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Atmospheric Measurement Techniques Discussions
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Interactive comment on "An analytical system for the measurement of stable hydrogen isotopes in ambient volatile organic compounds" *by* T. Meisehen et al.

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The paper presents a method for measurement of δD in atmospheric VOC and a thorough characterisation of this method. This is a substantial step towards expanding VOC stable isotope ratio studies (which previously are mainly limited to 13C) to δD. I specifically would like to point out that the use of a test mixture with known isotope ratios of the actually analyzed VOC is extremely important in evaluating possible bias (accuracy) instead of only evaluating reproducibility. Overall the results are of high quality and the methodology is well described and characterized. The paper is well structured and written and easy to read. The paper should therefore be published in

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AMTD after a few minor additions.

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. 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 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.

Some details that should be considered Page, line 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. 7096, 3-4: Needs to be rephrased, the study by Rice and Quay (cited later) and the roadside studies (also cited later) are exceptions. 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. I am also not sure why Table 1 contains several compounds for which no results (except the Agroisolad measurements) are presented here. 7100, 21-23: The statement about “plans for the future” should be 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 subchapter consisting of only one short paragraph. 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. 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. 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 ‰Ċonsidering 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. Are there any reasons why there seems to be a substantial bias for isoprene and trimethylbenzene? 7101 (3.5): The presentation of the ambient results and comparison with emissions would benefit from a table or bar graph giving an overview. 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. Figure 6: Y-axis is relative peak area, relative to what? Or is this just peak area in arbitrary units.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 7093, 2015.

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