

Atmos. Meas. Tech. Discuss., author comment AC1  
<https://doi.org/10.5194/amt-2021-362-AC1>, 2022  
© Author(s) 2022. This work is distributed under  
the Creative Commons Attribution 4.0 License.

## Reply on RC1

Magdalena Vallon et al.

---

Author comment on "LED-based solar simulator to study photochemistry over a wide temperature range in the large simulation chamber AIDA" by Magdalena Vallon et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-362-AC1>, 2022

---

**First of all we thank the reviewers for their constructive comments. Our answers are given in the following always directly after the individual comments in bold letters. Furthermore, corresponding modifications in the manuscript are given in parentheses.**

*Line 28: Please specify the location and seasonal conditions that the light source is compared with. Is it the Karlsruhe summer at noontime?*

**Answer: The light intensity equals to one third of the maximum light intensity at Karlsruhe (49.007° N, 8.404 ° E) at a clear summer day at 12:00 pm. We added this to the abstract as follows:**

**"Although, the light source only generates about 1/3 of the maximum solar irradiation at ground level at Karlsruhe (49.007° N, 8.404 ° E, 12:00 pm) at a clear summer day with a substantial intensity gradient throughout the simulation chamber, it could be shown that this type of light source allows reproducible experiments over a wide range of simulated atmospheric conditions and with a large flexibility and control of the irradiation spectrum."**

*Lines 60-79: The advantages and disadvantages of LEDs and xenon arc lamps are discussed in detail. How about black lights? Why are they excluded from the solutions?*

**Answer: Black lights were not considered, because they mostly emit light in the UV-A region. As we were trying to cover the light spectrum from around 300 nm to at least 500 nm, they are insufficient. It would have been necessary to combine them with other light sources, possibly making the construction and maintenance as a whole more complicated.**

*Section 4.3 Integral light intensity: Are the wall losses of NO<sub>2</sub>, NO, and O<sub>3</sub> accounted for when determining the light intensity? Also, it seems that the wall loss rates of gas-phase species at different temperatures were different. Will this impact the determination of the light intensity at different temperatures?*

**Answer: Fig. 4 shows the concentrations of the gas species NO<sub>2</sub>, NO, and O<sub>3</sub>. There is a distinct decline in the concentrations especially for NO<sub>2</sub> and O<sub>3</sub> during the illumination period. Without illumination, the wall loss is negligible for NO<sub>2</sub>**

on this time scale. To minimize the impact of wall losses on the photolysis frequencies, they were calculated using the concentrations measured during the first 10-12 min after reaching equilibrium. In this time period the wall losses are smaller than the uncertainty of the concentration measurements. Therefore, the impact on the photolysis frequencies is relatively small and included in the uncertainties given.

*Line 302: Why are the slopes different before and after illumination? Any explanations?*

**Answer: The adsorption rate is higher for higher 2,3-pentandione concentrations and the accommodation to the chamber wall is somewhat reduced for the aged or coated wall.**

*Line 317: Is it a summer day of Karlsruhe? Please clarify.*

**Answer: It refers to a clear summer day in Karlsruhe (49.007° N, 8.404 ° E). We have modified the sentence as follows:**

**“Regarding photolysis of 2,3-pentanedione alone, this corresponds to an atmospheric lifetime of about 40 minutes on a clear summer day in Karlsruhe (49.007° N, 8.404 ° E).”**

*Line 337: What are the uncertainties of wall losses? Why are the uncertainties higher at higher temperatures?*

**Answer: The uncertainties of the wall losses are calculated as the difference of the mean wall loss  $k_w$  (see Eq. 4) to the wall loss rates before respectively after illumination. For two (213 K and 298 K) of the five experiments the mean wall losses were calculated differently.**

**For 213 K the slope before illumination was higher than during illumination. In this case the photolysis frequency was calculated with regard to the wall loss rate after illumination, thus can only be considered as the upper limit of the photolysis frequency for this temperature. For the experiment at 298 K the data after illumination are missing due to technical problems. As the wall loss after illumination is generally lower than before, half of the maximum wall loss was considered as the mean wall loss and the maximum wall loss reflects the uncertainty.**

**This means only the uncertainties for the experiments at 243, 273 and 283 K are truly comparable and for these the trend is indeed, that with decreasing temperatures the uncertainties of the wall losses are getting smaller. The reason is that the wall loss rates before and after illumination are getting more similar. One explanation for this phenomenon could be that with decreasing temperature the effect of diffusion decreases and the influence of the mixing fan, transporting molecules from the chamber volume to the chamber walls gets more distinct. Furthermore, a wall coating may be achieved quicker at lower temperatures.**

*Lines 431-432: The photolysis of nitrate aerosols can produce OH radicals. Will this perturb the photolysis of DTDP?*

**Answer: Nitrate anions undergo photolysis in aqueous droplets, leading to the radicals OH $\cdot$  and NO $_2\cdot$ . According to Mack and Bolton (J. Photochem. Photobiol., A: Chem 1999) the absorption spectrum of NO $_3^-$  has a strong peak at 200 nm and a weaker peak at around 302 nm. Only the latter one is overlapping with the emission spectrum of the AIDA light source. As it is a weak band and only**

overlapping with the part of the emission spectrum which is lower in intensity. Furthermore, the quantum yield for OH radicals is only about 1% and not all potentially formed radicals will react with the DTDP. Therefore, this effect is significantly smaller than the direct photolysis of DTDP. The two products, which were already identified, have been shown to form also in the absence of nitrate (Mitsunobu et al., 1971 and Memarian et al., 2004). We have added this information to the manuscript as follows:

**“For these experiments we can assume that the absorption of photons through  $\text{NO}_3^-$  and the subsequent formation of OH radicals can be regarded as negligible as potential sink for DTPD in comparison to the direct photolysis. This is because the absorption spectrum of  $\text{NO}_3^-$  overlaps only weakly with the emission spectrum of the AIDA-light source and the quantum yields for OH radical formation is only about 1% (Mack and Bolton, 1999). The nitrate ion concentrations were too low to compensate for this. Nevertheless, experiments in the absence of nitrate ions would be beneficial.”**

*Lines 432-433: What are the phase states of DTDP at different temperatures? Were the slower production rates of products at lower temperatures caused by the reduced photolysis rate or the increased viscosity of particles?*

**Answer: Regarding the concentrations of salts and DTDP in the solution used for the aerosol production, the droplets should be liquid at 293 and 283 K, and highly viscous at 273 K and 263 K according to the AIM model (<http://www.aim.env.uea.ac.uk/aim/aim.php>, Clegg et al., 1998). As the light intensity is not substantially smaller for lower temperatures, the photolysis process itself should not be a decisive factor for the reduction of photolysis. However, the higher viscosity could hinder reactions of the excited DTDP with other reaction partners. We have added this information to the manuscript as follows:**

**“Please note that the DTDP containing particles droplets were liquid only at 293 and 283 K, but higher viscous at 273 K and 263 K (<http://www.aim.env.uea.ac.uk/aim/aim.php>, Clegg et al., 1998). This higher viscosity could hinder reactions of excited DTDP with other reaction partners.”**

*Lines 437-439: Are these components characterized by CIMS?*

**Answer: All of the organic components for the DTDP experiments were analysed with FIGAERO-CIMS. We have added this information as follows:**

**“During illumination the production of several components in gas and particle phase could be observed by CIMS measurements.”**

*Technical comments:*

*Line 100: Please remove the comma after “note”.*

**Answer: done.**

*Figure 3: Please add the labels “a” “b” to the figures.*

**Answer: done.**

*Figure 4: The labels “a” and “b” in the figures and captions are missing. Please check throughout the manuscript.*

**Answer: done.**

*Line 296: Wrong figure number.*

**Answer: We corrected the figure number to S5.**

*Figure 7: The caption of the x-axis should be "Time relative to start of the first illumination".*

**Answer: corrected accordingly.**

*Line 460: "pinen" should be "pinene".*

**Answer: corrected.**

*Line 501: "an" should be "and".*

**Answer: corrected.**