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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Possible heterogeneous hydroxymethanesulfonate (HMS) chemistry in northern China winter haze and implications for rapid sulfate formation" *by* Shaojie Song et al.

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The authors provide an interesting and comprehensive analysis of the likely contributions of hydroxymethanesulfonate (HMS) to Beijing PM1. This is a nice example of combining fascinating but often forgotten atmospheric chemistry of hydroxyalkylsulfonates from the 1980s and 90s with modern aerosol mass spectrometry techniques. Through the use of HR-AMS, single particle aerosol mass spec, and model simulations, the authors make a compelling case that HMS likely contributes significantly to the sulfur content of Beijing PM1 during humid winter haze conditions.

There are a few points that the authors should consider to improve the manuscript:

1. bottom of p. 9: The authors suggest that a good positive correlation between OS and AWC suggests that aerosol water is key to enabling OS production. One needs to be careful of using correlations to infer causation. My guess is that many Beijing PM1 aerosol species are positively correlated with AWC, both because humid conditions tend to accompany haze events and because AWC depends explicitly on hygroscopic aerosol mass. Is the correlation of OS and AWC higher than for other species (e.g., NH4NO3)?

2. bottom of p. 11: The addition of the SPAMS data, although just for one event when available, greatly adds to the case that HMS is important in this environment. I am puzzled, however, by the observation that the HMS m/z 111 signature was observed in just 10% of particles. If AWC is the main ingredient needed, why isn't HMS contained in most of the particles? I suspect that most Beijing haze particles have substantial AWC in these events. Perhaps differences in pH across particles are important. The authors predict a single pH for PM1 assuming an internal mixture when the aerosol may really be externally mixed. Do the SPAMS data suggest that the HMS occurs in particles of a certain type (e.g., mineral dust particles) that might have a higher pH than other particle types? Are there HR-AMS P-TOF data that can inform us about the HMS size distribution?

3. If there are not aerosol pH-driven differences in HMS production that result in HMS being observed in just a small fraction of particles, perhaps cloud processing is important after all and the HMS was formed in subset of aerosol particles that underwent cloud processing elsewhere in the NCP before being transported to Beijing...?

4. middle of p. 11: It would be helpful if the authors explained and justified their use of a modified HCHO emissions inventory here (or in the Methods section earlier), rather than leaving that explanation to the last page of the manuscript.

5. It would be interesting to look at the competition of aqueous sulfate and HMS formation in Beijing AWC. Both formaldehyde and various oxidants are competing for

dissolved S(IV) in the wet aerosol particles. How do the relative rates of HMS and sulfate production change with aerosol pH and plausible concentrations of reactants and catalysts? The aerosol droplets are small enough and the SO2 likely abundant enough, that the S(IV) oxidation and HMS formation pathways can proceed in parallel, but their relative rates for typical Beijing winter haze conditions would be interesting to outline.

6. The authors do not mention the recent Moch et al. GRL publication, involving several of the same authors that contribute to this paper, that takes a different look at HMS contributions to Beijing PM1. This is likely just a timing issue with submission of the two manuscripts, but should be corrected in production of a revised manuscript.

7. It would be useful for the authors to comment somewhere in the manuscript on the fate of HMS formed in wet haze particles if the RH drops enough for the particles to dry out. Will the HMS still be retained in the dry aerosol?

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