

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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Received and published: 22 April 2018

Author Response to RC1

We thank the first reviewer for providing these helpful comments. Although we are in the process of completing the work to address the reviewer’s reasonable concerns, we wanted to post a response immediately. The additional experiments are not overly burdensome and should address the concerns completely.

RC1: “I have a number of serious concerns about the evaporation experiments which I am not sure can be addressed. It may be necessary to cut this material from the paper,

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or heavily revise with additional control experiments. It seems that the experimental method involved leaving samples uncovered in a hood for a week.”

Yes, the reviewer is correct that for the evaporated samples, the vials are left in a clean, unused hood in laboratory used only by the PI for one week. We can address a number of the reviewer’s concerns with measurements we already have (that were not included in the original submission) and are happy to conduct additional control experiments for the final publication to confirm that the evaporation process does not significantly differ from droplet scale evaporation experiments. We believe that the findings regarding evaporation are important enough to merit further attention, and so hope they can be left in with the proposed additions.

Specific responses to individual concerns are addressed below.

1. “Cloud processing takes place on a timescale of minutes to hours, so this process does not resemble the experimental conditions. How does the timescale for drying affect the results?”

As the experiments were conducted, we analyzed the sample material after just a few hours, 24 hours, and 72 hours. In the case of the capped samples, the only change we observed from 24 hours to 1 week was the increase of all signals. All the products we observed after 1 week were visible in the initial spectra (will be added to the SI). The convenience of the 1 week old samples is purely in the signal to noise ratio of the spectra and easier interpretation of isotopically labelled products. As for the dried samples (more of a concern, I suspect), we see something different. The samples appear to change the product distribution over the final hours of drying resulting in the noticeable difference between capped and dried samples. Until the open samples actually dry, they resemble the capped samples (again, spectra will be added to the SI). The actual transition from a solution to dried material happens fairly quickly, despite the samples being allowed to dry for a week. Once dried, the samples do not change composition measurably, and we have verified this by analyzing dried material immediately follow-

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ing drying, and a week later. To compare this week long drying to rapid drying, we will conduct some additional experiments under two different mechanisms. First, we will dry samples (prepared in the same way) under high purity nitrogen. Past experience doing this suggests that drying will take place within 3 hours. Second, we will atomize a solution diluted by a factor of 1/100, dry the droplets by diffusion, and collect the particles by impaction onto the glass capillary used for APCI so that the dried particles will be directly analyzed following atomization. Again, preliminary work not included in the original submission suggests that the products will be the same but that the signal will be low. We will be sure to collect enough material to verify that the drying process in the hood has only served to increase the sample size/signal and not to distort the products. Any differences will be described in the manuscript text.

Using long drying time (or rotary evaporation with low heat) to understand the effect of cloud processing is not unique to this work (Nguyen et al. 2012; Powelson et al., 2013; Aiona et al., 2017), though the concerns about its relevance are the reason that cloud chamber facilities are desirable (when available) as the role of surface chemistry is not entirely known and sure to affect the product distribution somewhat. We intend to conduct further studies using atomization onto APCI capillary probes, with internal standards, to look further into this issue in our next study.

2. “How would one derive quantitative kinetic information from this complex combined reaction/dehydration process, and how could it be justified as being similar to what actually happens in the atmosphere? “

In order to obtain kinetic information, the study would have to be performed with a more quantitative method for determining product concentrations which necessarily requires standards of these compounds so that ionization efficiency can be determined. Only 2,5-DMP is available as a standard – the other products would have to be purified and a response in APCI quantified. While deriving kinetics is beyond the scope of this work, we hope that future studies will target one or more of the pyrazine products here for quantitative kinetic analyses. It is possible to use GC-MS, but that requires

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extraction of these products into more volatile solvents (much like the food studies included in our references). An alternative method might involve the use of an internal standard, such as pyrazine, that was not observed in our samples but might have similar ionization efficiency to 2,5-DMP. We propose that one might easily do a kinetic study on the capped samples, but that the kinetics of evaporation are far more difficult to quantify.

3. “Leaving samples uncovered in the lab is known to lead to BrC formation in SOA samples due to contamination (e.g. the early preliminary data of Bones et al. JGR 2010). How can the authors eliminate the possibility that contamination contributed to the enhanced absorption in the dried and reconstituted samples?” This is a good point – we did conduct control experiments with only methylglyoxal that was not included in the original submission. We will do a similar study with AS. We will include those in the revised SI to illustrate the difference in browning between the mixtures and the control experiments. Indeed, we do see a small amount of contamination, but it represents only a fraction of the browning in the mixtures. We are adding this to the text of the manuscript as well.

4. “It seems unnecessary to specifically compare the effects of pH and evaporation (line 34 page 3) when mechanistically these processes are distinct and not in competition with each other in ambient cloud droplets. It’s relevant to quantify both processes, but I doubt a meaningful direct comparison can be made based on the data here.”

We agree that the pH and evaporation processes are not in competition with one another; our point was more that the evaporation process can produce material with the absorptivity (or substantially greater absorptivity) than the effect of high pH. In previous studies (Yu et al., 2011; Kampf et al., 2012), the authors have asserted that this Maillard-type chemistry has limited brown carbon potential due to the acidic nature of atmospheric water and the unfavorable rate of these reactions under acidic conditions compared to basic conditions. While true, we assert that the effect of evaporation in forming brown carbon chromophores is so strong as to produce material with more

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absorptivity in pH 2 dried samples than that observed at pH 9 (arguably the most favorable for nucleophilic attack by ammonia). When the role of evaporation is correctly accounted for, we proposed that these reactions can in fact contribute to atmospheric brown carbon in acidic cloud and aerosol water. We will edit the manuscript text to make this point clearer.

Specific comment regarding the use of “Maillard type” – we used parentheses to distinguish the use of ammonium sulfate from intact amino acids, as is standard for Maillard reactions in food studies. But, we have omitted the parentheses in the revised version.

References cited in this response:

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-63>, 2018.

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