Answers to the reviews 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-RC1, 2021.

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.

RC1:

Vallon et al. described the implementation of a newly designed light source for the AIDA chamber. The illumination conditions were well characterized. In particular, with this newly designed light source, the photolysis of 2,3-pentanedione and a brown carbon proxy was investigated over a wide range of temperatures. It was demonstrated that this type of light source allows reproducible experiments for a wide range of atmospheric conditions. This paper has significant implications for the design of a smog chamber so is well within the scope for AMT. The experimental part is solid. It can be recommended for publication after the following comments are addressed.

Specific comments:

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 NO2, NO, and O3 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_2, NO, and O_3. There is a distinct decline in the concentrations especially for NO_2 and O_3 during the illumination period. Without illumination, the wall loss is negligible for NO_2 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 $NO2^{\cdot}$. 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 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 NO_3^- overlapps 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 to

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 viscus at 273 K and 263K 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 viscus 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.

RC2:

This manuscript describes the design of the illumination system developed for the AIDA chamber and provides results from a series of characterization and research experiments. The manuscript is clearly written, though it will require editing prior to publication. In addition to being helpful for any researchers involved in AIDA experiments or using data from AIDA, the novel integration of banks of LEDs to produce spectra similar to the solar spectrum would be of interest to a broad group of readers. The decision to use LEDs rather than more commonly used sources for solar simulation such as xenon arc lamps obviously made the system considerably more complex, but offers advantages of less heat generation and the ability to alter the spectrum for specific applications such as studying the wavelength dependence of photolysis reactions. Though I feel the manuscript should be published, there are some points that need to be clarified and several minor corrections that should be made.

One general recommendation is that the authors consider shortening the manuscript by removing either the section on photolysis of 2,3-pentanedione or photolysis of dissolved organic components. Both experimental datasets are interesting, but the manuscript is quite long and, for me, it was hard to maintain interest by the time I got to that last section. It also seems that either of those results could stand on their own in a separate manuscript.

Answer: It was our intention to show the reader the characteristics of the new light source but also some examples for potential applications that illustrate the options for future users even better. Therefore, we would like to keep the application examples in the manuscript.

The major issue I have with the manuscript is that, while there is a lengthy discussion of the light intensity gradient, there is not regarding the impact it will have on the different types of planned or possible experiments. On line 92 there is mention of use of a fan to rapidly mix the contents of the chamber, but then it is never mentioned again in the manuscript? Was it on for some or all of the experiments that are described? If not, what is the mixing time scale in the chamber? And even if it was on for some or all of the experiments presented in the manuscript, I am pretty certain that it would be undesirable for any experiments with cloud particles and so there should still be discussion of the mixing efficiency and time scale. In general, there is obviously a tradeoff between losses when the fan is on and, I assume, significant heterogeneity in time-averaged actinic flux for packets of air moving through the chamber. Or maybe there is enough natural convection that this isn't an issue. Either way, it needs to be discussed and, to the extent possible, discussed quantitatively. For which potential uses will the time scale of important reactions be comparable to or shorter than that of mixing in the chamber? Also, there needs to be some discussion of where the tubes to the gas and particle analyzers connect into the chamber as that could influence results for experiments such as the NOx/O3 system shown in Figure 4.

Answer: The mixing fan was working for all experiments discussed in this manuscript and the mixing time scale is given in line 92 as less than 2 minutes. To make this a bit clearer we have added the following information to the manuscript at line 92:

"Typical sampling tubes range 400 mm into the well mixed volume of the AIDA chamber. By rotating with 400 revolutions per minute, a fan inside the chamber ensures homogeneous dispersion of all components in less than 2 minutes during all experiments described in this manuscript."

Please note that is was our intention to show different potential applications of the light source ranging from gas phase photolysis, to photochemistry in aqueous aerosol, as well as photochemistry in cloud droplets (cf. figure S9). During all these experiments, the mixing fan was

working to ensure a homogeneous distribution of the components in the chamber. The AIDA simulation chamber is thus suitable for studying processes on timescales significantly longer than the mixing time of 1-2 minutes. If the light gradient is a problem for the experiments or not depends strongly on the type of the experiment. The experiments can be divided roughly in three categories. First, a reaction system which reaches an equilibrium during illumination like the actinometric experiments. As long as the time the system needs to reach the equilibrium is considerably longer than the maximum mixing time of the fan, the spatial light gradient is not a problem. This is especially the case for the actinometric experiments as only the equilibrium concentrations are relevant for the calculation of the photolysis frequency. After the start of the illumination the system reaches an equilibrium in around 8 min, which is considerably longer than the maximum mixing time of 2 min. Second, an irreversible photolytic reaction like the photolysis of 2,3-pentanedione. As long as one can easily measure either the decline of the educt or the formation of the product it should be possible to see if the light gradient leads to a considerable concentration gradient. As for the measured concentration of educt and product should change for up to two minutes after turning of the light due to the transportation of air parcels from higher or lower illuminated areas. As this could not be observed in any of the 2,3-pentanedione experiments, we assume that it is not an issue for these experiments. Third, more complex reaction mechanisms with possible intermediate products. If one would like to observe concentrations quantitatively on time scales of a few minutes, the light gradient could possibly be problematic and the positioning of the measurement lances should be considered appropriately. As for the experiments on the depletion of DTDP, the illumination and depletion process lasted two hours. Hence, any possible concentration gradient should be negligible with respect to the mixing time achieved by the fan.

The positions of sampling or injection tubes, which range typically 400 mm into the well mixed volume of the AIDA chamber, are well characterized but would only impact experiments on time scales close to the mixing time. These kind of experiments are typically not done in such a large simulation chamber but rather in e.g. flow tubes. The sampling or injection tubes comprise e.g. stainless steel tubes for aerosol particles, Teflon (FEP) tubes for reactive gases, and silco steel tubes for connecting mass spectrometers.

Minor comments:

Line 199: The discussion at this point is focused on the light intensity gradient. Unless I am missing something, absorption of light along the walls of the flange collar (and therefore before entering AIDA) will not contribute to the top-to-bottom gradient.

Answer: Here we refer to the changing light spectrum and try to explain why the UV is reduced more than the visible part. Due to the relatively wide emission angles of the individual LEDs substantial fractions of the photons are reflected from the flange collar and especially the upper parts of the chamber wall. This contributes to the gradients in light intensity and spectrum.

Line 201: Stating just the wavelength of maximum reflectivity of aluminum is not especially useful without some discussion of the extent of fall-off on either side of the maximum.

Answer: Considering the fact that the aluminium walls of the chamber are oxidized, the reflecting properties of aluminium oxide are actually more important. In a publication of Pavlovic and Ignatiev (Thin Solid Films, 138 (1986) 97-109) the reflective properties for different anodically oxidized aluminium are depicted. Even though these are slightly different for each oxidation method it is plausible to assume that the general trend is the same. The reflectance spectra shows a plateau from 670 nm to 500 nm with a reflectance of 0.7 starting to decline to 0.65 at 350 nm depending slightly on the oxidation procedure. The spectrum shows no further data for the

reflectance at even shorter wavelengths. We have added this information to the manuscript as follows:

"This is also in accordance with the reflectivity of oxidized aluminium which shows a plateau from 670 nm to 500 nm with a reflectance of 0.7 starting to decline to 0.65 at 350 nm (Pavlovic and Ignatiev, 1986). Please note that the aluminium wall in the AIDA chamber is oxidized. However, also the reflectivity of non-oxidized aluminium, like the reflectors added to the flange collars, decreases for wavelengths below 400 nm (Bartl and Baranek, 2004)."

Figure 2: I realize that the figure is already busy, but it really needs a curve showing the ratio of the intensity in AIDA to that outside (or two to show the winter and summer ratios).

Answer: We have added the ratios for summer and winter to the supplement to avoid to busy figures in the main manuscript. We have added this information to the manuscript at the captions of figure 2 as follows:

"The ratios of the mean intensity inside the AIDA chamber and the maximum values outside are given in figure S3 for summer and winter."

Figure 3: The relevance of the temperature-dependent shift for the shortest UV depends a lot on the type of experiment conducted. The authors should add some discussion of impacts for any photochemistry experiments for which photolysis of ozone is a significant source of OH. Related to this, the authors should explain if there is anything that can be done to recover the <320 nm UV for the highest temperature with the current LED bank or possibly with additions to it.

Answer: It is actually possible to keep the UV intensities relatively constant with varying temperatures by adjusting the LED currents. Furthermore, it is possible to add more UV LEDs to increase the <320 nm UV to adapt for experiments employing ozone photolysis at higher temperatures. We have added the following changes to the manuscript text at line 220:

"Alternatively, it is in principle possible to apply lower currents at lower temperatures to keep the emission spectrum nearly constant compared to warmer conditions. However, it is also possible to add more or stronger UV LEDs to increase the UV intensity also for higher chamber temperatures."

Line 352: I assume that CO yield is in % and not a fraction like the other two.

Answer: This is indeed correct. We have modified the sentence as follows:

"For a temperature of 298 K and without OH radical scavenger Bouzidi et al. (2014) reports yields 0.41 ± 0.7, 0.39 ± 0.6 and 0.076 ± 0.005 for formaldehyde, acetaldehyde, and CO, respectively."

Line 468: I assume there should be a "decreasing" in front of temperature.

Answer: This is correct. We have modified the sentence as follows:

"Decomposition of pinic and pinonic acid as well as the formation of products reduce significantly with decreasing temperature, which might be partially due to the increased viscosity of the aerosol particles."

RC3:

The authors present an LED based lightning system for the simulation chamber AIDA. The lightning within the chamber is very well characterized in terms of gradients, photolysis of relevant species like NO2, effects of chamber temperatures and perturbation of chamber conditions while the lights are on. The methodology, figures and discussion are well done. However, the presentation while good, suffers from an introduction that is not written in a fluent and precise way. Improving the introduction would help the manuscript but it stands as a great piece of work regardless. I would accept the manuscript baring some minor comments below.

Line 35-36: Odd way of saying that light enables photochemical pathways that are not available by merely increasing the temperature. Rephrase.

Answer: We agree and modified the sentence as follows:

“From a chemical viewpoint, light enables, besides the thermodynamic, photochemical pathways by specific electronic excitation of the molecules.”

Line 39-40: This sentence is vague in the way it is written. The authors provide examples in the next paragraph but I would rephrase this sentence to be more specific.

Answer: We agree and modified the sentence as follows:

“Various photochemical reactions like the formation of ozone and OH-radicals or the fragmentation of halocarbon compounds have been studied widely in the last few decades, now offering a good understanding for many photochemical reactions of atmospheric relevance. However, for many of the multiple organic compounds in the atmosphere additional research is still needed (Goldstein, 2007).”

Line 43: Should read “In principle”

Answer: We changed this accordingly.

Line 125: Did the experiments after using NO2 differ in any way?

Answer: The photolysis of 2,3-pentanedione in the presence of NO_2 did not show a significant difference compared to those without. We could not identify any interaction of NO, NO_2, or O_3 with 2,3-pentanedione or its photolysis products.

Figure 4: j(NO_2) seems fairly constant even though the emissions profiles are quite different in Figure 3. For figure 3 electrical settings were adjusted, is that the same case for Figure 4? If so it should be stated.

Answer: Although the UV light intensities increased for lower temperatures as indicated in figure 3a, the measured j(NO_2) did not increase significantly, at least not for the lowermost temperature of 213 K. This is somewhat surprising and may partially be due to a not completely representative intensity measurement at low temperatures. These measurements were done through a window at the bottom of the chamber and may have a small bias due to temperature dependent reorientations. Furthermore, the NO_2 photolysis is dominated by the higher photon fluxes and absorption in the visible spectral range.

Line 305 and Figure 5: How consistent are kW values? Did they change with temperature? Also, did the authors perform exclusively wall loss experiments?

Answer: No exclusive wall loss experiments were done for 2,3-pentanedione. We used the time periods before and after the photolysis experiments to determine the wall losses. The differences between the wall losses observed before and after the photolysis were used to estimate their uncertainties. These differences decreased with decreasing temperatures and so the uncertainties we estimate.

Figure 6: Formaldehyde and acetaldehyde yields increase with temperature, is this the result of faster wall losses artificially reducing the yields? Or increased adsorption leading to different product distributions? The suggested changes to alkoxy radical chemistry are a plausible reason but there could be other reasons.

Answer: Indeed, there could also be other reasons. However, the uncertainties resulting from the wall losses are included in the uncertainties of the yields.

Figure 9: Figure S7 and lines 435-440: The authors mention that product formation for the DTDP photolysis experiments is slower at lower temperatures but the photolysis rate is the same. Any explanation for this? Figure S7 only shows one temperature.

Answer: We don’t find a significant change of the DTDP photolysis rate with temperature but a weaker formation of the two products potentially due to changing branching ratios for reactions following the photolysis.

Line 460: Should read pinene

Answer: corrected.

Line 463: Numbers should be subscript

Answer: corrected to NH_4NO_3.

References:

Clegg, S. L., Brimblecombe, P., Wexler, A. S.; A thermodynamic model of the system H^+ - $NH4^+$ - $SO4^{2-}$ - $NO3^-$ - H2O at tropospheric temperatures. J. Phys. Chem. A, 102, 2137-2154, doi: 10.1021/jp973042r 1998.

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Mack, J., Bolton J. R.; Photochemistry of nitrite and nitrate in aqueous solution: a review, Elsevier J. Photochem. Photobiol., A: Chem, 128, 1-13, doi: 10.1016/S1010-6030(99)00155-0, 1999.

Pavlovic, T., Ignatiev, A.; Optical and microstructural properties of anodically oxidized aluminium, Elsevier Thin Solid Films, 138, 97-109, doi: 10.1016/0040-6090(86)90220-8, 1986.