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Interactive comment on “Challenges associated with the sampling and analysis of organosulfur compounds in air using real-time PTR-ToF-MS and off-line GC-FID” by V. Perraud

Anonymous Referee #2

Received and published: 17 February 2016

The authors describe a detailed study on organosulfur-compound measurements using PTR-ToF-MS and GC-FID. The application of both techniques is demonstrated by laboratory measurements of standards and ambient measurements from complex, high emission sources. Overall, the study is carefully designed, addressing the uncertainties and pitfalls of the two methods. Thus, the manuscript is appropriate for publication within the scope of AMT.

The presentation of the results is well structured and understandable. The authors provide a comprehensive overview on work that has been undertaken in this field and the language is fluent and precise.

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I recommend publication in AMT, after addressing the following minor comments:

AMTD

8, C5508–C5511, 2016

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Abstract

p. 13158, l. 6: The ordering of visibility, climate and human health seems unusual. Aerosol effects on climate are rather considered as beneficial, not as “negative”, as they are counteracting greenhouse gas forcing.

l. 7: I doubt that it will be possible to “predict particle formation” events, even if one knows OSC emissions in detail. Still, improving emission inventories (which include OSC emissions) might help to reduce uncertainties in sulfuric acid production, which is linked to new particle formation.

Introduction

The unexperienced reader would appreciate if reported ranges of mixing ratios were included for pristine marine environments and being contrasted to other natural sources (e.g. wetlands) and anthropogenic sources.

p. 13160, l. 19: Is the probability of fragmentation in PTR-MS only a matter of size of the molecules? What is about fragmentation probability considering different functionalities of small (<200 amu) molecules?

Materials and methods

p. 13161, l. 18-21: Please provide a reference for that?

p. 13162, l. 13: replace “two standard deviations” with 2σ .

p. 13162, l. 26-28: How sure is it that the modified Gaussian function fit from another instrument applies to the used instrument? Are peak shapes changing with time, depending e.g. on ambient temperature? How does the applied modified function fit match with your reagent ion signal (which can be used to determine an instrument specific peak shape function)?

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p. 13162, l. 29: resolution of ~5000 at which m/z?

p. 13165, l. 5: Out of curiosity: Can the higher emission rate of MTO vs H₂S be explained, although the H₂S vapour pressure is ten times higher than that of MTO?

p. 13165, l. 15: Consider renaming into: Sampling from a complex, high emission source.

p. 13165, l. 28: Replace “inlet of the container” with “sampling line of the bin” in order to be consistent with the paragraph.

Results and discussion

p. 13167, l. 25: Does the mass defect of the unidentified signal suggest it contains sulfur? Does the signal height of the isotopic signal at m/z 98 tells how much sulfur one would expect?

p. 13169, l. 17: Can one still apply the per-carbon-response-factor, if the analytes contain different numbers of heteroatoms? See also: Holm, T., J. Chromatogr. A 782 (1997), 81-86.

p. 13170, l. 5-7: Were the canisters filled simultaneously?

p. 13170, l. 13: As cyclohexane (CH) has a different retention time than the analytes, do you still expect that FID detector saturation can be an issue? In Fig. 2, the CH signal is clearly separated from the OSC signals.

p. 13170, l. 19: P'T'R-ToF-MS

p. 13171, l. 20: If by “stainless steel pre-concentration system” the stainless steel canister is meant, then please be consistent with the terminology.

p. 13172, l. 3: Consider renaming into: Application to a complex, high emission source. General comment on section 3.4: Is it possible to identify OSC compounds in PTR ToF MS spectra, other than DMS, DMDS, DMTS and MTO? Can you show mass spectra

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of the waste bin measurements to indicate the relative intensities of OSC versus VOCs or OVOCs?

Table 1: Do accurate mass measurements with R=5000 provide four decimal places?

Figure 1: What is the origin of the high background signals in (c) and (d)?

Short summary: “Gas phase organosulfur compounds in air serve ‘as’ precursors of particles [...]”

Interactive comment on *Atmos. Meas. Tech. Discuss.*, 8, 13157, 2015.

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