

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 formation 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 ($2.21 \pm 1.08\%$ vs. $1.79 \pm 0.80\%$, 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.

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).“

1 **Hydroxymethanesulfonic acid in size-segregated aerosol particles at**
2 **nine sites in Germany**

3
4 Sebastian Scheinhardt, Dominik van Pinxteren, Konrad Müller, Gerald Spindler, Hartmut
5 Herrmann*

6 Leibniz-Institut für Troposphärenforschung (TROPOS),
7 Permoserstraße 15, 04318 Leipzig, Germany

8
9 scheinhardt@tropos.de, dominik@tropos.de, konrad@tropos.de, spindler@tropos.de,
10 herrmann@tropos.de

11
12 Keywords: hydroxymethanesulfonic acid, HMSA, size-segregated particles, Berner impactor,
13 Germany

14
15
16
17
18
19
20
21
22
23
24
25 | [Revised version](#) submitted to
26 Atmospheric Chemistry and Physics
27 | [November-March](#) 2013
28

29
30
31

*Corresponding author, Phone: +49 341 2717 7024; Fax: +49 2717 99 7024
32 E-mail address: herrmann@tropos.de (H. Herrmann)

1 **Abstract**

2 In the course of two field campaigns, size-segregated particle samples were collected at nine sites in
3 Germany, including traffic, urban, rural, marine, and mountain sites. During the chemical
4 characterisation of the samples some of them were found to contain an unknown substance that was
5 later on identified as hydroxymethanesulfonic acid (HMSA). HMSA is known to be formed during the
6 reaction of S(IV) (HSO_3^- or SO_3^{2-}) with formaldehyde in the aqueous phase. Due to its stability, HMSA
7 ~~may~~ can act as a reservoir species for S(IV) in the atmosphere and is therefore of interest for the
8 understanding of atmospheric sulphur chemistry. However, no HMSA data are available for
9 atmospheric particles from Central Europe and even on a worldwide scale, data are scarce. Thus, the
10 present study now provides a representative dataset with detailed information on HMSA
11 concentrations in size-segregated Central European aerosol particles. HMSA mass concentrations in
12 this dataset were highly variable: HMSA was found in 224 out of 738 samples (30%), sometimes in
13 high mass concentrations exceeding those of oxalic acid. In average over all 154 impactor runs,
14 31.5 ng/m^3 HMSA were found in PM_{10} , contributing 0.21% to the total mass. The results show that
15 the particle diameter, the sampling location, the sampling season and the air mass origin impact the
16 HMSA mass concentration. Highest concentrations were found in the particle fraction $0.42 - 1.2 \mu\text{m}$,
17 at urban sites, in winter and with eastern (continental) air masses, respectively. The results suggest
18 that HMSA is formed during aging of pollution plumes. A positive correlation of HMSA with sulphate,
19 oxalate and PM is found ($R^2 > 0.4$). The results furthermore suggest that the fraction of HMSA in PM
20 slightly decreases with increasing pH.

21

22 **Abbreviations**

23	HMSA	hydroxymethanesulfonic acid
24	HASA	hydroxyalkanesulfonic acid
25	Su	summer
26	Wi	winter
27	W	west
28	N	north
29	E	east
30	ME	Melpitz
31	DD	Dresden
32	OB	Oberbärenburg
33	AU	Augsburg
34	LT	Leipzig-TROPOS
35	LE	Leipzig-Eisenbahnstraße
36	HP	Hohenpeißenberg
37	SI	Schauinsland
38	BÖ	Bösel

1 1. Introduction

2 In the course of two field campaigns (REGKLAM and GUAN, cf. Scheinhardt et al., 2013a, and
3 Birmili et al., 2009), numerous size-segregated particle samples were collected at nine sites in
4 Germany. During the chemical characterisation of the samples a fraction of the samples were found
5 to contain hydroxymethanesulfonic acid (HMSA, HO-CH₂-SO₃H).

6 HMSA and other hydroxyalkanesulfonic acids (HASA; HO-CHR-SO₃H with R = -(CH₂)_nH) were
7 suggested to be involved in atmospheric sulphur chemistry, notably regarding sulphate formation.
8 Sulphate is one of the main constituents of atmospheric aerosol particles. It is mainly formed from
9 the oxidation of S(IV) by H₂O₂ in the atmospheric ~~liquid-aqueous~~ phase and especially in cloud
10 droplets. Dissolved S(IV) originates from gaseous SO₂, which, in Central Europe, is mainly emitted by
11 human activities, e.g. coal burning. SO₂ dissolution is described by a Henry's law equilibrium,
12 followed by the formation of hydrogen sulphite (HSO₃⁻) or sulphite (SO₃²⁻). However, in various field
13 studies, it has been observed that S(IV) concentrations in the atmospheric aqueous ~~liquid~~-phase were
14 often higher than expected from Henry's law (Richards et al., 1983; Munger et al., 1984). Rapidly, the
15 reaction of dissolved SO₂/HSO₃⁻/SO₃²⁻ with dissolved aldehydes, yielding hydroxyalkanesulfonic acids,
16 was identified as an explanation for this observation (Munger et al., 1984). Hydroxymethanesulfonic
17 acid turned out to be the most important HASA since formaldehyde, its organic precursor, is the
18 most common aldehyde in the atmospheric aqueous ~~liquid~~-phase (Olson and Hoffmann, 1989;
19 Takeuchi et al., 2001).

20 An overview of the HMSA formation mechanism is given in Figure 1. HMSA formation is most
21 rapid at pH > 5, but HMSA decomposition as well is enhanced at higher pH. The highest stability is
22 thus observed at acidic pH (Sorensen and Andersen, 1970; Munger et al., 1986). HMSA is comparably
23 stable and not readily oxidised (Hoigné et al., 1985; Martin et al., 1989; Ojo et al., 2004). It therefore
24 accumulates in the atmosphere and can be found in high concentrations. Katagiri et al. (1996) found
25 hydroxymethanesulfonate to be the third most important anion in dew samples collected in Japan. It
26 has been suggested that the high HMSA concentrations may act as a reservoir species for
27 atmospheric S(IV) (Richards et al., 1983; Munger et al., 1984 and 1986; Voisin et al., 2000) and might
28 thus impact S(IV) oxidation kinetics (McArdle and Hoffmann, 1983) by shielding S(IV) from the direct
29 oxidation by non-radical oxidants such as H₂O₂.

30 The HMSA dataset obtained here was evaluated because HMSA, on the one hand, is of great
31 interest for the understanding of atmospheric-S(IV) oxidation processes but, on the other hand, has
32 only rarely been quantified in atmospheric particles (Suzuki et al., 2001). The aim of the present
33 study is thus to investigate HMSA concentrations in size-segregated atmospheric aerosol particles at
34 selected sites in Central Europe in order to identify the main factors determining HMSA mass

1 concentrations. To this end, the influences of particle diameter, sampling location, sampling season
2 and air mass origin are studied.

3

4 **2. Material and Methods**

5 2.1 Particle sampling

6 Size-segregated aerosol particle samples were collected in two field campaigns in Germany in
7 2009 and 2010 as described by Scheinhardt et al. (2013b). Sampling was performed on ring-like
8 aluminium foils using five stage Berner impactors. Inside the impactors, particles are separated
9 depending on their aerodynamic diameter, the 50% cut-offs being 0.05 – 0.14 – 0.42 – 1.2 – 3.5 –
10 10 µm for impactor stages 1–5, respectively. Sampling was performed at nine sites in Germany
11 (Figure 2, cf. Birmili et al., 2009):

12 (1) Leipzig-Eisenbahnstraße (LE; 51.34°N, 12.37°E, 119 m a.s.l.) is a traffic site located about half-way
13 between Leipzig city centre and Leipzig-TROPOS (LT) in a street canyon arranged in west-east
14 direction. The air inlet is installed about 6 m above the ground level at the northern side of the
15 canyon.

16 (2) Leipzig-TROPOS (LT; 51.35°N, 12.43°E, 125 m a.s.l.) is an urban site located at the roof of TROPOS
17 building, 4 km northeast of the city centre of Leipzig (530,000 residents). The air inlet is installed
18 16 m above the ground level. The site is not directly affected by local particle sources like traffic.

19 (3) Dresden-Winckelmannstraße (DD; 51.04°N, 13.73°E, 112 m a.s.l.) is an urban site in the city of
20 Dresden (530,000 residents). The site is not directly affected by local particle sources like traffic.

21 (4) Augsburg (AU; 48.36°N, 10.91°E, 484 m a.s.l.) is an urban site located about 1 km south-east of
22 the city centre of Augsburg (270,000 residents). There are no local particle sources nearby.

23 (5) Melpitz (ME; 51.54°N, 12.93°E, 86 m a.s.l.) is a well characterised rural site in the German
24 lowlands (Spindler et al., 2010, 2012, 2013). It is surrounded by meadows.

25 (6) Oberbärenburg (OB; 50.78°N, 13.72°E, 735 m a.s.l.) is a rural site 30 km south of Dresden. It is
26 located in a low mountain range and is surrounded by forests.

27 (7) Bösel (BÖ; 53.00°N, 7.96°E, 16 m a.s.l.) is a rural site located 30 km southwest of Oldenburg
28 (160,000 residents), 80 km south of the North sea coast.

29 (8) Schauinsland (SI; 47.91°N, 7.91°E, 1205 m a.s.l.) is a rural site located on the mountain with the
30 same name, around 10 km southeast of Freiburg im Breisgau (220,000 residents), in the black
31 forest.

32 (9) Hohenpeißenberg (HP; 47.80°N, 11.00°E, 988 m a.s.l.) is a rural site located 50 km south of
33 Munich on top of a hill that rises about 300 m above the surrounding landscape.

1 Sampling was started whenever the weather forecast predicted favourable meteorological
2 conditions (i.e. no precipitation and a constant air mass origin throughout the sampling day). The
3 sampling period was 24 hours, corresponding to a sampled air volume of 108 m³.

4 Prior to use, the aluminium foils were pre-heated at 300 °C for at least two hours in order to
5 remove organic traces. After sampling, the foils were stored at -21 °C until analysis.

6 7 2.2 Classification of sampling days

8 Out of the complete dataset, only sampling days with unambiguous air mass origins were
9 selected and chemically analysed. This was the case for 30 sampling days, corresponding to 156
10 impactor runs or 738 Berner impactor foils. Depending on the season and the air mass origin during
11 sampling, sampling days were classified into six categories: Winter West (WiW), Winter North (WiN),
12 Winter East (WiE), Summer West (SuW), Summer North (SuN), and Summer East (SuE). This empirical
13 categorisation has proven to be successful in former studies in Central Europe (Spindler et al., 2010,
14 2012, 2013) and considers differences in PM mass concentrations and compositions under different
15 meteorological conditions. Summer included sampling days between May and October and winter
16 included days between November and April. The air mass origin was determined using 96-hours-
17 backward trajectories from the NOAA HYSPLIT transport model (Hybrid Single Particle Lagrangian
18 Integrated Trajectory Model; Draxler and Hess, 1998; <http://ready.arl.noaa.gov/HYSPLIT.php>).
19 Backward trajectories were calculated for each sampling day and each sampling site at 10:00 CET and
20 18:00 CET for arrival heights of 200, 500 and 1,000 m above the ground level. An overview of the
21 sampling events is given in the Supplementary Material.

22 23 2.3 Weighing and chemical analysis

24 The determination of the collected particle mass was done gravimetrically using a
25 microbalance (UMT-2, Mettler-Toledo, Switzerland) after at least 48 hours of equilibration at
26 (20±1) °C and a relative humidity of (50±5)%. After weighing, the foils were cut with ceramic scissors
27 and chemically analysed.

28 Chemical analysis was performed after extraction of an aliquot of an aluminium foil in 2 ml of
29 deionised water (> 18 MΩ·cm) following a standard protocol (10 min shaking, 10 min ultrasonic
30 treatment, 10 min shaking). After extraction, the solution was filtered using syringe filters with a pore
31 size of 0.45 µm.

32 Main inorganic ions (chloride, nitrate, sulphate) were determined from the aqueous extracts
33 using ion chromatography with conductivity detection (ICS3000, Dionex). Cations were separated
34 applying a methylsulfonic acid eluent and a CS16 (3 mm) column, anions were separated applying a

1 KOH eluent in a AS18 (2 mm) column. Calibration was done daily, using a four point standard (Fluka,
2 Switzerland).

3 HMSA and oxalate were determined from the aqueous extracts using a capillary
4 electrophoresis method described by Kramberger-Kaplan (2003) and Scheinhardt et al. (2013b).
5 Shortly, a background electrolyte consisting of 2 mM 5-sulfosalicylic acid, 8 mM
6 tris(hydroxymethyl)aminomethane and 0.001% hexadimethrine bromide at a pH of 8.2 was used in
7 an Agilent 7100 capillary electrophoresis system. An uncoated fused-silica capillary with an inner
8 diameter of 75 μm and a total length of 80.5 cm (72 cm to the detector) was used. The capillary was
9 maintained at 20 °C. Separation of HMSA from other compounds was reached within 13 min,
10 applying a voltage of -30 kV (corresponding to a current of about -5 μA) following hydrodynamic
11 sample injection with 750 mbar-s (corresponding to 1% of the capillary length). Indirect UV detection
12 with a measurement wavelength of 260 nm (bandwidth: 20 nm), a reference wavelength of 208 nm
13 (bandwidth: 36 nm) and a time resolution of 20 Hz was used for quantification. Migration times and
14 peak areas were very well reproducible (n = 10, RSD 0.08% and 2.16%, respectively). No significant
15 blank values were found. The HMSA detection limit (LOD; three times the standard deviation of the
16 background signal) was 1.15 μM (127 ppb) and the quantification limit (LOQ; LOQ = 3 LOD) was
17 3.44 μM (382 ppb).

18 HMSA concentrations above the LOD were found in 224 of 738 samples. From these 224
19 samples, 157 had HMSA concentrations between the LOD and the LOQ. Even though concentrations
20 in this range are less reliable, they were still considered in this study, since the concentrations
21 uncertainties associated with such concentrations are regarded less problematic than setting all
22 those HMSA concentrations to zero. Thus, in the present study, all HMSA concentrations above the
23 LOD are reported. In atmospheric units, the LOD corresponds to mass concentrations of about 6-
24 7 ng/m^3 (depending on the impactor stage and the extraction protocol). Values below the LOD were,
25 however, taken as zero. The HMSA quantification method in this study has a slightly better LOD than
26 the method applied by Suzuki et al. (2001), who for the first time investigated particulate HMSA by
27 ^1H NMR.

28 The amount of organic and elemental carbon (OC/EC) was quantified using a thermographic
29 method (C-mat 5500, Ströhlein, Germany) following VDI guideline 2465, Part 2 with minor
30 modifications. In the first step, an aliquot of an aluminium foil was heated to 650 °C in a nitrogen
31 atmosphere. Under these conditions, organic compounds evaporated and were flushed towards a
32 CuO catalyst. There they were oxidised, forming CO_2 that was subsequently quantified with a NDIR
33 detector (OC). In the next step, after cooling to at least 75 °C, the foil was again heated to 650 °C in
34 an oxygen atmosphere oxidising EC, which was quantified as CO_2 , too. Compared to other methods,
35 this method tends to overestimate EC and to underestimate OC (Schmid et al., 2001). However, due

1 to the melting point of aluminium (660 °C), the method is limited to a temperature of 650 °C, and
2 thermo-optical methods applying the EUSAAR-2, NIOSH or IMPROVE protocols cannot be applied. For
3 details see Spindler et al. (2012).

5 2.4 Particle ~~aqueous liquid~~-phase pH

6 The charge balance in our particle samples, considering main inorganic ions (NH_4^+ , Na^+ , K^+ ,
7 Ca^{2+} , Mg^{2+} , SO_4^{2-} , NO_3^- , Cl^-) and organic ions (oxalate, malonate, tartronate, succinate, malate and
8 hydroxymethanesulfonate), was generally equalised and varied only within analytical errors.
9 Contrary to recent studies from China (Cheng et al., 2011; Zhou et al., 2012), charge balances could
10 thus not be applied to calculate particle ~~aqueous liquid~~-phase pH in this study. They were instead
11 determined applying measurements of the aqueous extracts' pH and a model that was able to
12 calculate the particle liquid water content. The particle ~~aqueous liquid~~-phase pH was then calculated
13 back from the pH of the aqueous extracts, assuming its dilution due to the extraction protocol
14 mentioned above. A comparable approach was applied by Li et al. (1997) and Keene and Savoie
15 (1998).

16 The pH of the aqueous extracts was determined using a micro pH electrode (PHR 146S
17 microelectrode, Lazar Research Laboratories, Los Angeles, USA). The particle water content was
18 calculated using the E-AIM model (Wexler and Clegg, 2002; www.aim.env.uea.ac.uk), which has been
19 shown to show good agreement with measured data (Engelhart et al., 2011). In former studies, E-
20 AIM Model III was found to be the most suitable E-AIM type for our samples (Scheinhardt et al.,
21 2013b). The average relative humidity during the measurement and the mass concentrations of the
22 main constituents (NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , and Cl^-) are the model input parameters. The mass
23 concentrations of H^+ and OH^- were adjusted to assure the particles' charge neutrality. The formation
24 of insoluble solids was enabled in the calculation. The model output provided the water content.

26 **3. Results and Discussion**

27 3.1 Absolute mMass concentrations and contributions to PM

28 The HMSA mass concentrations determined in atmospheric samples were highly variable
29 within the set of 224 samples with HMSA above the detection limit (out of a total of 738 samples, cf.
30 supplementary material). The highest observed value of 625 ng/m³ was determined in a sample from
31 Augsburg on December 16, 2009 under Winter-East conditions on impactor stage 2. Since this value
32 was disproportionally high (more than 2.5 times higher than the second largest value), it was
33 identified as an outlier, most likely due to a local pollution episode at that site (analytical errors were
34 excluded by means of repetition experiments). It was therefore regarded as being not representative

1 and is thus not considered in the following discussions. Concentrations below detection limit were
2 set zero for all calculations.

3 The dataset was investigated regarding the influence of sampling location, particle diameter
4 and the meteorological conditions on HMSA mass concentrations (Figure 3). Although some
5 exceptions exist, urban sites generally exhibited higher HMSA mass concentrations than rural sites
6 (Figure 3a; average of the urban sites: 37.9 ng/m³, average of the rural sites: 23.8 ng/m³). Moreover,
7 rural lowland sites show higher HMSA mass concentrations than mountain sites. Generally, HMSA
8 mass concentrations in Central Europe seem to be slightly higher than those in Japan (14.7 ng/m³ in
9 urban aerosols, 1998 – 1999; Suzuki et al., 2001). To judge on the relative contribution of HMSA to
10 total PM, the fraction of HMSA in PM was calculated and compared for different sample types
11 (Figure 4). We found HMSA to be enriched by a factor of 1.23 in urban samples (2.21 ± 1.08‰ vs.
12 1.79 ± 0.80‰, Figure 4a). Even though this is not a statistically significant difference, it is consistent
13 with the precursors of HMSA originating from anthropogenic emissions.

14 Regarding the impact of the particle diameter, a strong dependency was observed, the
15 highest HMSA mass concentrations being found on impactor stage 3 (Figure 3b). A similar size
16 distribution was found by Suzuki et al. (2001). Since particles of that size have the longest
17 atmospheric lifetime and can therefore be transported over long distances, this observation might
18 suggest that HMSA was formed during aging of particles, e.g. in pollution plumes, and/or in fog or
19 cloud processing prior to the sampling time of the aerosol particles. In fact, from its abundance in
20 single particles with diameter > 0.7 µm and its coincidence with periods of fog or high relative
21 humidity, HMSA has been suggested to represent a tracer for fog processing (Whiteaker and Prather,
22 2003; Healy et al., 2012). In contrast to impactor stage 3, short-lived particles (stages 1 and 5) contain
23 only small amounts of HMSA. The relative contribution to PM is also largest on stages 2 and 3 (Figure
24 4b). However, this might be due to the low absolute amounts of HMSA on the other stages, which
25 makes the calculation of the HMSA/PM fraction on those stages susceptible to errors.

26 Regarding the air mass origin, highest HMSA concentrations in total PM₁₀ (sum of impactor
27 stages 1–5) were observed for eastern (continental) air mass origins (Figure 3c; West: 23.9 ng/m³,
28 North: 7.7 ng/m³, East: 51.0 ng/m³). This reflects the high HMSA precursor concentrations (VOCs,
29 SO₂) in continental air masses and shows that the high anthropogenic SO₂ emissions in Eastern
30 Europe not only promote the formation of main inorganic PM constituents such as sulphate, but
31 might also enhance the formation of organic trace compounds such as HMSA. It can be presumed
32 that similar conclusions could be drawn from the analysis of other sulphur-containing organic
33 compounds, too. From the fraction of HMSA in PM₁₀ it again appears that HMSA is enriched in some
34 samples (Figure 4c).

1 In summer, HMSA mass concentrations were lower than in winter (Figure 3c; Summer:
2 23.9 ng/m³, Winter: 31.2 ng/m³), most likely again due to stronger anthropogenic emissions of HMSA
3 precursors, e.g. from individual heating systems.

4 It should be noted that, besides emissions, the meteorological conditions in winter and
5 during eastern air mass origin (i.e. low mixing layer height, low temperatures, decreased turbulence,
6 few precipitation) generally favour high PM loads, too. Clearly, this applies for HMSA as well as for all
7 the other PM constituents and might partly explain the HMSA concentration differences observed
8 between the seasons and air mass origins.

9 10 3.2 Correlations with other parameters

11 In the previous section, absolute HMSA mass concentrations were found to show
12 dependencies generally resembling the behaviour of total PM (i.e. highest concentrations on
13 impactor stage 3, at urban sites, in winter and with eastern air mass origins, respectively; cf. Spindler
14 et al., 2010 and 2012; Scheinhardt et al., 2013a). This is to some extent confirmed by correlating
15 HMSA mass concentration and the total PM mass concentration (Figure 4Figure 5a).

16 The correlation of HMSA with sulphate (Figure 4Figure 5b) is comparably strong, confirming
17 that both HMSA and sulphate are formed from the same precursor (SO₂) and under comparable
18 conditions (secondary formation in the atmospheric aqueous phase). Oxalate, which is
19 photochemically formed from higher organic compounds, also correlates with HMSA (Figure 4Figure
20 5c). This also might be interpreted in a way that both substances are formed under comparable
21 conditions (secondary formation in the atmospheric ~~liquid~~ aqueous phase via photochemical
22 multiphase oxidation processes occurring in pollution plumes), even though both substances have
23 different precursors.

24 Oxalate is one of the main contributors to the sum parameter OC, but the correlation of
25 HMSA with OC is weak (Figure 4Figure 5d). This is probably due to the various sources of the
26 different OC components, including, for example, direct emissions. Traffic emissions, which are
27 characterised by high EC (diesel soot) contents, seem to affect HMSA concentrations only to a minor
28 extent (Figure 4Figure 5e). The same is true for potassium, a tracer for biomass burning (Figure
29 4Figure 5f). The combination of Figures 4b-4f suggests that HMSA is formed in sulphur-rich aged air
30 masses. Future discussions of HMSA formation should include direct SO₂ and formaldehyde
31 measurements to identify possible impacts on HMSA concentrations in more detail.

32 33 3.3 HMSA relative to PM

34 In Figure 4a, HMSA mass concentrations were found to be somewhat related to the total PM
35 mass concentration. However, the relationship was not totally linear, so there might be other

1 parameters affecting HMSA concentrations. Therefore, the fraction of HMSA in PM was calculated
2 and compared for different sample types (Figure 5). We found HMSA to be enriched by a factor of
3 1.23 in urban samples (2.21% vs. 1.79%, Figure 5a). Regarding the particle diameter, the fraction is
4 largest on stages 2 and 3 (Figure 5b). However, this might be due to the low absolute amounts of
5 HMSA on the other stages, which makes the calculation of the HMSA/PM fraction on those stages
6 susceptible to errors. Regarding the impact of the meteorological category, it again appears that
7 HMSA is enriched in some samples (Figure 5c). This means that high HMSA values cannot only be
8 explained by high PM values.

10 3.34 Impact of pH

11 Since the formation and degradation kinetics of HMSA is pH-dependent, the impact of the
12 particle aqueous liquid-phase pH on HMSA mass concentrations was investigated. In our study,
13 particle aqueous phase pH was found to vary between about 0.5 and 2.5. These values are somewhat
14 higher than those found in Los Angeles' particles (-2.4 – 0.2; Li et al., 1997) and lower than pH in
15 marine particles (2.48 – 3.48; Keene and Savoie, 1998). The impact of pH on absolute HMSA mass
16 concentrations is weak (Figure 6a; R^2 and slope close to zero). Interestingly, the fraction of HMSA in
17 PM shows a small dependency and decreases with increasing pH. Although the scatter is large, this is
18 in qualitative agreement with the decreasing stability of HMSA at increasing pH. In our samples, an
19 empiric relationship of $f \approx -0.16 \cdot \text{pH} + 0.72$ was found between pH 0 and 4, with f being the
20 percentage of HMSA in PM_{10} . It has to be noted, that HMSA formation is much more effective at pHs
21 higher than the ones estimated for the samples of this study. Olson and Hoffmann, 1989, predict the
22 formation rate to strongly increase at pHs above approx. 4.5. It is thus plausible to assume that the
23 formation of HMSA might have taken place at higher pH in cloud and fog water. Upon cloud/fog
24 dissipation, HMSA will then be stabilized due to a much lower water content (i.e. higher apparent
25 acidity) of the residual particles.

27 **4. Summary**

28 The present study presents data from a unique dataset regarding HMSA concentrations in size-
29 segregated ambient aerosol particles. HMSA mass concentrations were found to be highly variable.
30 Highest concentrations were found in urban environments during winter and eastern advection on
31 Berner impactor stage 3 ($D_p = 0.42\text{-}1.2 \mu\text{m}$). The fraction of HMSA in PM generally showed similar
32 trends. HMSA concentrations correlated with sulphate ($R^2 = 0.53$), Oxalate ($R^2 = 0.46$) and PM ($R^2 =$
33 0.42) mass concentrations. Correlations with EC ($R^2 = 0.37$), OC ($R^2 = 0.23$) and potassium ($R^2 =$
34 $0.23/0.06$) were also observed, but to a lesser extent. The fraction of HMSA in PM seems to be
35 slightly influenced by pH, eventually possibly due to its pH-dependent stability. Overall, the results

1 are consistent with well-known aqueous phase formation of HMSA in polluted air masses from
2 anthropogenic precursors SO₂ and formaldehyde.

3

4 **Acknowledgements**

5 This study has been supported by the German Federal Ministry of Education and Research under
6 grant no. 01LR0802 (REGKLAM) and by the German Federal Environment Ministry under grant no.
7 F&E 370343200 (GUAN). We thank all our project partners in GUAN and REGKLAM. We would also
8 like to thank our technical staff: A. Dietze, S. Fuchs, A. Grüner, R. Rabe and A. Thomas as well as two
9 undergraduate students: A. Rau (Universität Leipzig) and E. Charlesworth (Seattle University), for
10 whom DAAD RISE support is gratefully acknowledged. [Input of two anonymous reviewers to our](#)
11 [manuscript is much appreciated as well.](#)

12

13

14 **References**

15 Birmili, W., Weinhold, K., Nordmann, S., Wiedensohler, A., Spindler, G., Müller, K., Herrmann, H.,
16 Gnauk, T., Pitz, M., Cyrys, J., Flentje, H., Nickel, C., Kuhlbusch, T.A.J., Löschau, G., Haase, D.,
17 Meinhardt, F., Schwerin, A., Ries, L., Wirtz, K.: Atmospheric aerosol measurements in the German
18 Ultrafine Aerosol Network (GUAN), *Gefahrstoffe - Reinhaltung der Luft*, 69(4), 137-145, 2009.

19

20 Cheng, S.H., Yang, L.X., Zhou, X.H., Xue, L.K., Gao, X.M., Zhou, Y., Wang, W.X.: Size-fractionated
21 water-soluble ions, situ pH and water content in aerosol on hazy days and the influences on
22 visibility impairment in Jinan, China, *Atmos. Environ.*, 45, 4631-4640, 2011.

23

24 Draxler, R.R., Hess, G.D.: An overview of the HYSPLIT_4 modelling system for trajectories, dispersion
25 and deposition, *Austr. Met. Mag.*, 47, 295-308, 1998.

26

27 Engelhart, G.J., Hildebrandt, L., Kostenidou, E., Mihalopoulos, N., Donahue, N.M., Pandis, S.N.: Water
28 content of aged aerosol, *Atmos. Chem. Phys.* 11, 911-920, 2011.

29

30 [Healy, R. M., Sciare, J., Poulain, L., Kamili, K., Merkel, M., Müller, T., Wiedensohler, A., Eckhardt, S.,](#)
31 [Stohl, A., Sarda-Estève, R., McGillicuddy, E., O'Connor, I. P., Sodeau, J. R., and Wenger, J. C.:](#)
32 [Sources and mixing state of size-resolved elemental carbon particles in a European megacity:](#)
33 [Paris, *Atmos. Chem. Phys.*, 12, 1681-1700, 2012.](#)

34

1 Hoigné, J., Bader, H., Haag, W.R., Staehelin, J.: Rate constants of reactions of ozone with organic and
2 inorganic compounds in water – III Inorganic compounds and radicals, *Water Res.*, 19, 993-1004,
3 1985.
4
5 Katagiri, Y., Sawaki, N., Arai, Y., Okochi, H., Igawa, M.: Enhanced dissolution of SO₂ into dewwater by
6 forming hydroxyalkanesulfonate, *Chem. Lett.*, 197-198, 1996.
7
8 Keene, W.C., Savoie, D.L.: The pH of deliquesced sea-salt aerosol in polluted marine air, *Geophys.*
9 *Res. Lett.*, 25, 2181-2184, 1998.
10
11 Kramberger-Kaplan, H.V.: Carbonsäuren und Dicarbonsäuren in atmosphärischen
12 Mehrphasenprozessen, Ph.D. Thesis, Technische Universität Darmstadt, Germany, 2003.
13
14 Li, S.M., Macdonald, A.M., Strapp, J.W., Lee, Y.N., Zhou, X.L.: Chemical and physical characterizations
15 of atmospheric aerosols over southern California, *J. Geophys. Res. Atmos.*, 102(D17), 21.341-
16 21.353, 1997.
17
18 Martin, L.R., Easton, M.P., Foster, J.W., Hill, M.W.: Oxidation of hydroxymethanesulfonic acid by
19 Fenton's reagent, *Atmos. Environ.*, 23, 563-568, 1989.
20
21 McArdle, J.V., Hoffmann, M.R.: Kinetics and Mechanism of the Oxidation of aquated sulfur dioxide by
22 hydrogen peroxide at low pH, *J. Phys. Chem.*, 87, 5425-5429, 1983.
23
24 Munger, J.W., Jacob, D. J., Hoffmann, M. R.: The Occurrence of Bisulfite-Aldehyde Addition Products
25 in Fog- and Cloudwater, *J. Atmos. Chem.*, 1, 335-350, 1984.
26
27 Munger, J.W., Tiller, C., Hoffmann, M.R.: Identification of hydroxymethanesulfonate in fog water.
28 *Science*, 231, 247-249, 1986.
29
30 Olson, T.M., Hoffmann, M.R.: Hydroxyalkylsulfonate formation: its role as a S(IV) reservoir in
31 atmospheric water droplets, *Atmos. Environ.*, 23, 985-997, 1989.
32
33 Ojo, J.F., Otoikhian, A., Olojo, R., Simoyi, R.H.: Oxyhalogen-Sulfur chemistry: nonlinear oxidation
34 kinetics of hydroxymethanesulfonic acid by acidic iodate, *J. Phys. Chem. A*, 108, 2457-2463, 2004.
35

1 Richards, L.W., Anderson, J.A., Blumenthal, D.L., McDonald, J.A., Kok, G.L., Lazrus, A.L.: Hydrogen
2 peroxide and sulfur (IV) in Los Angeles cloud water, *Atmos. Environ.*, 17, 911-914, 1983.
3
4 Scheinhardt, S., Spindler, G., Leise, S., Müller, K., Iinuma, Y., Zimmermann, F., Matschullat, J.,
5 Herrmann, H.: Comprehensive chemical characterisation of size-segregated PM10 in Dresden and
6 estimation of changes due to global warming, *Atmos. Environ.*, 75, 365-373, 2013a.
7
8 Scheinhardt, S., Müller, K., Spindler, G., Herrmann, H.: Complexation of trace metals in size-
9 segregated aerosol particles at nine sites in Germany, *Atmos. Environ.*, 74, 102-109, 2013b.
10
11 Schmid, H., Laskus, L., Abraham, H.J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier,
12 H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H.M., Giesen, K.P., Hitzenberger, R., Hueglin,
13 C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.P., Toom-Sauntry, D., Puxbaum, H.: Results of the
14 "carbon conference" international aerosol carbon round robin test stage I, *Atmos. Environ.*, 35,
15 2111-2121, 2001.
16
17 Spindler, G., Brüggemann, E., Gnauk, T., Grüner, A., Müller, K., Herrmann, H.: A four-year size-
18 segregated characterization study of particles PM10, PM2.5 and PM1 depending on air mass
19 origin at Melpitz, *Atmos. Environ.*, 44(2), 164-173, 2010.
20
21 Spindler, G., Gnauk, T., Grüner, A., Iinuma, Y., Müller, K., Scheinhardt, S., Herrmann, H.: Size-
22 segregated characterization of PM10 at the EMEP site Melpitz (Germany) using a five-stage
23 impactor: a six year study, *J. Atmos. Chem.*, 69(2), 127-157, 2012.
24
25 Spindler, G., Grüner, A., Müller, K., Schlimper, S., Herrmann, H.: Long-term size-segregated particle
26 (PM₁₀, PM_{2.5}, PM₁) characterization study at Melpitz – influence of air mass inflow, weather
27 conditions and season, *J. Atmos. Chem.*, 70, 165-195, 2013.
28
29 Sorensen, P.E., Andersen, V.S.: The formaldehyde-hydrogen sulphite system in alkaline aqueous
30 solution. Kinetics, mechanisms, and equilibria, *Acta Chem. Scand.*, 24(4), 1301-1306, 1970.
31
32 Suzuki, Y., Kawakami, M., Akasaka, K.: 1H NMR application for characterising water-soluble organic
33 compounds in urban atmospheric particles, *Environ. Sci. Technol.*, 35, 3656–2664, 2001.
34

1 Takeuchi, M., Okochi, H., Jgawa, M.: Dominant factors of major and minor components and
2 formation of hydroxyalkanesulfonate in urban dew-water, Water Air Soil Poll., 130, 613-618,
3 2001.

4

5 Wexler, A.S., Clegg, S.L.: Atmospheric aerosol models for systems including the ions H^+ , NH_4^+ , Na^+ ,
6 SO_4^{2-} , NO_3^- , Cl^- , Br^- , and H_2O , J. Geophys. Res. Atmos., 107(D14), 4207, 2002.

7

8 [Whiteaker, J. R., and Prather, K. A.: Hydroxymethanesulfonate as a tracer for fog processing of
9 individual aerosol particles, Atmos. Environ., 37, 1033-1043, 2003.](#)

10

11 Voisin, D., Legrand, M., Chaumerliac, N.: Scavenging of acidic gases ($HCOOH$, CH_3COOH , HNO_3 , HCl ,
12 and SO_2) and ammonia in mixed liquid-solid water clouds at the Puy de Dôme mountain (France),
13 J. Geophys. Res., 105(D5), 6817-6835, 2000.

14

15 Zhou, Y., Xue, L.K., Wang, T., Gao, X.M., Wang, Z., Wang, X.F., Zhang, J.M., Zhang, Q.Z., Wang, W.X.:
16 Characterization of aerosol acidity at a high mountain site in central eastern China, Atmos.
17 Environ., 51, 11-20, 2012.

18

19

20

21

22

23

24

25

26

27

28

29 Figure Captions

30

31 Fig. 1: Formation pathways of HMSA (Munger et al., 1984; Olson and Hoffmann, 1989). All reactions
32 are equilibrium reactions. ~~Backward reactions were omitted for clarity.~~ The circle indicates an
33 atmospheric droplet.

34

35 Fig. 2: Sampling sites (cf. Scheinhardt et al., 2013b). See text for explanations.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26

Fig. 3: (a) HMSA mass concentrations in PM₁₀ (sum of impactor stages 1-5) as a function of the sampling site. (b) HMSA mass concentrations as a function of particle size. (c) HMSA mass concentrations in PM₁₀ (sum of impactor stages 1-5) as a function of the meteorological category. Boxes indicate the 25%, 50% and 75% quartiles, whiskers indicate the minimum and maximum values. ♦ indicates the respective mean value. The number of samples is given below each column. See text for discussion.

[Fig. 4: \(a\) Fraction of HMSA in PM₁₀ \(sum of impactor stages 1-5\) as a function of the sampling site. \(b\) Fraction of HMSA in PM as a function of the particle size. \(c\) Fraction of HMSA in PM₁₀ \(sum of impactor stages 1-5\) as a function of the meteorological category. The symbols and numbers of samples are consistent with Figure 3. See text for discussion.](#)

Fig. 45: Correlations of HMSA mass concentrations with (a) the respective PM mass concentration and (b-f) the mass concentrations of sulphate, oxalate, organic carbon, elemental carbon and potassium, respectively. In f), R² is given with and without the consideration of an outlier (0.96 µg m⁻¹ K⁺). The charts comprise the complete dataset (738 samples). See text for discussion.

~~Fig. 5: (a) Fraction of HMSA in PM₁₀ (sum of impactor stages 1-5) as a function of the sampling site. (b) Fraction of HMSA in PM as a function of the particle size. (c) Fraction of HMSA in PM₁₀ (sum of impactor stages 1-5) as a function of the meteorological category. The symbols and numbers of samples are consistent with Figure 3. See text for discussion.~~

Fig. 6: (a) HMSA mass concentrations and (b) fractions of HMSA in PM as functions of the particle liquid phase pH. The charts comprise only samples with HMSA concentration above the detection limit (224 samples). See text for discussion.











