Reply to Referee 1

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).

The manuscript presents extensive observations of HMSA in size-segregated particles for a range of different types of sites. Although HMSA can represent an important sulfur species, in particular as reservoir of S(IV), there exist only limited measurements. Thus, the work adds to the existing datasets, which is a valuable contribution. Generally, HMSA foramtion is expected to depend on formaldehyde and SO2 (and pH), so pollutant plumes are likely as HMSA sources. The results of this work indeed suggests that HMSA is formed during aging of pollution plumes, based on the correlation with oxalate and sulfate. Furthermore, weak pH dependence was observed, which also is reasonable. The experimental work is thorough and the presentation is clear. Due to the limited data available for HMSA, this work fits well for ACP. I recommend publication after the consideration of the following comments:

Author reply:

We thank the reviewer for his/her kind remarks on our manuscript. All issues raised by this reviewer are being addressed in the following.

My main comment is that the motivation for studying HMSA is presented as its role as S(IV) reservoir species. It would be useful to address this aspect: How important for the sulfur budget is this role as judged by the presented measurements or can this not be evaluated?

Author reply:

The reviewer poses an interesting question here. However, from the dataset of our study we don't think we can really address it. To judge on the role of HMSA for the sulfur budget, it would be crucial to know S(IV) concentrations in the particles as well. As these are not available, we unfortunately cannot evaluate this point.

Minor comments:

1. It would be helpful if the authors added a figure of the HMSA decomposition pathways to figure 1, or make a separate figure if this would make figure 1 too complicated. This will also help highlight the relationship to atmospheric sulfur chemistry, mentioned in the abstract.

Author reply:

The reactions given in Figure 1 are all equilibrium reactions (as indicated in the Figure caption). Decomposition pathways are therefore just the same as the formation pathways.

2. P. 32628 line 3-5 "understanding of atmospheric oxidation processes": This statement is too general. I recommend specifying what (aspects of) atmospheric oxidation processes.

Author reply:

We modified this sentence to: „understanding of S(IV) oxidation processes"

3. First and second paragraph of section 3.1: It would be very helpful to discuss the contribution to total PM for the mentioned measurements already here. I realize this is in section 3.3., but to me it makes more sense to add this in here, especially as section 3.3 is very brief.

Author reply:

In the revised version, we now discuss the relative contribution to PM directly after the absolute mass concentrations in section 3.1. Section 3.3. has been removed and the order of appearance of Figures 4 and 5 has been changed (including renaming the references in the text etc.). Also, we changed the section title to „Mass concentrations and contributions to PM".

4. P. 32635, line 13: "liquid phase" Do the authors mean aqueous? I am not sure this is necessarily synonymous, although aqueous particles or cloud droplets are certainly liquid.

Author reply:

We fully agree with the reviewer and corrected „liquid" to „aqueous" here and anywhere else in the manuscript.

5. Section 3.3: What is the uncertainty of the numbers given and is the difference (2.21 vs 1.79) statistically significant?

Author reply:

The uncertainty (in terms of standard deviation of the mean value) is 1.08 and 0.08 for urban and rural sites, respectively. We added these data and modified this paragraph as follows:

„We found HMSA to be enriched by a factor of 1.23 in urban samples (2.21 ± 1.08‰ vs. 1.79 ± 0.80‰, Figure 4a). Even though this is not a statistically significant difference, it is consistent with the precursors of HMSA originating from anthropogenic emissions."

6. Section 3.4: Does this mean that larger particles have higher pH? The question is whether multiple properties are correlated.

Author reply:

We're not sure we can follow the reviewer here. Coarse particles can usually be expected to have a somewhat higher pH due to the presence of sea salt and/or crust material. In section 3.4, however, there is no size-resolved information discussed (Fig. 6 presents PM10 data).

We're afraid we're also unable to comment on the question of „multiple properties" being correlated, as we don't see where the reviewer is aiming at here.