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.

Major comments

- 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 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.
- 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.

Minor and technical comments

- Page 1, line 4: including in their complexity
- Page 2, line 22: Fu 2008 is not properly cited and does not show in the bibliography.
- Page 4, line 5: "TOC" appears for the first time here but is not properly introduced. Meanwhile, it is introduced later twice (Page 4, lines 16 and 19).
- Page 5, line 21: "with clear shoulders at 350". It appears to me that the capped samples also exhibit shoulders at 350 nm. It is more obvious from the log-log figure (Figure 1B). If the shoulder is not an important part of the discussion, I would suggest that the authors removed this part.
- Page 6 Line 12 (awkward sentence): "The masses observed in the pH 2 samples in Figure 2 compose most but not all of the products observed across all samples though the ratio of products is pH-dependent."
- Page 6 line 29: 2,5-dimethylpyrazine appears here for the first time, hence (2,5-DMP) should be defined here instead of line 30.
- Page 6, line 31: "m/z 162 is proposed as an imine-substituted dehydration product of m/z 181 formed as shown in Scheme 3." The authors refer to Scheme 3 here before Scheme 1 or 2. I would suggest a reorder of either the sentences or the schemes.

- Page 10, line 28: “Because the absorptivity metric accounts for OC concentration, we cannot simply attribute the higher absorptivity to higher a concentration of chromophores driven by the faster reaction rate under basic conditions.” This statement is puzzling. The TOC concentrations in the capped samples should remain relatively constant regardless of the initial pH. Even after normalization with TOC (equation 1), the higher absorptivity may still simply represent the faster formation of BrC in basic conditions. I think the current statement is correct only if the absorption were to be normalized against BrC concentration (which cannot be quantified).
- Although the evidence for PBC is strong, it seems that PBCs do not contribute to the strong light absorptivity at under more basic conditions. In Conclusion, the authors should briefly comment on the current “unknowns” for aqBrC. This should serve as a guidance for future research.

Reference

(1) Lee, A. K.; Zhao, R.; Li, R.; Liggio, J.; Li, S.-M.; Abbatt, J. P. Formation of Light Absorbing Organo-Nitrogen Species from Evaporation of Droplets Containing Glyoxal and Ammonium Sulfate. *Environ. Sci. Technol.* **2013**, *47* (22), 12819–12826.