

Interactive comment on “A portable dual smog chamber system for atmospheric aerosol field studies” by Christos Kaltsonoudis et al.

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Main comments:

(1) *In the “Experimental procedure” it is not clear how many experiments were performed (it is ambiguous for the blank experiments and missing for the experiments themselves). The authors should clearly state upon how many replicates are based their conclusions and provide a table for various initial conditions and main results.*

The paper is based on the results of 51 chamber characterization experiments and 7 field test experiments. The characterization experiments include 15 blank or contamination related experiments, 14 experiments characterizing wall losses, 6 experiments quantifying the ambient air sampling efficiency, 3 experiments for the measurement of

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J_{NO_2} , 9 experiments related to RH and UV variations, and 4 VOC loss experiments. A table with the details of these experiments has been added to the Supplementary Information of the revised manuscript. The number of experiments on which the various conclusions are based is now clearly stated.

(2) *Sometimes, the analysis is oversimplified. Some key measurements are not given (see below my comments) and the literature survey is not wide enough.*

We have followed the reviewer’s suggestion and extended the literature survey (including those in Comments 3 and 4). In the original paper we focused on the historical development of smog chamber experiments. We now include more smog chamber studies focusing on their methodological contributions. We have also added information about the suggested measurements. Additional experiments have been performed during the revision stage to better characterize the behavior of the chamber with respect to the NO, NO₂, and O₃ losses to the walls and OH production.

(3) *The authors should have tried to better define the behavior of the chamber walls toward the NO_x/air/light system. This is a valuable exercise which is required for most of the chamber application. This is especially important since HONO was used as a source of OH radicals. They should perform deeper analysis and to build an auxiliary mechanism made of pseudo-elementary reactions with rate constants parameterized upon their experimental data. See for instance: Jeffries et al., 1976; Akimoto et al., 1979; Bloss et al., 2005; Carter et al., 2005; Hynes et al., 2005; Rohrer et al., 2005; Metzger et al., 2008; Wang et al., 2011; Wang et al., 2014.*

We have performed additional experiments characterizing the losses of NO, NO₂, and O₃ to the walls of the chambers as well as the OH production. These are described in the revised paper. A basic auxiliary mechanism has been developed and has been to the paper.

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(4) Previous simulation chamber studies observed a significant background OH production that could not be attributed to known OH radical precursors (Rohrer et al., 2005). A heterogeneous formation of HONO and its subsequent photolysis was suggested to explain this so called "background reactivity" within simulation chambers (Akimoto et al., 1987; Carter et al., 1982; Glasson and Dunker, 1989; Killus and Whitten, 1990; Sakamaki and Akimoto, 1988). It was postulated that HONO is formed by the heterogeneous dark hydrolysis of NO₂ on the humid chamber surfaces (see for example Carter et al., 1982; Finlayson-Pitts et al., 2003; Jenkin et al., 1988; Kleffmann et al., 1998; Pitts et al., 1984; Sakamaki et al., 1983; Svensson et al., 1987) the mechanisms of which are still under discussion. Did the authors calculate the ratio of HONO_{walls}/HONO_{injected}. This background HONO production could differ at varying light conditions. Higher light intensities as it is the case in this study ($J(\text{NO}_2) = 0.1 \text{ min}^{-1}$) would increase the quasi-stationary background OH concentrations. More significant HONO and OH background production rates can only be determined by especially dedicated experiments including systematic variations of RH and light intensity.

Following the reviewer's suggestion, we performed several additional experiments focusing on the production of OH due to the walls as a function of RH and light intensity. The OH levels were estimated by the decay of d-butanol that was added to the clean chambers. Assuming pseudo-steady state for the OH radicals we then estimated their effective production rate. The production rate was practically negligible at low RH but it did increase at 50 percent and depended on light intensity. These results are described in the revised paper. The OH produced from our HONO injection, and not the OH due to the walls, is the dominant source of OH in our perturbation experiments. One important note for our experiments is that because d-butanol is injected in all of them, the OH is estimated directly and therefore the OH exposure reported is already taking into account the wall source.

(5) There is no information about the estimated water quantity adsorbed on the Teflon wall or about the VOCs adsorbed on the wall. As mentioned above the blank experi-

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ments can lead to a HONO production from the chamber walls. What could be the zero order constant in ppt/s of HONO production from the chamber walls? The photolytic wall source of HONO is proportional to the J_{NO_2} (Rohrer et al., 2005) and somewhat related with the NO₂ concentration (for example Hynes et al., 2005 or Wang et al., 2011 or Wang et al., 2014).

We have performed vapor loss experiments for a few selected VOCs. The loss rates were quite low (less than 1 percent per hour). These results have been added to the revised paper. The estimation of the water adsorbed on the Teflon walls of our chambers is not possible right now. As discussed in our responses to Comment 4 we have performed additional experiments to quantify the magnitude of the wall OH source. Our estimated HONO production rate is less than 1 ppt/s for the J_{NO_2} and RH ranges used in this study. This information has been added to the revised paper.

Minor comments

(6) What is the mixing ratio of HONO introduced in the chamber?

HONO was not measured directly. The concentration of OH was estimated in all experiments by the decay of d-butanol over time. The estimated levels are of the order of 100 ppb.

(7) As the wall material seems to have a significant importance, please provide the precise reference of the material: producer, ref number, and product name.

We used Dupond PTFE 2 mil, 0.5 m wide to construct the chambers. This information has been added to the revised manuscript.

(8) As the Teflon foil is new and used just before the preliminary experiments how the blank experiments were distributed during the campaign? If, they were evenly

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distributed among experiments, did you notice any evolution of the wall chemical behavior?

The chambers were built by us in our laboratory in Patras and were thoroughly cleaned and conditioned before the characterization experiments. Their cleaning procedure involved first passing of high O₃ concentrations with the UV lights on and heating to approximately 50 C. Clean air passed then through chambers for several hours. A blank experiment was performed every few experiments both in the lab (during the characterization phase) and in the field. The wall losses are measured in each field experiment. We did not observe any evolution of the wall chemical behavior in these initial tests, but it something that we will keep investigating in future work.

(9) *Adsorbed organics on the chamber wall can also come from the foil production process (see Carter et al., 1982 for example), it is hence not relevant to only refer to the level of VOCs coming from the ambient air.*

This is correct, so we have rephrased the corresponding sentence. We did our best to clean the walls after the construction of the chambers from any residue of the Teflon production process (see also our response to Comment 8) but some volatile or semi-volatile material could be still in theory present.

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