little - aerosol offgassing is observed.

Unfortunately, we did not have access to a LOPAP instrument in order to measure the HONO offgassing. Nevertheless, we have added discussion about the NO_x and HONO offgassing in the manuscript.

More explanation is needed as to why photolyzing highly humidified air with O_3 present was chosen as the method to "clean" the chamber. Ideally there should also be data showing that it indeed cleans a contaminated chamber – though they would need to do experiments like pure air irradiations to assess the level of contamination, and if the results are always negative they won't be able to show that it works. The high level of humidity may give a concern about water condensing on the walls, which may exacerbate background effects.

The method was chosen because we assumed it would enhance the cleaning of the chamber. A humid air is used in surface cleaning. The high ozone concentration was thought to oxidize compounds on the chamber walls. The lamps were used, not only for photolyzing but also as an attempt to raise the temperature of the walls and detach semi-volatile compounds from the walls.

During the cleaning process, the relative humidity was 92 % at its highest (Fig. R3), so there may indeed have been condensation on the walls at some local cold spots. However, since the high humidity was used in the beginning of the cleaning process, we estimate that during the overnight flushing of at least 12 hours with drier (RH ~50 %) purified air the possibly condensed water evaporates from the walls.

In the latter experiments we did not use this purification procedure, i.e. photolyzing with highly humidified, ozonized air, since it is quite time-consuming but emptied the chamber after an experiment and filled and flushed it with the purified air (conditioned at around 50 %RH) overnight before the next experiment, and will use this latter method in the future experiments. Our aim is to build an automatic filling-emptying system so this can be repeated multiple times between the experiments; a method which has also been reported e.g. by Carter et al. (2005).

Why did they add O_3 in the toluene-HONO experiments? It seems to me it would be more comparable to experiments in other labs if it weren't present. I wonder if a toluene - H_2O_2 irradiation (no NO_x or HONO) might have been better (or also useful) as a comparison with previous results. Experiments with no NO_x remove the complications of SOA yields being dependent on NO_x levels, and toluene has higher SOA yields when NO_x is absent.

We chose HONO dissociation to be the source for OH radicals. The HONO production itself produces NO and NO_2 as by-products, and when HONO photodissociates, NO is produced. We used O_3 for converting the NO to NO_2 before UV irradiatione in order to start the photochemistry initiated by the NO_2 photodissociation as soon as possible after turning the lights on. Also, we strove for an initial ozone concentration of about 30-50 ppb found in the ground-level atmosphere. Furthermore, in our first setup, the 365 nm blacklights would have been able to dissociate H_2O_2 into OH radicals only in a very small degree.

It is stated that there is no dilution in the chamber because of the flexible nature of the chamber and operation under positive pressure. However, they do not provide data to show that this is the case. Including an inert tracer in the chamber and monitoring its concentration during the experiments would provide the needed verification of no dilution. The chamber of Carter et al (2005) has a similar design in this regard (though not stated in this manuscript), and we occasionally observe dilution in this chamber despite the positive pressure. This is attributed to leaks, which is always a problem with Teflon film reactors, and which generally gets worse as reactors become more extensively used.

Because leaks can also introduce contamination as well as giving invalid calculations of amounts of compound reacted, tracers need to be included and leaks measured routinely with each experiment, not just when the chamber is first characterized. If dilution is observed, the source of the leaks need to be found and repaired, or the Teflon film walls need to be replaced.

We performed test injections of combustion aerosol into the chamber and monitored the CO_2 concentration in the chamber for 4 hours after the injection (Fig. R4 and R5). In these tests, dilution was observed. By taking into account the 380-390 ppm CO_2 concentration outside the chamber, we obtained a dilution factor of 0.0026 h^{-1}, i.e. 0.26 % h^{-1}, and 0.0058 h^{-1}, i.e. 0.58 % h^{-1}, in Test 1 and Test 2, respectively. Since the dilution indeed seems to vary from experiment to experiment, we do not state any fixed dilution factor for our chamber but will calculate the dilution factor for each experiment separately. CO_2 may not always be the best trace gas for dilution calculation, because it can be a reaction product, and therefore another inert tracer, such as SF_6, should be used.

Technical Corrections:

Figure 4 should be referenced when the blacklight light source is first mentioned in the section describing the construction of the chamber. As it is, it isn't referenced until the methods of the actinometry experiments are discussed.

We now refer to Figure 4 in Section 2.1 when the lights are first mentioned.

It is unclear whether the "N/A"'s for the particle levels and yields in Table 2 for run T130909 is because the run formed no measurable PM or because the measurement was lacking. I assume it is the latter because Table 1 shows that this experiment seems quite close in conditions to the following experiment. In that case, they should add a note meaning that no data were taken, so the reader won't think that no PM was formed. If the N/A means that PM was monitored but below the measurement sensitivity, then it needs to be discussed why this run has such different results than the following run. A similar comment can be made about the "N/A"'s in Table 3.

The measurements of particle size distribution (Table 2, Run T130909) and concentrations of gas phase oxidation products (Table 3, Run T130912) were lacking due to problems in the instruments.

FIGURES

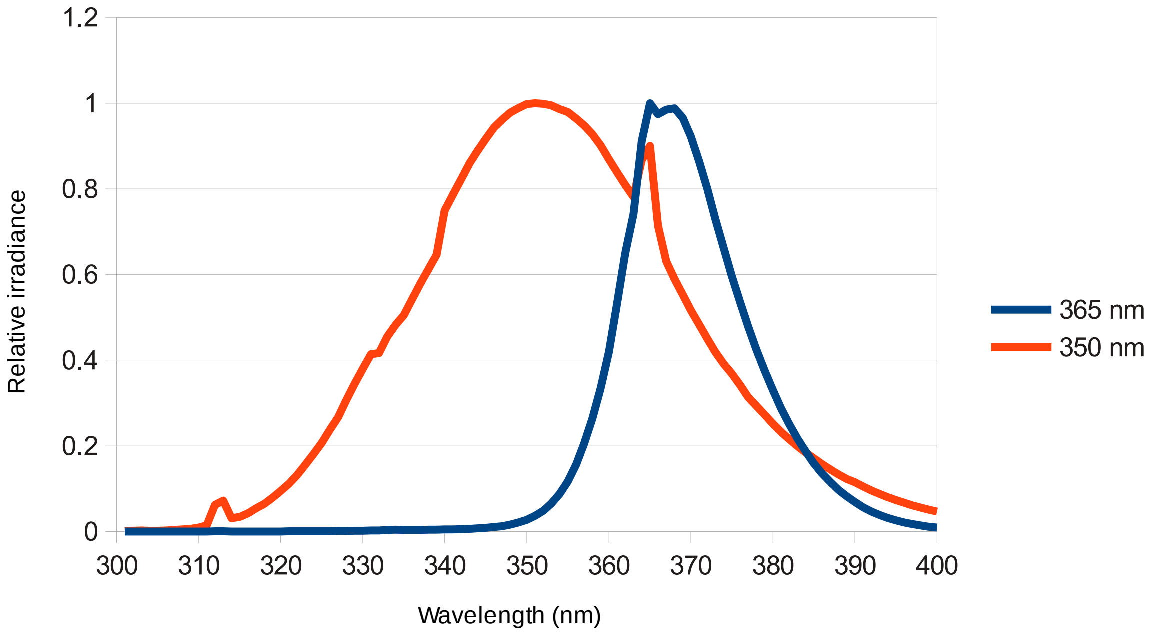

Figure R1: The relative irradiance spectra of the 365 nm lamps and the 350 nm lamps used in characterization of the Ilmari chamber.

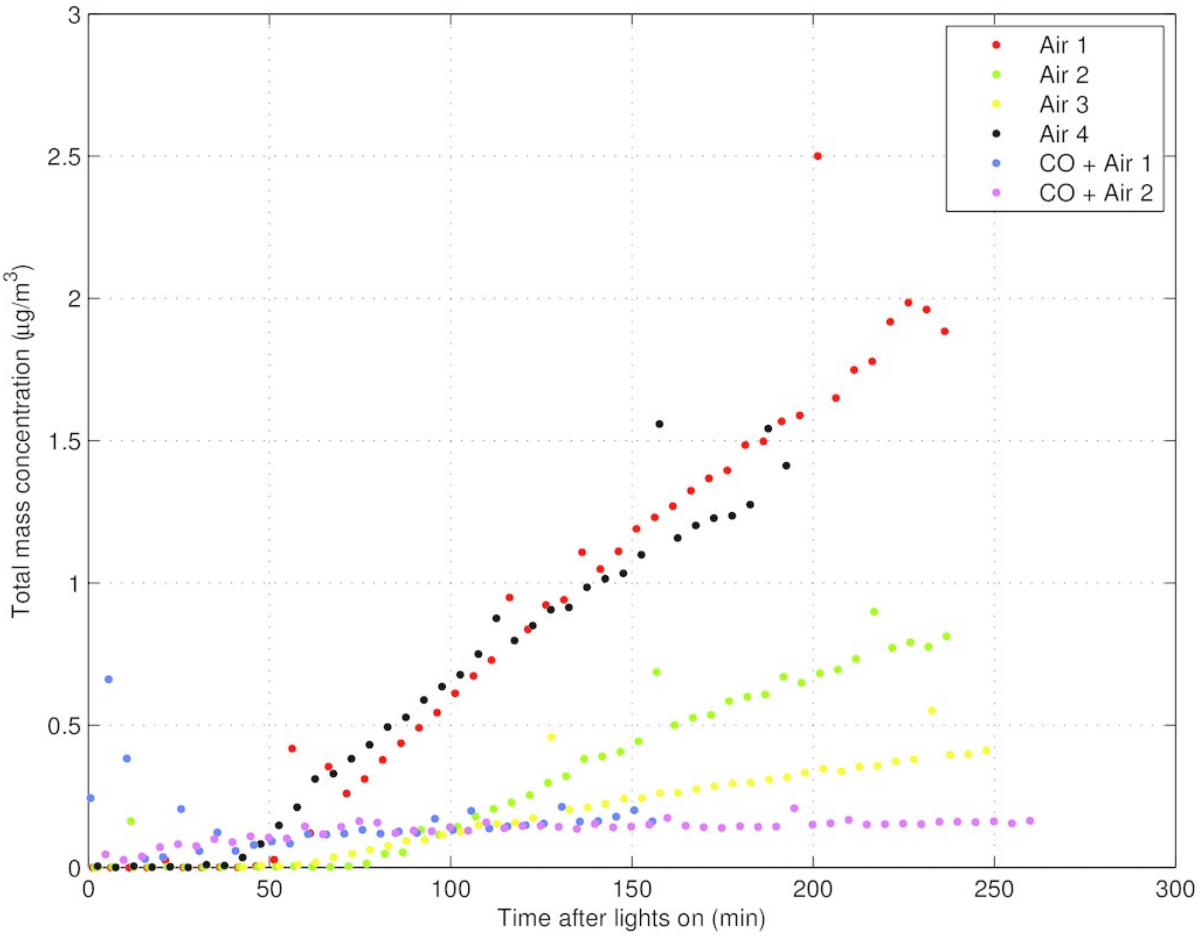

Figure R2: Wall loss corrected total mass concentration in pure air irradiation experiments. In "CO + Air" experiments carbon monoxide was added to the chamber as an OH radical scavenger.

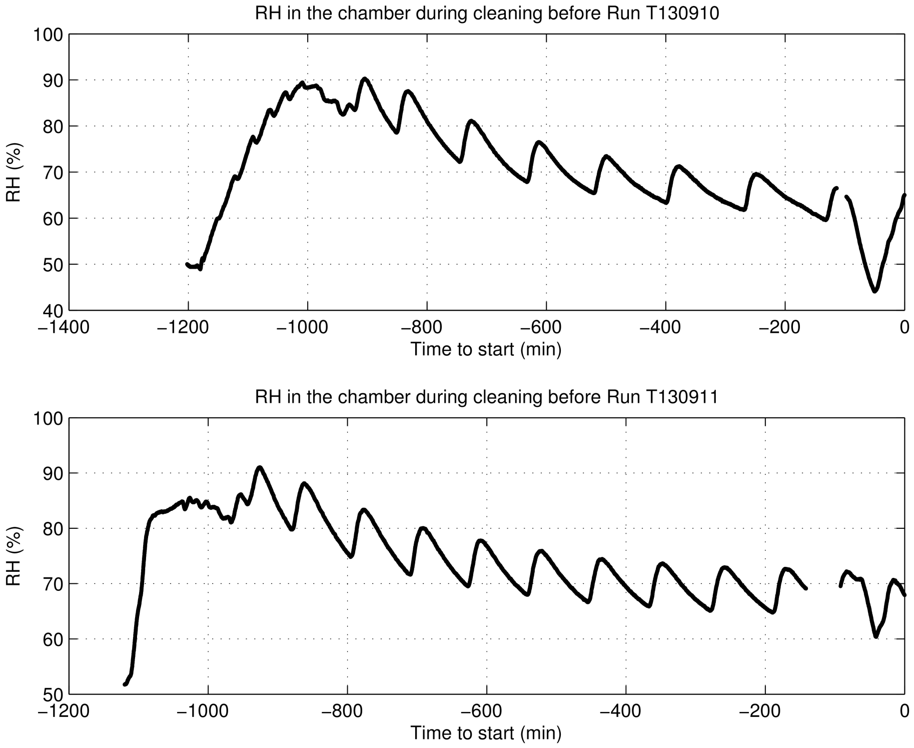

Figure R3: Relative humidity in the chamber during flushing and pure air irradiation.

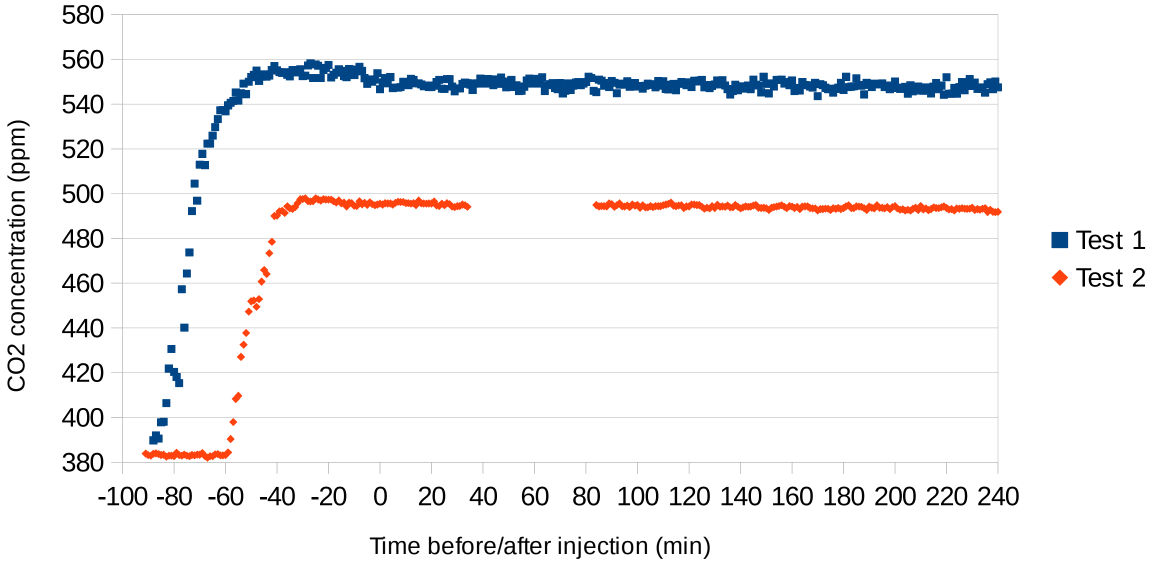

Figure R4: CO_2 concentration in the chamber in three injection tests with combustion aerosol. The aerosol was in the dark for 240 minutes after injection.

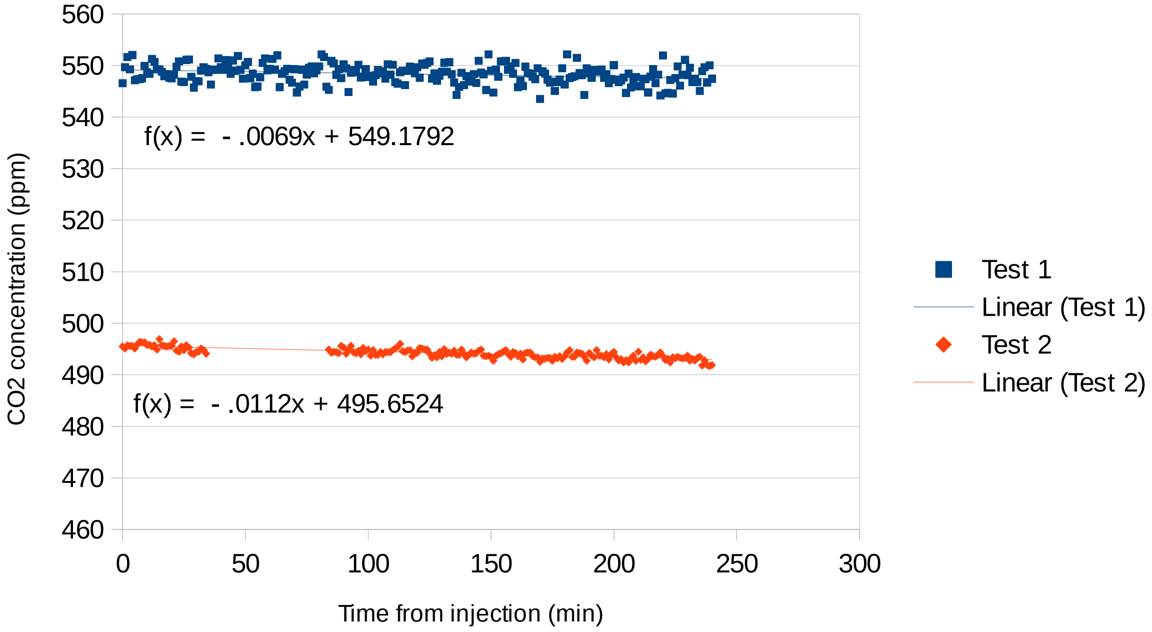

Figure R5: A detail of Fig. R4 for the time period of 0-240 min after injection. Also given are linear trendlines and their equations for the data points.