

**Paper entitled “Challenges associated with the sampling and analysis of organosulfur compounds in air using real-time PTR-TOF-MS and off-line GC-FID”**

**Response to Referee #1**

We would like to sincerely thank Dr. Armin Hansel for his comments on the paper. Please find below our point-to-point responses to the referee’s minor comments and technical corrections as follows: Referee’s comments are presented in blue and our corresponding responses follow in black.

V. Perraud et al. describe analytical challenges associated with sampling and analysis of organosulfur compounds (OSC) in air using real-time PTR-ToF-MS and off-line GCFID methods. OSC are naturally emitted reactive compounds forming MSA and sulfuric acid vapors that are important precursor gases for new particle formation (NPF). This manuscript shows that both techniques produce accurate and quantitative results for DMS. Fragmentation of DMDS and DMTS occurs in the real-time PTR-ToF-MS instrument resulting in fragment ions containing sulfur, which were identified due to the high mass resolution of the PTR-ToF-MS. Off-line canister sampling coupled with GC-FID provides excellent sensitivity for DMS, DMDS and DMTS. MTO was observed to react on metal surfaces producing DMDS and when H<sub>2</sub>S is present even DMTS. This manuscript is very well written, the methodology is clearly presented and the topic is within the scope of AMT. The manuscript provides useful and new information for the atmospheric community dealing with OSC. I recommend this manuscript for publication in AMT, following consideration of my minor comments and technical corrections.

Abstract, page 2, line 6 “Their oxidation to methanesulfonic and sulfuric acids leads to the formation and growth of atmospheric particles, which are known to have negative effects on visibility, climate and human health.”

Explain the "negative" effects of sulfate particles on climate – more cooling?

=> We modified the text to read: *“Their oxidation to methanesulfonic and sulfuric acids leads to the formation and growth of atmospheric particles, which are known to influence clouds and climate, atmospheric chemical processes, visibility and human health.”*

Introduction, page 3, lines 21 ff “These newly formed particles then grow to sizes able to scatter sun light and impact clouds...”

According to Kulmala et al. (DOI: 10.1126/science.1227385) Science 2013 (Fig.4) new particles are not "automatically" growing to larger sizes necessary for light scattering. The availability of other vapors than sulfuric acid, amines/ammonia seems important. Please comment or revise your statement.

=> We agree with the referee, other atmospheric organic species, apart from sulfuric acid (or methanesulfonic acid) play a significant role in the growth of those freshly nucleated particles.

We revised the text to read (the addition is underlined): *“These newly formed particles can ultimately grow, by uptake of organic vapors, amines/ammonia and/or water, to sizes capable of scattering sun light and impacting clouds, thus influencing the Earth’s energy balance and climate (Finlayson-Pitts and Pitts, 2000; Kulmala and Kerminen, 2008; Hallquist et al., 2009; Zhang et al., 2012; Kulmala et al. 2013). In addition, atmospheric particles have been previously linked to negatively affect health and visibility (Dockery et al., 1993; Hinds, 1999; Pope III et al., 2002; Pope III and Dockery, 2006).”*

Materials and methods, page 5, line 17 “Because of the low energy ion source, the ionization process is generally considered “soft”..

This is not the reason of being soft in PTR-MS!

=> We agree with the referee and we removed this segment from the main text. The text now reads: *“Collisions of the  $H_3O^+$  ions with a volatile organic compound generally results in a proton transfer reaction if the compound has a proton affinity (PA) higher than that of water ( $PA(\text{water})=691 \text{ kJmol}^{-1}$ ). The chemical ionization process is generally considered “soft”, and in most cases generates a single parent ion at  $[M+H]^+$ .”*

Fig 1) Explain the high count rates of the grey peaks in Fig 1 d)

=> The high count rates of the grey peak in Figure 1d correspond to fragments observed from cyclohexane ( $m/z$  41, 43, 55, 69 and 83; PA  $686.9 \text{ kJ mol}^{-1}$ ), which was used as the solvent for the generation of DMTS using the dynamic liquid injection system. A sentence was added to the figure caption as follows (the addition is underlined): *“Figure 1. Individual PTR-ToF-MS mass spectra from each organosulfur compound: (a) methanethiol (MTO) from the laboratory generated gas phase standard, (b) dimethyl sulfide (DMS) and (c) dimethyl disulfide (DMDS) from injection of the individual pure liquid standards into air in a 100 L Teflon chamber, and (d) dimethyl trisulfide (DMTS) from the dynamic injection system. The peaks shown in grey correspond to background peaks. In (d), the grey peaks correspond to ion fragments resulting from the ionization of cyclohexane which was used here as the solvent.”*

Fig 3) What are the errors of expected mixing ratios? Include these errors also in Fig 3.

=> The error of the expected mixing ratios are mentioned in our original manuscript in the experimental section (section 2.3, page 8, line 15-17) as follows: *“The mixing ratios after dilution were estimated using error propagation analysis (Harris, 1991), with an estimated accuracy of  $\pm 10\%$  ( $2s$ ) for the DMS/DMDS gas cylinder, and  $\pm 20\%$  ( $2s$ ) for the mixtures from the dynamic injection system.”* A new sentence was added to Fig. 3 caption as follows: *“The error bars for the expected mixing ratios after dilution were estimated as  $\pm 10\%$  ( $2\sigma$ ) for the DMS/DMDS gas cylinder, and  $\pm 20\%$  ( $2\sigma$ ) for the mixtures from the dynamic injection system,*

*based on error propagation analysis*". In addition, the error bars on the expected mixing ratios were added to the figure.

Page 15, line 26 Please check the peak area ratio of MTO to DMDS. In Fig 6b this ratio does not look like 7.5!

=> We thank the referee for noticing this. We replaced Figure 6b with the correct chromatogram.

Fig. 8 What is the reason to draw a line between symbols of individual bins?

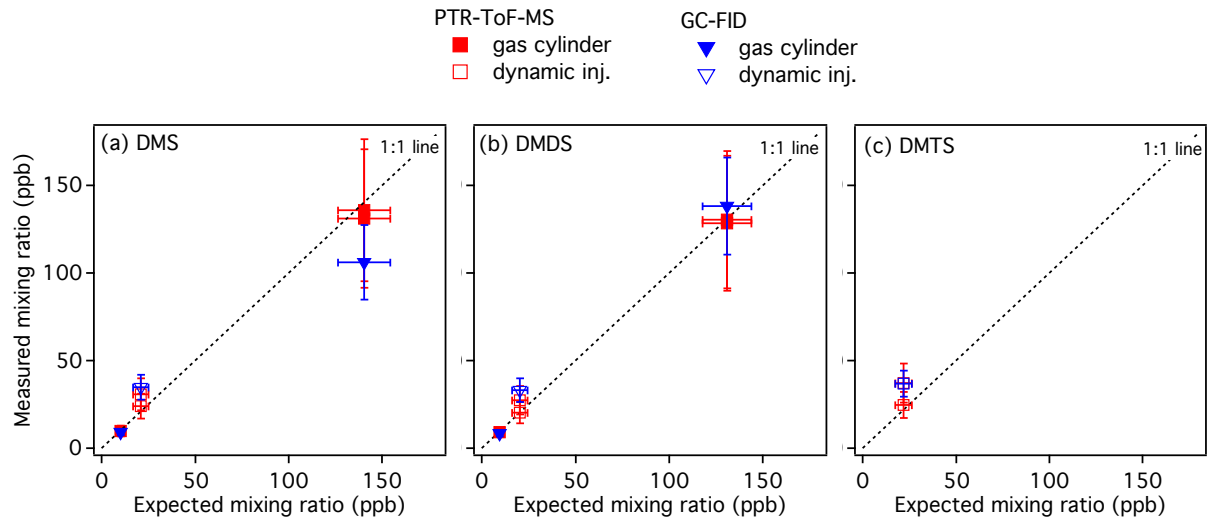
=> There is no significance for the line between the symbols of individual bins in Fig. 8. They were included to aid the visuals. The alternative would be to make a bar graph, but we think the data would be difficult to see when reduced in size to match AMT format requirements. We have therefore left Figure 8 intact. We added a sentence in Fig. 8 caption as follows: *"The lines between symbols of individual bins are simply a visual aid."*

In section 3.4 organosulfur emissions from waste bins were investigated. Please have a look at the following paper and consider including it as a reference.

Mayrhofer et al. ENVIRONMENTAL MICROBIOLOGY, Volume 8, Issue 11, Pages: 1960-1974 (2006), Microbial community related to volatile organic compound (VOC) emission in household biowaste. DOI: 10.1111/j.1462-2920.2006.01076.x

=> We thank the referee for this reference. This reference was added on section 3.4 as follows: *"Sources of OSC in urban and rural areas include those of non-marine origin such as human breath (Tonzetic, 1971; Taucher et al., 1996; Van den Velde et al., 2008, 2009), agricultural activities and pet waste (Burnett, 1969; Williams et al., 1999; Filipy et al., 2006; Shaw et al., 2007; Trabue et al., 2008; Feilberg et al., 2010; Papurello et al., 2012; Meinardi et al., 2013; Zhang et al., 2013) as well as household biowaste (Mayrhofer et al., 2006)."*

New Figure 3.



New Figure 6.

