

Reply to Referee 2

Notes: Referee comments are printed in italic, author replies in plain text. All page and line references refer to the original manuscript (not the revised version).

I read through the manuscript twice and I did not find major flaws that I could identify. I am delighted that a field-oriented group led by Hartmut Herrmann went looking for hydroxyalkylsulfonates in aerosols and determined their presence in about a 1/3 of the collected samples.

Author reply:

We're glad to read that the reviewer is pleased with our work. His/her comments will be addressed in the following.

The paper would be strengthened significantly if Herrmann and co-workers could address their observations in the context of the predictions that by Olson and Hoffmann (1989). In this paper, the authors made quantitative predictions based on the known equilibria, measured kinetics of formation for HMSA over the broad ranges of pH and species variation, the dehydration of the gem-diol form of formaldehyde, and detailed mass transport considerations that influence the rate of formation, and the overall stability of the reaction products. There is a delicate balancing of all these factors that may help to explain their field observation. This should be discussed more quantitatively in the paper.

Author reply:

We are very well aware of the landmark Olson and Hoffmann 1989 paper. Within the present study, emphasis was, however, on performing one of the first studies to quantify HMSA for central European particle samples. We have considered to apply the kinetic and thermodynamic parameters available to calculate HMSA concentrations depending on aerosol (a) LWC, (b) pH and gas phase concentrations of (c) HCHO and (d) SO₂. However, we have restricted our present study on reporting HMSA concentrations in aerosol particles for now as a formation calculation under the conditions of aerosol sampling with the above parameter set (a)-(d) might be un-related to the actually found HMSA levels, as HMSA is expected to form already during particle transport to the sampling site and also during cloud periods during that transport along a given trajectory.

We would like to note that many of the parameters determined and collected in the Olson and Hoffmann paper are used in our CAPRAM multiphase chemistry model and it surely is a worthwhile follow-up study to undertake a set of box-trajectory model calculations with CAPRAM to better understand the operative formation mechanisms of HMSA.

Herrmann and co-workers, in light of their results, remind us that there are other organic sulfur compounds in secondary aerosol samples in addition to those that form during photochemical transformations (in the troposphere and chamber studies). These alternative pathways seem to be consistently overlooked in studies of secondary aerosol formation and in various field campaigns. Northeast China including Beijing should be very fertile sampling grounds to explore this chemistry in field to a much greater extent.

Author reply:

We fully agree with the reviewer here and appreciate his/her idea to study HASA chemistry in China. We'll keep this in mind.

The Olson and Hoffmann predicts that HMSA should be formed at higher pH than those that are predicted by the authors and then stabilized at lower pH. This is due to the higher kinetic reactivity of the sulfite ion in the nucleophilic attack on the carbonyl carbon of small fraction of formaldehyde that is present in the carbonyl form. Thus, the formation may have taken place in clouds or fogs and when the cloud and fog dissipated, the resulting post-processing aerosol had a higher apparent acidity due to a much lower water activity.

Author reply:

This is a valid point, indeed. To account for this possibility, we inserted the following paragraph into the „Impact of pH“ section (P32636 L24):

„It has to be noted, that HMSA formation is much more effective at pHs higher than the ones estimated for the samples of this study. Olson and Hoffmann, 1989, predict the formation rate to strongly increase at pHs above approx. 4.5. It is thus plausible to assume that the formation of HMSA might have taken place at higher pH in cloud and fog water. Upon cloud/fog dissipation, HMSA will then be stabilized due to a much lower water content (i.e. higher apparent acidity) of the residual particles.”

In addition, the following paragraph has been added to section 3.1 (P32634 L14):

“...this observation might suggest that HMSA was formed during aging of particles, e.g. in pollution plumes, and/or in fog or cloud processing prior to the sampling time of the aerosol particles. In fact, from its abundance in single particles with diameter > 0.7 μm , HMSA has been suggested to represent a tracer for fog processing (Whiteaker and Prather, 2003; Healy et al., 2012).”