

Interactive comment on “Measurement techniques of identifying and quantifying sulfur compounds in fog and cloud water” by Eleni Dovrou et al.

Eleni Dovrou et al.

edovrou@g.harvard.edu

Received and published: 29 July 2019

We would like to thank Referee #3 for the comments that have helped improve the manuscript. The reviewer comments are in italic followed by our replies in normal text.

Comment 1 (“Title”): The title as it stands now is very broad. Maybe it could be phrased a bit more specific ? Wouldn’t it make sense to clearly mention HMS ?

The title has been revised to: “Measurement techniques of identifying and quantifying Hydroxymethanesulfonate in cloud water and particulate matter”

Comment 2 (“Introduction”): It covers quite some aspects, but at times there could be some more coverage. Maybe the authors can check again, HMS has been discussed a bit more often.

C1

Information regarding the formation, chemistry and field measurements of HMS is presented throughout the introduction. As HMS is an important compound discussed in this work we provide information in all the paragraphs of the introduction.

Comment 3 (“Page 3 Section 1.2”): I find it strange that here the very successfully applied CE (capillary electrophoretic) separation and determination is not described. This is a major flaw and needs to be corrected. See Scheinhardt et al., but especially references therein, Kramberger et al.

We have added a description of the CE method in page 4 lines 34-40: “Scheinhardt et al. (2014) provided evidence of identification of HMS during two field campaigns conducted in nine sites in Germany. Capillary electrophoresis (CE) was used resulting in efficient separation of HMS from other compounds when a voltage of -30 kV followed by hydrodynamic sample injection with 750 mbars was applied. Quantification was achieved through indirect UV detection at 260 nm wavelength and time resolution of 20 Hz. The detection limit of HMS was reported equal to $6-7 \text{ ng}\cdot\text{m}^{-3}$ and higher concentrations were observed during winter time. The method resulted successful quantification of HMS in concentration $\geq 18-21 \text{ ng}\cdot\text{m}^{-3}$. Concentrations in the range of $6-18 \text{ ng}\cdot\text{m}^{-3}$ were reported, however this range was characterized as less reliable in the study. (Scheinhardt et al., 2014)”

Comment 4 (“Page 5 line 29”): For MSA you should possibly reference Huang, Shan, et al. “Latitudinal and seasonal distribution of particulate MSA over the Atlantic using a validated quantification method with HR-ToF-AMS.” Environmental science & technology 51.1 (2016): 418-426.

The citation of the recommended work has been added to the revised manuscript in page 6 line 11: “(Phinney et al., 2006; Huang et al., 2016; Chen et al., 2019)”.

Comment 5 (“Page 6 Section 3.1”): Maybe it would be good to carry the conclusion of this section into the abstract: It is very difficult if not even impossible to identify or even quantify HMS through AMS only.

C2

The conclusion of Section 3.1 is presented in the abstract in page 1 lines 18-22: "In cases where the dominant sulfur-containing species are ammonium sulfate or HMS, differences in AMS fragmentation patterns can be used to identify HMS. However, the AMS quantification of HMS in complex ambient mixtures containing multiple inorganic and organic sulfur species is challenging due to the lack of unique organic fragments and variability of fractional contributions of H_xSO_y^+ ions as a function of matrix."

Comment 6 ("HPLC"): Also, the HPLC method presented here does not fully convince. Please give numbers of merit for it and compare to all existing offline analytical techniques. Could you discuss whether AMS paralleled by filter sampling and CE analysis wouldn't be a valuable option? In this view, the discussion at the end of the paper should be widened.

Information and concentration ranges according to the study of Zuo and Chen (2003) are presented in page 4 lines 33-39. The study provides evidence of separation and quantification of HMS, sulfate and sulfite and the reported numbers that are relevant to the separation of these species are included in the manuscript. The present work does not aim to provide a literature review of the techniques that have been used to identify HMS thus Section 1.2 serves as a short discussion of methods previously used. The AMS coupled with CE analysis is an interesting option however since CE is not used in the present work, we could not comment on the efficiency of such a method. According to our finding AMS identification quantification of HMS is challenging. As pointed out by the referee #3, CE has successfully been used for the identification and quantification of HMS, however it is uncertain that the combination of the two system, AMS and CE, would result in better results.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2019-127, 2019.