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Reply on RC2

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-AC2, 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.

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."