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Atmospheric Chemistry and Physics
Discussions

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 #1

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This manuscript describes a study aimed at determining how photochemistry of water soluble organic matter in aerosol droplets affects the ability of these aerosols to be cloud condensation (CCN) or ice nuclei (INP). Natural organic matter collected directly from rivers in the Southeastern U.S. and a fulvic acid isolate from the international humic substances society (IHSS) were photolyzed for a length of time approximately equivalent to the lifetime of an aerosol droplet in the atmosphere. The solutions were atomized into a cloud condensation nuclei chamber to determine their kappa-values (measure of hygroscopicity from Koehler theory) or studied for their ice nucleating abil-

ity in an immersion freezing apparatus. The authors found that irradiation of solutions led to significant mineralization of carbon (loss of CO and CO2) and formation of small carboxylic acids due to fragmentation induced by direct and indirect photochemistry promoted by chromophores within the dissolved organic matter; total dissolved organic carbon decreased over time of photolysis. Interestingly, hygroscopicity values increases with decreasing dissolved organic matter concentrations while INP efficiencies decreased. This suggests that photochemical aging makes aerosols better CCN and worse INP. The data provides valuable information that can be used to model aerosol/cloud processes and their corresponding radiative properties.

The manuscript is excellent in all respects, from the quality of the writing to the figures, and of course the science. Regarding the science, there are several aspects of this manuscript that make the work novel. Aside from the fact that the CCN and INP measurements were carried out using state of the art instrumentation, measuring both CCN and INP activity on the same types of samples is quite unique and allow critical insights to be made; I am not aware of another study that has done this. Another unique aspect of this work, which stems from the multidisciplinary approach of this work, is the use of dissolved organic matter collected from the Great Dismal Swamp in Virginia and the Suwannee River in Florida, USA. These are more realistic surrogates of dissolved organic matter since they were not subjected to the type of extraction protocol that the typical commercially available humics or fulvics are subjected to that artificially change their composition and reactivity relative to unaltered samples. Finally, another strength of the manuscript lays in the quality and quantity of supporting photochemical (actinometry) and analytical chemistry measurements (CO(g), CO2(g) loss and production of small organic acids) that help explain the trends in CCN and INP efficiencies.

The most significant findings are that in situ photochemistry driven by water soluble organic matter leads to significant organic carbon mass loss and this loss impacts CCN and INP efficiencies and concentrations. Indeed, the fact that the photochemistry occurred within the aerosol solutions and were not impacted by gas phase oxidants, suggests that photochemistry from within the particle may be more important factors driving CCN and INP efficiencies than heterogeneous oxidation mechanisms involving gas-to-particle partitioning of oxidants. This will be a significant finding for the aerosol modeling community and I very much appreciated the clear discussion of the impacts of their work on predicted aerosol size distributions, aerosol properties, and the impact on cloud formation and optical properties. I feel the manuscript is ready for publication and I congratulate them on some very nice work.

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