

Interactive comment on “Characterisation of organic contaminants in the CLOUD chamber at CERN” by R. Schnitzhofer et al.

The authors want to thank the anonymous reviewers for their valuable comments and suggestions that helped to improve the quality of the manuscript.

Anonymous Referee #1

General comments

This paper presents results from measurements made to identify organic contaminants and their sources in the CLOUD chamber. The paper is well-written, the measurements are of high quality and the interpretation of the results is well done. However, it is a very technical paper and its relevance is mainly limited to researchers working with large simulation chambers operating very close to atmospheric conditions. It could also be argued that the work does not fit squarely within the aims and scope of Atmospheric Measurement Techniques. Nevertheless, the results of this work are useful since they identify and quantify the contaminants and pinpoint their source. The possible role of inlet lines, chamber processes and various instruments in adding to contamination of the air in chamber experiments is also highlighted. On balance therefore, I recommend this article is published.

Specific comments

Referee #1:

The paper is very carefully written and there are only a few trivial corrections to be made:

1. page 7711 line 18: Should be "background levels"

Reply:

The dash has been deleted.

Referee #1:

2. Page 7714, line 8: Again, no dash is required between H3O+ and ions.

Reply:

The dash has been deleted.

3. Page 7721, lines 19-20: The term "rather low ozone levels" is subjective and it is suggested that this sentence is changed.

Reply:

The term 'rather low' has been deleted.

Anonymous Referee #2

Specific comments

Referee #2:

It is stated in line 264 (Results) that a total of 36 different VOCs above their individual LOD could be detected. Table 1 includes the 5 most abundant. It is of interest to have some information about the other 31 compounds. Could this info be given as part of supporting information?

Reply:

We could provide a separate list of the other ions having a rather low count rate (abundance).if needed.

Referee #2:

It is stated that the paper by Almeida et al (Molecular understanding of amine-sulphuric acid particle nucleation in the atmosphere) is submitted. Which journal?

Reply:

The paper has been published in Nature on October 6th 2013. The complete reference is now cited.

Referee #2:

It is stated that the paper by Schlobesberger et al (Molecular understanding of atmospheric particle formation from sulphuric acid and large oxidised organic molecules) is submitted, 2013. Which journal?

Reply:

The paper has been published in PNAS on October 7th 2013. The complete reference is now cited.

Anonymous Referee #3

General comments

The paper describes the background conditions of VOCs determined in the CLOUD chamber at CERN. The influence of experimental conditions like varying humidity, temperature, SO₂- and O₃-concentrations on the VOC background concentrations were investigated and discussed. The manuscript is well written and the results are presented well. The experimental data are of high quality and the interpretation of the results is appropriate.

Specific comments

Referee #3:

Table 1 provides the relative abundance of certain VOCs during CLOUD3. Fig. 7 show that relative abundances can differ significantly while experimental conditions change. To account for the variability of the relative abundance please provide the respective min- and max-values to table 1.

Reply:

We included the min- and max-values in table 1.

Referee #3:

It is unclear whether the given relative abundances in table 1 are representative for all campaigns. Please specify their reproducibility for the different CLOUD campaigns.

Reply:

For comparison we included min-, mean-, and max-values from the CLOUD2 campaign in table 1 and changed the text consistently. The longest background contamination datasets CLOUD2 (12 days) and CLOUD3 (31 days) are included in table 1 now, whereas we didn't include CLOUD7 data since background measurements were only conducted for less than 5 days at the very beginning of the CLOUD7 campaign.

Referee #3:

Page 7721 Line 22. The authors state that ozone yields to VOC formation by heterogeneous reaction on the chamber walls. While the influence of the ozone generator on VOC is clearly shown in Fig. 6 evidence for a further VOC formation process due to ozone (e.g. heterogeneous reaction) is not obvious from the presented results.

Reply:

It is quite obvious that the VOC background contamination is related to the ozone concentration. To locate the exact source within the whole chamber and the inlet system is not as straight forward. The plastic seals of the ozone generator were one possibility and replacing the "plastic" seals of the ozone generator with new all stainless steel ones could reduce the amount of VOCs released. Nevertheless the VOC contamination is still connected to ozone (Fig. 6). Fig. 7 shows a strong increase in total VOCs when ozone is introduced into the chamber. However, the VOC background contamination decreased after some hours, indicating a finite reservoir. In our interpretation this reservoir are non volatile precursor compounds sticking on the chamber walls. The detected VOCs are formed during heterogeneous reactions of ozone on the chamber walls with the finite reservoir compounds. In contrast the plastic parts in the old ozone generator, represents a rather 'infinite' reservoir.

Referee #3:

At the end of the conclusion section the authors propose a cleaning cycle for the chamber including a heating cycle (100 °C) together with a high ozone concentration and humidified air. According to the statement on page 7719, line 15 no influence of temperature on the VOC background concentration was found. Based on this result a heating cycle could be omitted and it is not clear why it has been included to the proposed cleaning cycle. The reasons for the chosen conditions could be justified in more detail. The conditions for a cleaning cycle could also be more specific (duration of a cycle, ozone and humidity levels) as they may provide guidance for other chamber experiments.

Reply:

During the heating cycles no VOC increase has been found for the experiments without addition of VOC like pinanediol or alpha-pinene. Those data are shown in this paper since it is about the background contamination. Whenever the physic experiments require the addition of VOCs, a washoff of VOCs during heating cycles could be observed. We tried to clarify this in the manuscript and added the sentence: 'Nevertheless the chamber cleanliness benefits from a heating cycle, after a specific VOC has been added to the chamber for experimental reasons.' to the result section.

Technical corrections

Referee #3:

Page 7717, Line 13: The use of "number" might be misleading in that context. Replace by "mixing ratio"?

Reply:

'number' has been replaced by 'mixing ratio'.

Referee #3:

Fig. 7, Top panel: The sum formula "C3H6OH" is unclear

Reply:

The formula is referring to acetone/propanal and should read C3H6O. The exact mass detected with the PTR-ToF-MS refers to the protonated compound (i.e. C3H6OH+). Inconsistently we wrote the sum formula for the protonated compound in Fig.7, and changed it to C3H6O in the revised version of the manuscript.