

Interactive comment on “Effect of ions on the measurement of sulphuric acid in the CLOUD experiment at CERN” by L. Rondo et al.

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The manuscript “Effect of ions on the measurement of sulphuric acid in the CLOUD experiment at CERN” explores the role that weakly-bound clusters of sulfuric acid and oxidized organic compounds (OxOrg), which are formed and ionized within in the chamber, may play in biasing the measurement of sulfuric acid monomer in a selected ion chemical ionization mass spectrometer (CIMS). In this manuscript, the authors present evidence that shows an increase in sulfuric acid signal as detected by CIMS could be the result of increased transmission of the OxOrg-HSO₄⁻ clusters in the CIMS inlet, and the breakup of those clusters in the collisional dissociation chamber. Additionally the

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authors explore whether this enhancement effect has atmospheric implications during a recent field campaign in a forest. Having read this article several times, I generally feel that the presentation is more con-fusing than it needs to be; eventually, and after multiple readings, most of the main details of the manuscript make sense. I have a few questions that I will outline below, but generally I would encourage the authors to review their manuscript and strive to simplify the presentation if possible. Once the issues are addressed I feel this manuscript would be suitable for publication.

We thank the referee for his helpful comments and suggestions. We are aware that the topic in our manuscript is very specific and will mainly be of interest for the community dealing with Chemical Ionization Mass Spectrometry (CIMS) measurements. Nevertheless, we feel that this is an important topic and deserves some attention. We have tried to improve the readability and the structure of the paper by considering all the raised points and comments by the referees.

questions/comments:

6602/18: this sentence suggests that there are alkene contaminants in CLOUD. If true, please provide a simple sentence that states this (e.g., a summary of the relevant results from the cited study by Schnitzhofer et al.).

Here we added a sentence in order to provide clarification on the observed alkenes impurities that were reported by Schnitzhofer et al. (2013), page 6602/ line 22: ... These organic impurities (mainly formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid) which have a rather high vapor pressure and are therefore not important for aerosol nucleation and growth, are reported to occur at rather low concentrations (below 1 ppbv in total, see Schnitzhofer et al. (2013)) .

Typically, sulfuric acid CIMS instruments directly measure OH concentrations using isotopically labeled SO₂, was this not the case in the current study?

For this study no isotopically labeled SO₂ was used and a direct measurement of OH

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was not attempted. OH measurements are challenging for this system due to the relatively high wall losses. The OH transmission efficiency would be only ~13% for the 0.9 m long sampling line, a limited maximum flow rate of 7.6 slpm and a diffusion coefficient of 0.2 cm²/sec for OH.

6604/25: This is a major observation of the manuscript: the observation that a major part of the bisulphate ions from the chamber, is probably being lost before reaching the ion drift tube due to diffusion or electrostatic forces.” What evidence suggests this to be the case? Or is this just a hypothesis? The subsequent text seems to suggest that this loss mechanism is a fact, as it details the possible locations for the loss.

Indeed we agree with the above comment that our statement of the possible losses of bisulphate ions during sampling it is of a high importance of this study. Nevertheless, (as stated in the text: 6605/1...is probably being lost. . .) we clarify that we did not claim experimental evidence of the loss mechanisms described in the paper. However, our hypotheses are consistent with the observed difference in bisulphate ion concentration between the two different environments (binary and organic oxidized ternary case). The described loss mechanism is the most likely one from our experiences regarding H₂SO₄ measurement using CIMS. Probably, most of the ion loss occurs between the end of the sampling line and the beginning of the drift tube as the ions cross a repulsing electric field. In case of heavier ions, the repulsing force will probably have a smaller effect and promote the ion detection efficiency. We try to better address this issue now by changing the following sentence page 6605/2: Although, there is no direct experimental evidence that ions are lost at one specific location in the CIMS sampling line and ion drift region we can presume several possible locations for such effects to occur (see Fig. 6).

6606: I am somewhat confused about the results shown in Figure 7. Are these the result of the parameterization? If not, then why are the pinanediol data displayed here?

In Figure 7. a comparison of the parameterization data (y-axis) versus the measured

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data (x-axis) for binary and ternary organic nucleation runs (pinanediol) is displayed in order to show the good agreement for the binary case (red points) and the significant deviation for the pinanediol case under the ion influence (green points). In order to clarify this we modified the relevant sentence (page 6606, line 15): Fig. 7 shows that the predictive ability of the derived [H₂SO₄] in an ion-free environment is good (red points) whereas for the ion-induced pinanediol case (green points) the observed deviation indicates the ion effect on the CIMS measurements.

Minor correction: page 6607/3. . . (Fig. 6) is changed to (Fig. 7)

6607/12: As the authors state, one would expect ambient observations to be similar to chamber GCR data, that is, a slight enhancement of the HSO₄- signal due to ambient ions. Could this be due to the fact that the OxOrg produced by CLOUD is not representative of the actual atmosphere? This seems to be the suggestion presented by the authors in this paragraph.

At this point we feel that we need to clarify that it is not our intension to derive such conclusions as the one mentioned above. Indeed, due to our findings from the CLOUD-04 experiment concerning the ion enhancement in the presence of pinanediol and its oxidized products, we conducted sulphuric acid atmospheric measurements (during the PARADE campaign) in order to explore the possible ion effect in an ambient environment. The fact that our ambient results did not show the same effect as in CLOUD does not necessarily lead to the conclusion that the CLOUD experiments are not representative of the actual atmosphere. To the contrary, CLOUD experiments are designed in such a way that they simulate the desired atmospheric conditions and reproduce nucleation rates similar to that observed for ambient conditions (Riccobono et al., 2014). In particular, pinanediol was chosen as a representative compound of first-generation SOA vapors, with its oxidation products being also atmospherically relevant. The CLOUD experiment simulates the conditions of atmospheric pinanediol and its OxOrgs products, so the actual reason of the discrepancy of the ambient bisulphate ions could possibly rely to different sampling challenges (e.g. sampling conditions as

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well as ion source geometries and the applied electric fields). The overall actual effect of the complex chemical system to bisulphate ion enhancement is therefore highly convoluted. In order to make clear that the OxOrg produced by CLOUD is representative of the actual atmosphere, we introduce a sentence in page 6607, line 14: . . .A question related to the discussed observations is to what degree atmospheric measurements could be affected by this phenomenon. Because the CLOUD-04 experiment simulated to a great extent atmospherically relevant oxidation products (Riccobono et al., 2014), there was a need of further investigation of the ambient bisulphate ion enhancement effect on the CIMS measurements.

minor points:

6596/4: the phrase following i.e. should correspond to the previous phrase (that is, it should state “i.e., without and with the presence of ions, respectively,” We thank the reviewer for the correction. Changed to: nucleation experiments, i.e., without and with the presence of ions, respectively,

6598/4: “detectable”

Changed to: was only detectable under. . .

6602/2: “the” not needed in front of pinanediol

Changed to: In order to study the effect of oxidised organic compounds on the nucleation rates pinanediol (PD, C₁₀H₁₈O₂) vapour was introduced into the chamber. . .

6604/24: reword the awkward phrase: “fragments the ions less strongly pronounced”

Changed to: The APi-TOF, however, appears to fragment the ions less strongly than the CIMS does and therefore the mixed HSO₄–OxOrg clusters are clearly detected.

6605/2: suggest “possible locations” instead of “possibilities”

Changed to: . . . several possible locations for such effects to occur (see Fig. 6)

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Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/7/C2904/2014/amtd-7-C2904-2014-supplement.pdf>

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 6595, 2014.

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