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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Light induced conversion of nitrogen dioxide into nitrous acid on submicron humic acid aerosol" *by* K. Stemmler et al.

K. Stemmler et al.

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We would like to thank this reviewer for thoroughly reading this manuscript and the constructive comments. In our response, we directly refer to the numbered specific comments raised by the referee.

1)Choice of humic acid

The Humic Acid (Aldrich) was chosen for practical reasons because it is available in sufficient quantities for the aerosol experiments, see also our response to referee 1; this choice further allowed us to extend and compare previous photoreactivity studies on solid films of humic acids. Moreover, the higher reactivity was necessary to obtain a quantifiable HONO production in addition to the background formation on the reactor walls. We follow the argument of the referee and add a proper caveat in the "Dis-

cussion" and "Conclusions and atmospheric implications" section with a statement, in which we point out that the estimated upper limit is based on the comparatively high reactivity of the used HA material, which further confirms our conclusion. We also note that the similarity between fulvic acids and complex organic material in atmospheric aerosols is based on comparable behaviour in exchange columns and several other physical parameters, however not on chemical properties. Nevertheless, we are aware that oxidized atmospheric aerosol has not as much aromatic moieties as present in humic acids. Biomass burning aerosol may be the only example, which contains phenolic monomers comparable to those present in HA.

2)Effect of particles on light scattering in the reactor

As mentioned in the Experimental section, we attributed background formation of HONO to heterogeneous reactions of NO_2 and adsorbed H2O and of NO_2 with deposited HA particles on the inner walls inside the aerosol flow-tube. The gas phase chemistry forming HONO is considered too slow. Therefore aerosol scattering would not influence HONO formation on the flow tube walls (actinic flux may increase by scattering but irradiance on the surface should be almost not effected or even decrease by absorption of light by the particles). Moreover scattering and absorption by the aerosol is estimated insignificant (less than 0.01) considering the path length, particle size, particle concentration and typical optical properties of humic-like aerosols. Thus, our increasing HONO formation during the "aerosol on" experiments cannot be attributed to a changing background photochemistry, but is caused by the photo-induced heterogeneous conversion on the particles. We will add a sentence about this estimate at the end of the section discussing the dependence of HONO formation on light intensity.

3)HONO formation on aerosol vs HONO formation on soil

The hypothesis presented at the end of the manuscript (page 4052 line 29) is a conclusion of a previous paper (Stemmler et al., 2006), which evaluated the photoreactivity of solid films of HA and real soil samples towards NO_2. The quantitative estimations were

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based on experiments with real soil surfaces (soil dust on a glass surface substrate), which is very realistic for irradiated atmospheric ground surfaces (for example: farm land, or any surfaces with wind blown soil dust like buildings, streets etc.). Therefore, this last paragraph is only added as a comparison to the conclusions about the HONO source strength for HA aerosol from the present study. We will carefully check the formulation of this paragraph to avoid the impression that the source strength from ground is estimated from the present study.

References

Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., and George, C.: Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, Nature, 440, 195-198, 2006.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4035, 2007.