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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Photosensitised heterogeneous oxidation kinetics of biomass burning aerosol surrogates by ozone using an irradiated rectangular channel flow reactor" *by* S. M. Forrester and D. A. Knopf

Anonymous Referee #2

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The work presented here is of atmospheric relevance since the studied compounds levoglucosan (LEV), Pahokee peat (PP), and 5-nitroguaiacol (NG) are widely present in the atmosphere emerging from the combustion processes. In this work the authors explore the potential of triplet state of Pahokee peat (3PP*) to photosensitize levoglucosan and 5-nitroguaiacol in the presence of ozone. The uptake coefficients of ozone towards levoglucosan, Pahokee peat, and 5-nitroguaiacol have been evaluated under dark conditions and in presence of UV-VIS light using the newly developed rectangular channel flow reactor. Various mass ratios of Pahokee peat with levoglucosan and

5-nitroguaiacol, were exposed to ozone under both visible and UV-A irradiation. The authors show that the effect of UV light on the reactive uptake of ozone is more important in comparison to the influence of the visible range of the solar spectrum.

The manuscript is well written, consistent and the obtained results follow the pattern of the previous work done by the group of Knopf. In fact, these results represent a continuation of the efforts of Knopf's group to strengthen the knowledge about an emerging topic such as photosensitized heterogeneous chemistry. I recommend publication of this article in Atmospheric chemistry and Physics and I strongly encourage the authors to continue their research on this topic.

However, I have few comments and/or suggestions which may help to improve the quality of this manuscript.

The PP/LEV mixture was prepared in water and the PP/NG mixture was prepared in methanol. Methanol is somewhat less polar than water so many organic compounds have a significantly higher solubility in methanol than in water. Did the authors consider the possibility of solvent effect on both mixtures of the organics modifying the photosensitizing properties of PP prior deposition of the substrate on the glass block? How relevant is the concentration of 1 mg ml-1 of PP with respect the atmosphere?

In the legend of Figure 2, please indicate where this spectral irradiance was measured and zenithal angle, as well. Between 550 and 650 nm there are important peaks from the lamps used in this study, considerably higher that the intensity of the solar spectrum. However, these peaks might not have an influence on the reactive uptake since the organic compounds under study does not absorb in this region, as shown in Figure 5. Please clarify this in the text. Further, in the legend of Figure 5 please indicate in the composition of solution used to obtain the absorbance spectrum for PP as was done for the other compounds. Was it an aqueous solution? The black line shows that obviously there are particles in suspension in the solution that cause diffusion of light. Also it seems that the concentration of PP is so high that the spectrum (black line) is

ACPD
13, C1529–C1531, 2013

Interactive Comment

saturated. Can you please shed some light on this? Overall, in my opinion the light sources should be better adjusted with respect the absorption properties of the organic compounds and should better mimic the solar spectrum.

It would be interesting to test the photosensitizing properties in the absence of ozone, which could in turn also serve as blank experiments. In this sense on page 7568 the authors state: "but this enhancement is most likely due to PP, and not to an energy transfer between PP and LEV". This hypothesis could be easily checked by performing experiments in the absence of ozone. I recommend to check this possibility in future studies.

In Figure 6 at mass ratio 1:1, the observed uptake coefficients in the presence of UV or VIS are almost the same. Further, it is not clear whether the uptake coefficients increase is due to the effect of light or to the increased mass ratio 1:100. In this figure it is not clear in which case the light is enhancing the uptake coefficients and when they increase is due to the change of mass ratio. Can you please explain this phenomenon?

Please remove the a.u on y axis in Figure 4, 6, 7 and Figure 8 since the uptake coefficients are dimensionless. Figure 7 and Figure 8 show that the light source is not appropriate for this kind of study. In Figure 8 it can be seen that both uptakes under UV and under VIS irradiation exhibit almost the same values. This is somewhat strange since 5-NG absorbs well in the UV and not in the visible at least not at the wavelengths that could overlap with the spectrum of the lamp.

The last minor comment is that reference Alvarez et al., 2012 should be Gomez Alvarez et al., 2012.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 7553, 2013.