

Response to Reviewer #1

We thank Jochen Rudolph for his valuable comments and suggestions, which helped to clarify some statements and thus to improve the paper.

The ambient samples analysed were obtained by using an inlet line directly connected to the analytical system. This seriously limits the general applicability of the method for atmospheric studies. This should be mentioned and options to overcome this limitation should be briefly discussed.

The measurements of ambient air samples were a first test of the system. Therefore, we used an inlet line taking air samples from outside the institute's building. We have at our disposal various whole air sampling systems, which have been applied during a Zeppelin and various aircraft campaigns. For offline measurements of $\delta^2\text{H}$ we presently use a compressor and specially prepared high pressure cylinders, which allow the sampling of up to 1500 L of air. However, we did not discuss this in detail in the paper.

Page 7106, lines 3-9: The linear range and determination of the minimum peak area for reliable isotope ratio measurement is a very important consideration in the evaluation of a GC-IRMS method. Here much more detail such as examples of plots of isotope ratio versus peak area (sample mass) including reproducibility, has to be provided to allow the reader an own evaluation of the linear range, possible bias due to deviations from linearity and so on.

We added a more detailed description of the mentioned parameters in the text. We further added a Figure ($\delta^2\text{H}$ versus peak area) for different preconcentrated masses taking n-octane as example. In Table 1 we added a column giving the necessary minimum mass of the compounds corresponding to the determined detection limit.

The “required signal” is given as nA, which is the actual measured value. However, for potential users it would be extremely important to also know the minimum mass of hydrogen required.

The minimum mass of hydrogen is about 50 ng. We added this information in the text.

Some details that should be considered: In general: The use of “VOC standard mixture” should be replaced by “VOC test mixture”. The term “standard” implies more than just having a mixture with reasonably well known isotope ratio and concentration for method testing purposes. The use of “standard” may result in misunderstandings.

We changed “VOC standard” into “VOC test mixture” throughout the text.

7096, 3-4: Needs to be rephrased, the study by Rice and Quay (cited later) and the roadside studies (also cited later) are exceptions.

The reviewer is right. We rephrased this sentence.

7102, Table 1: It should be explained if the uncertainties stated for the Agroisolab data are standard deviation, error of the mean or accuracy. In the latter case some more explanation is needed how the accuracy was determined.

The uncertainties given by Agroisolab are the standard deviation of the measurements and the uncertainties of the three different secondary standards (calibrated against IAEA-SMOW, IAEA-GISP, IAEA-SLAP) used for the calibration. We added this information in the text.

I am also not sure why Table 1 contains several compounds for which no results (except the Agroisolab measurements) are presented here.

We removed the compounds for which no results are available.

7100, 21-23: The statement about “plans for the future” should be deleted.

The statement has been deleted.

The whole subchapter 2.3 should be removed and the three short sentences describing the operation of the MSD moved to 2.2. By the way, this is a bit of general irritation, there are many subchapters consisting of only one short paragraph.

The original chapters 2.2 and 2.3, and the original chapters 2.5 and 2.6 have been merged.

7100, 6 and following: Not sure what is meant by “for additional separation during a single measurement”. The next sentence mentions an advantage of the used column combination. Advantage compared to what? There are numerous columns and column combinations described in literature for VOC separation. Is this one better suited for this purpose than those described in literature? These statements should be deleted or more specifics about difference in separation quality etc should be given.

The statement was just that two columns of different polarity yield a better separation. But this sentence was obviously capable of being misunderstood. This sentence has been deleted without losing information.

7104, 3.1: The use of Tenax TA has advantages, but there is also the problem of high benzene artifacts. Since benzene is an important atmospheric VOC, some caveat about the usefulness of Tenax TA should be added.

That's absolutely right. We are aware of this problem and did mention this caveat in Chapter 3. The use of TENAX was a first test to get rid of CO₂ in the preconcentrated sample. We indeed plan to investigate the influence of different adsorbents.

7105, 21: I am not sure about the “perfect agreement”. The number of repeat GC-IRMS measurements is 18. Based on standard deviations ranging from 2.5 to 9 ‰ the

statistical error of the mean is only in the range of 0.6 to 2 %. Considering this some of the differences may be statistically significant. I agree that overall (except for isoprene and trimethylbenzene) the differences are small, but some more detailed statistical evaluation should be given.

We used the standard deviation here because we think that due to the few available data points stating the error of the mean and a detailed statistical analysis may be a bit overdone. We changed “perfect” to “good” in this sentence.

Are there any reasons why there seems to be a substantial bias for isoprene and trimethylbenzene?

Trimethylbenzene showed some larger variations of the peak areas, maybe due to the stickiness of the compound. For isoprene we presently do not have a reasonable explanation for this behaviour.

7101 (3.5): The presentation of the ambient results and comparison with emissions would benefit from a table or bar graph giving an overview.

These measurements were some first tests of the system with ambient air samples. We are not sure if a plot would really increase the information content. Therefore, we decided not to add a plot here.

7112, 25: Since available mass of hydrogen will depend on sample volume and VOC concentration giving only the required volume is of very limited value for the reader.

That's right. We changed the sentence accordingly.

Figure 6: Y-axis is relative peak area, relative to what? Or is this just peak area in arbitrary units.

In the figure caption we now referred to the text where the calculation of the “relative peak areas” is explained.