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Interactive comment on "Photomineralization mechanism changes the ability of dissolved organic matter to activate cloud droplets and to nucleate ice crystals" *by* Nadine Borduas-Dedekind et al.

Anonymous Referee #2

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Overview

Borduas-Dedekind et al. report on systematic laboratory studies of the photo-degradation of representative dissolved organic matter bulk solutions and its impact on cloud condensation nuclei (CCN) and ice nuclei activity (IN). Their main finding is that photochemical oxidation promotes CCN activity and suppresses IN activity. A perhaps remarkable finding is that the hygroscopicity of these organic mixtures increases from $\sim$0.1 to upwards of $\sim$0.45 with increasing irradiation. This is where I feel the authors need to strengthen their argument - can such an increase be reconciled? The meth-

ods, techniques, and analyses appear well executed and cited, and the authors did an excellent job discussing caveats and experimental limitations. I support publication in Atmospheric Chemistry and Physics after the authors address my comments. In addition to addressing the large enhancement in κ, the paper could really be improved by including a schematic to connect the different chemical processes the authors propose are happening.

Comments

Abstract, line 13: Be careful with phrasing here – the authors are measuring the CCN and IN activity, not necessarily ability to form mixed-phase clouds. I suggest dropping ". . .ability to form mixed-phase clouds, by acting as. . ." and connect so that it reads, ". . .on its cloud condensation nuclei (CCN) and ice nuclei (IN) activity."

Page 7, line 25: Please clarify how the wet diameter was determined in the calculation of critical supersaturation if such data was not measured. Do you mean it was a fitting parameter as part of the activated fraction curve?

Page 10, lines 10-13: I much appreciate the authors' statement of caveats and potential differences in their bulk measurements compared to aerosol phase processes. Beyond the kinetic considerations due to differences in concentrations between the aerosol phase and bulk solution, other factors such as mixing state, phase, morphology (i.e., matrix effects) might also impact photochemical processes differently in aerosol compared to the bulk solution (Lignell et al., 2014).

Page 10, section 3.2: This discussion needs some revision – please describe in detail why κ varies between 0.12 and 0.45. Would you expect κ to increase this much, and why? This is significant given that κ for organic aerosol is generally $\sim$0.1-0.2 (Petters and Kreidenweis, 2007). See also comment (6) below.

Page 13, line 25: What are the units referring to carbon loss? Is it by mass, volume, molar concentration?

It's difficult for me to make a clear connection between the increase in hygroscopicity and the production of small organic acids/loss of carbon, except that the author's state there is a dependency of CCN activity on the decrease in organic carbon content. Is the reasoning that the production of small organic acids increases average O/C of the particles and thus κ? Is there any evidence that shows such an enhancement in CCN activity attributed to an increase in O/C and how much of a change in O/C is expected? Perhaps the significant loss of carbon (up to 63%) during irradiation, likely due to volatilization, decreases average DOM molar mass, thus increasing κ, e.g., as in Slade et al. (2017) for Suwannee River Fulvic Acid particles reacting with OH? The following relationship relates molar mass to κ (Mikhailov et al., 2013):

κ=J*(density/M)/(density_w/M_w)

Where J is the van't Hoff factor, M is average particle molar mass, and the subscript "w" refers to water. Assuming constant particle density and unity van't Hoff factor, a decrease in molar mass would increase hygroscopicity. I understand the authors did not analyze the mixtures using mass spectrometry, however, performing such a calculation relating κ to molar mass could help support the argument even further.

Page 13, line 21: I found the result that pH of the solution remained at ∼5 during the irradiation quite surprising. If more organic acids are generated with increasing irradiation, would not the pH further decrease?

The paper could really benefit from an overall schematic of the proposed processes (mechanisms) occurring. For example, a reaction scheme that shows the production of oxidants internal of the solution, the oxidation of a representative DOM structure and formation of the small organic acids, etc. There are many (exciting and cross-cutting) points discussed in the paper. However, connecting them without a clear schematic, makes it very difficult to follow in the paper.

References

Lignell, H., Hinks, M. L., Nizkorodov, S. A.: Exploring matrix effects on photo-chemistry of organic aerosols, Proc. Natl. Acad. Sci. USA, 111, 13780-13785, 10.1073/pnas.1322106111, 2014.

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Petters, M. D., and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, 10.5194/acp-7-1961-2007, 2007.

Slade, J. H., Shiraiwa, M., Arangio, A. M., Su, H., Pöschl, U., Wang, J., and Knopf, D. A.: Cloud droplet activation through oxidation of organic aerosol influenced by temperature and particle phase state, Geophys. Res. Lett., 44, 10.1002/2016GL072424, 2017.

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