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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evidence for pyrazine-based chromophores in cloudwater mimics containing methylglyoxal and ammonium sulfate" *by* Lelia Nahid Hawkins et al.

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Author Response to RC2

RC2: "Hawkins et al. present a laboratory experiment to simulate the formation of aqueous-phase brown carbon (aqBrC) from methylglyoxal and ammonium sulfate. The reactions of methylglyoxal (or glyoxal) + ammonium sulfate (or amines and amino acids) have been employed as a canonical chemical system to mimic BrC formation. Despite numerous studies on this topic, the chemical insights of the chromophores remain unclear. Using an innovative APCI technique with isotopically labeled ammonium sulfate, the authors present convincing evidence for pyrazine-based chromophores

present in the reaction mixture. The chemical analyses are highly detailed. I believe that the molecular-level information on BrC chromophores presented in this work will lay the foundation for understanding the environmental impact of BrC. I strongly recommend publication of this work in Atmospheric Chemistry and Physics. However, I have several comments/suggestions to improve the manuscript."

The authors are grateful for the thoughtful comments and find the major suggestions to be entirely reasonable and manageable in the time frame provided. Indeed, some of the suggested measurements have been completed already, but were carelessly excluded from the SI document upon submission.

Specific responses to individual concerns are addressed below.

1. "I am concerned that the conclusion "droplet evaporation can overcome the pH barrier" is an overstatement. Personally, I think there is no doubt that evaporation accelerates BrC formation. For example, Lee et al.1 have shown that diffusion-drying atomized droplets gave rise to BrC within seconds (I think the authors should consider citing this paper). However, the current experimental approach (i.e., free-drying in a vial for 7 days) cannot conclusively show that droplet drying can overcome acidity barrier under atmospherically realistic conditions (i.e., rapid drying, evaporation of volatile compounds)."

The authors agree with this assessment and have planned to both modify the text to perform preliminary studies using an atomizer to determine if any of the observed product are visible upon rapid drying. These measurements will be included in the SI.

2. "The authors only present APCI spectra after one week of drying. Something missing from the current analytical protocol is the initial MS and TOC concentration (i.e., immediately after mixing of methylglyoxal and AS). It may seem trivial, but it is essential to show that the peaks presented by the authors are indeed from the reaction. It is also a good way to test whether APCI is indeed insensitive to methylglyoxal."

The authors did obtain spectra immediately after mixing as well as 24 and 72 hours later, those will be included in the SI along with the blanks suggested by Reviewer #1. Initial TOC measurements as well as absorbance spectra will be collected on new samples prepared prior to submission of the revised draft.

3. “Despite a detailed discussion on the effects of evaporation, the authors seem to have neglected the fact that evaporation also occurs during the APCI measurement (from the ASAP probe). In particular, the capped samples are in liquid while the dried samples are in solid. The authors should discuss how this may affect the APCI interpretation.”

The authors agree that evaporation during APCI analysis could be important in product formation. A discussion of this will be added to the revised manuscript. While nothing can be done to prevent the liquid samples from evaporating during analysis, we were able to re-dissolve the dried material and collect spectra to compare with the dried (original) material. Those spectra were identical within instrumental uncertainty. In almost all cases, the capillary became coated with a dark brown material after exposure to heat and dry N2, indicating that the method does indeed generate additional brown products beyond reaction. However, the observance of masses matching our pyrazine chromophores in previous studies using other methods (and in our GC-MS samples that never experience drying) gives us confidence in the formation of pyrazine chromophores prior to APCI analysis.

The authors are willing to make all of the suggested minor and technical corrections.

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