Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-198-RC1, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous OH oxidation of secondary brown carbon aerosol" *by* Elijah G. Schnitzler and Jonathan P. D. Abbatt

Anonymous Referee #1

Received and published: 30 April 2018

This manuscript reports experiments, in which the evolution of brown carbon (BrC) aerosol upon exposure to OH is followed by the optical properties (scattering and absorption) at low (15%) and higher (60%) relative humidity. BrC aerosol was produced from the aqueous photooxidation of solutions containing resorcinol and H2O2, thus resembling aged biomass burning aerosol with high aromaticity. The results are that at 60% RH, oxidation of this BrC aerosol first induced an enhancement of absorption, followed by bleaching, with an inverse behavior observed for the single scattering albedo (SSA). At 15% RH, only a slowly increasing absorption was observed during the time scale of the experiments. Interpretation of the results is facilitated by a multilayer kinetics model, in which chemistry is lumped into a simple oxidation scheme involving one parent BrC leading to one second and one third generation oxidation product with

Printer-friendly version

Discussion paper

differing optical properties. Comparison to experimental data in terms of optical properties, indicate that strongly contrasting diffusivity must be assumed between 15% RH and 60% RH to reproduce the experimental data. This allows speculating about different pathways of oligomerization and fragmentation to occur at various time periods. The evolution of BrC properties is a highly relevant topic of atmospheric aerosol chemistry due to ubiquitous presence of BrC compounds in a large variety of primary, aged primary or secondary organic aerosol.

The experiments seem to be well performed and carefully analyzed. Proper control experiments are performed to distinguish between photolysis and OH oxidation. Since the experiments are not accompanied by more detailed chemical analysis, the application of the kinetic model remains poorly constrained, though it provides a useful link between expected chemical processes and the optical properties, as they evolve under different humidity and thus likely differing diffusivity.

The manuscript is well written and structured; the conclusions are adequately supported by the experimental findings; and the kinetic model is presented and used with care and proper caveats. I recommend publication of this work with maybe just a few small revisions, following some specific comments below.

1) The model is based on chemical reactions just occurring at the surface, and the bulk only serves as a medium for reactants and products to diffuse; this seems reasonable for the reaction with OH. However, second generation oxidation may involve O2 or other reactive oxygen species deriving from the first and second step and may also proceed in the bulk. Of course, considering such would rapidly lead to more variables that would need to be tuned and would make the results more ambiguous. But maybe the authors could make an attempt in checking the sensitivity of the model results and parameters towards the experimental observables. I would also expect that O2 has quite different diffusivity than the large aromatic oligomers.

2) The estimated diffusivity at 60% RH and also the fact that diffusion limitations are

Printer-friendly version

Discussion paper

so apparent are a bit surprising. The authors are explaining it with the high aromatic content and the ease with which aromatic oligomers are formed. Can the hygroscopic growth be estimated from the experiment between 15% and 60% RH. The lack of significant water uptake could support the semi-solid character of these particles at 60% RH.

3) Based on the reported results, under the conditions of the experiments, OH oxidation dominated the changes in optical properties in comparison to pure photolysis alone. Could the authors try estimating the relative impact of photolysis and OH under atmospheric conditions. Photolysis of BrC or reactions of their triplet excited states may also lead to later generation radical processes, similar to those initiated by OH; therefore the relative impact of OH versus that of BrC induced photochemistry on aerosol aging may require some attention.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-198, 2018.

Printer-friendly version

Discussion paper