

We thank the referee for taking the time evaluating our manuscript. We have responded to each comment and give suggested changes to the manuscript text as bold-faced letters. The page and line numbers refer to the discussion paper.

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?

We thank the referee for bringing up this point. We do not know if the distribution of PP and LEV or PP and NG changes due to the presence of different solvents upon drying and solidification. The results in Table 2 likely indicate that both mixtures are well mixed. The mean γ of 1:1 PP/LEV under VIS irradiation is less than for pure PP, indicating that the surface of PP/LEV represents a mixture. The same applies for the PP/NG mixtures where γ under VIS decreases as NG amount increases, indicating that the surface composition follows the solution composition. These results suggest that there is not a significant bias of the location of PP, and thus its photosensitising properties, due to the usage of two different solvents.

A concentration of 1 mg ml⁻¹ PP in water for acidic to neutral conditions will result in only partial solubility of PP (Graber and Rudich, 2006; Klučáková and Pekař, 2005). Since atmospheric aerosol is more likely to be neutral or acidic (Facchini et al., 1999; Graber and Rudich, 2006), we would expect a similar effect on PP. However, the concentration of 1 mg ml⁻¹ aqueous PP was not chosen as an atmospherically relevant concentration. It was chosen for comparison with previous studies and to ensure enough material coated the glass block.

In the legend of Figure 2, please indicate where this spectral irradiance was measured and zenithal angle, as well.

We add the following sentence to the manuscript on page 7561, line 4 to clarify the zenith angle:

“The light sources are positioned directly above the flow reactor so that the zenith angle is 0°.”

Between 550 and 650 nm there are important peaks from the lamps used in this study, considerably higher than 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.

In regard to the peaks between 550 and 650 nm, the authors realize that the VIS light source is not ideal for the absorption of irradiation by NG, but a trade-off was made in order to have sufficient irradiation output power. We agree that this is a caveat to our experiment, and would like to look into other light sources in the future. We have mentioned this caveat at numerous places within the manuscript:

Results and Discussion (Section 3.1, 3.4.2), Atmospheric Implications, and Conclusions.

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?

In Figure 5 we do not indicate solution composition for NG and only give the composition of the solvent. The exact solution compositions are unknown, and therefore we do not report an absolute absorbance. The absorbance scale is in arbitrary units for comparison of absorption wavelengths only. Furthermore, the PP solution was centrifuged to remove particulate matter, therefore reporting a solution concentration is not possible.

For clarity, we modify the following sentence to the figure caption of Figure 5: **“Absorbances as a function of wavelength. Pahokee peat is shown in black and 5-nitroguaiacol in a 0.01M HCl solution (pH = 2) and a 0.01M NaOH solution (pH = 12) are shown in green and purple, respectively.”**

becomes

“Comparison of relative absorbances as a function of wavelength. Aqueous Pahokee peat, centrifuged to remove particulate matter, is shown in black and 5-nitroguaiacol in a 0.01M HCl solution (pH = 2) and a 0.01M NaOH solution (pH = 12) are shown in green and purple, respectively.”

The black line shows that obviously there are particles in suspension in the solution that cause diffusion of light.

The authors agree that the spectrum shown for aqueous PP is quite similar to a spectrum that is dominated by Rayleigh scattering. However, we believe this is only a coincidence since other studies have shown that humic acid absorbance spectra exhibit the same overall trend as shown in our spectrum (D'Anna et al., 2009; Monsallier et al., 2001).

Also it seems that the concentration of PP is so high that the spectrum (black line) is saturated. Can you please shed some light on this?

The aqueous PP solution was diluted several times to ensure that the spectrophotometer was not saturated. The absorbance values on the y-axis are arbitrary since we do not record absolute absorbance, and thus do not reflect a known aqueous PP concentration.

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.

Please see comment above. We have mentioned this caveat a couple of times in the manuscript. It is difficult to find an irradiation source that possesses the necessary photon flux in the visible wavelength range and which sufficiently irradiates the entire substrate surface.

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.

The referee brings up an interesting point that in the absence of ozone, potential reactions may occur between PP and LEV resulting, for example, in new volatilized or condensed phase products. However the CIMS was operated and optimized for operation in negative ion mode to determine the changes in O_3 due to uptake and thus the heterogeneous kinetics. This is a good idea to investigate in future studies in which we are aiming to also monitor volatilized organic compounds.

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?

Figure 6 is a graphical representation of some of the data from Table 2. It shows the enhancement from either VIS or UV irradiation as a function of mass ratio of PP to NG. We can observe from Fig. 6 that the average γ for 1:1 PP/NG is enhanced under VIS and UV irradiation compared to pure NG. As the amount of PP to NG decreases, under VIS irradiation the average γ decreases. Under UV irradiation, as the mass ratio of PP to NG decreases the mean γ seems to be increasing. However, within the experimental uncertainty, one could also conclude that there is no further enhancement of γ when decreasing the amount of PP. These effects may be explained when looking at the absorbance of NG with respect to VIS and UV irradiation. NG does not efficiently absorb VIS (in the spectral distribution of our light source). Therefore under VIS irradiation, the increasing amount of little/non-absorbing NG shields PP and thus the overall reactivity decreases. However, NG absorbs strongly at lower wavelengths. Therefore under UV irradiation, γ of the PP/NG substrates are enhanced even when PP is decreased.

We modify the following sentence on page 7568 for clarity:

“This is most likely due to the increasing dominance of NG, which does not efficiently absorb VIS radiation.” becomes

“This is most likely due to the increasing dominance of NG, which does not efficiently absorb VIS radiation, and because there is less PP available to transfer energy to NG.”

Please remove the a.u on y axis in Figure 4, 6, 7 and Figure 8 since the uptake coefficients are dimensionless.

We have corrected the figures according to the referee’s suggestion.

Figure 7 and Figure 8 show that the light source is not appropriate for this kind of study.

Please see comments above.

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 uptakes indeed are similar in Figure 8. Although NG does not absorb well in the visible regime of our light source, PP is still able to absorb at these wavelengths and transfer excitation energy to NG. Also, Fig. 6 indicates that 1:1 mass ratio PP/NG mixtures show similar enhancements when exposed to VIS and UV irradiation.

Furthermore, it should be taken into account that the total UV photon flux reaching the organic substrate during the experiments is 2 orders of magnitude smaller than that of the VIS irradiation.

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

We have corrected the references according to the referee's suggestion.

References

- D'Anna, B. et al., 2009. Light-induced ozone depletion by humic acid films and submicron aerosol particles. *J. Geophys. Res.-Atmos.*, 114, D12301.
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