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Discussions

Interactive comment on “Hydroxymethanesulfonic acid in size-segregated aerosol particles at nine sites in Germany” *by* S. Scheinhardt et al.

Anonymous Referee #2

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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.

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.

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.

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 nuclephillic 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 32625, 2013.

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