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Interactive comment on “A method for stable carbon isotope ratio and concentration measurements of ambient aromatic hydrocarbons” by A. Kornilova et al.

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We like to thank the referees for their useful comments. Most of the comments deal with details of the presentation and clarification of ambiguous statements and are the basis of several minor changes made (see below). Referee 1 comments in detail on the bias in $\delta^{13}\text{C}$ measurements for n-alkanes: - Page12Lines24-26: The authors state: ‘The methodology has been specifically developed and tested for the purpose of accurate measurement of light aromatic hydrocarbons, but this does not exclude its use for analysis of other VOC’. Yet, the systematic bias of up to 2 ‰, which was found between the n-alkane off-line and on-line δ values and which is definitively beyond the

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hitherto reported uncertainty range for compound specific isotopic measurements, indicate the necessity of completely revising the method suitability for VOC classes other than aromatics. The first hypothesis explaining this bias on Page8Lines14-17: 'One possibility is that for heavy alkanes isotopic fractionation might have taken place inside the stainless steel canisters where the mixtures were stored and since ^{12}C containing molecules are more reactive compared to ^{13}C molecules, it is expected that any loss of n-alkanes with time will result in enrichment of ^{13}C .' infers that ca. 60% n-hexane have already 'reacted' when exhibiting a fractionation from -31 to -29‰. Is this likely to happen? The authors may want to comment this issue. The second hypothesis needs to be similarly discussed (Page8Lines17-20: 'Another possible explanation for the bias between off-line and on-line is incomplete oxidation during off-line combustion. This also would result in a decrease of the isotope ratio in the CO_2 formed, since ^{12}C containing VOC will oxidize more readily than ^{13}C containing VOC.') Reply: Indeed, extending the methodology to other VOC classes than aromatics may require further method development, and definitely will require detailed testing. There is no completely convincing explanation for the discrepancy between on-line and off-line results for n-alkanes. The two basic possibilities are an error in the $\delta^{13}\text{C}$ values of the n-alkanes in the artificial mixture or an isotope fractionation occurring during one of the steps in the GC-IRMS measurement. There are several explanations for both possibilities, but due to the lack of additional, independent information none of them can be ruled out. As explained in the manuscript, the artificial mixtures were not prepared with the calibration of concentration measurements in mind and therefore we cannot rule out loss or contamination of the artificial mixtures during preparation or storage of the mixtures. Furthermore, the carbon isotope fractionation for a possible n-alkane loss is unknown and cannot even be estimated as long as the loss process is not identified. From the referee's comment we assume that the referee is using the KIE for the reaction of n-hexane with the OH radical for the estimate of 60% required loss. However, there is no convincing reason to assume that n-alkane loss during preparation or storage of the mixtures should have the same carbon isotope effect as a reaction

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of n-alkanes with OH-radicals. Similarly, the influence of a possible contamination on the isotope ratio of n-alkanes cannot be estimated since the carbon isotope ratio of a possible contamination cannot be determined if the source of the contamination cannot be identified. We modified our discussion of the possible origin of the discrepancy between the isotope ratio of the test mixture and the GC-IRMS results as follows, but since the actual source of the discrepancy cannot be identified, we tried to keep this part of the discussion as short as possible and replaced lines 8-21, page 1376 (Page 8, Line 16 to Page 9, Line 8 in revised manuscript) as follows: “No certified standards or equivalent internationally accepted reference mixtures suitable for tests of the accuracy of isotope ratio measurement of atmospheric VOC are available and consequently the accuracy tests had to be conducted using mixtures prepared in house. In the case of good agreement between GC-IRMS analysis and the isotope ratio of the test mixtures this gives confidence in the accuracy of the GC-IRMS measurements. However, in case of a systematic discrepancy between off-line and GC-IRMS results this makes it difficult to identify the source of bias. While isotope fractionation during sampling on the adsorbent cartridges can be ruled out since the isotope ratios obtained from direct analysis of the test mixtures agreed with isotope ratios determined from samples of the test mixtures collected on adsorbent cartridges, uncertainty in the carbon isotope ratio of the test mixture as well as biased GC-IRMS isotope ratio measurements are possible explanations. Although the mixtures were not prepared for the purpose of concentration calibration, the decrease in peak area from n-hexane to n-decane in the test mixture suggests the existence of a loss for heavier n-alkanes. However, it is not possible to identify at which stage such a loss may have occurred. Error in the $\delta^{13}\text{C}$ in the test mixture can be due to loss or contamination during preparation of the mixture or error in the off-line $\delta^{13}\text{C}$ determination for the bulk n-alkanes. Since the mixtures were not prepared for the purpose of calibrating concentration measurements, it is not possible to exclude or verify the existence of losses or contaminations from comparison of peak areas or calibration curves. The uncertainty of conventional dual-inlet $\delta^{13}\text{C}$ measurements in carbon dioxide is much lower than the observed discrepancy in

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the n-alkane carbon isotope ratios. However, incomplete oxidation of n-alkanes during the off-line combustion of the bulk n-alkanes could result in significant carbon isotope fractionation. Since n-alkanes are less reactive than benzene and alkylbenzenes, this would be consistent with the absence of bias for aromatic VOC. Bias in the GC-IRMS analysis can be caused by contamination or losses during adsorption or desorption of VOC in the TSPS, problems in the chromatographic separation such as peak tailing or baseline drift, and incomplete oxidation in the combustion interface. A significant impact from contamination or artifacts can be ruled out since this would result in a decrease of bias for high sample masses, which is not found (Fig. 3). Although in principle none of the other explanations can be ruled out, there is no direct evidence which would support them. The good reproducibility of the measured n-alkane carbon isotope ratios would require that any loss in the TSPS would be highly reproducible, which is unlikely and the tests of the TSPS showed no indication for significant loss of n-alkanes in the TSPS. Except for n-pentane there also is no indication for problems due to chromatographic separation, peak shape, or baseline drift for n-alkanes. Due to the higher chemical stability of n-alkanes incomplete oxidation in the combustion interface could result in isotope fractionation for n-alkanes without influencing the results for aromatic VOC, although this would require inverse isotope effects for the catalytic oxidation of n-alkanes in order to explain the bias towards higher carbon isotope ratios.” Comment: The referee also specifically mentions “which is definitively beyond the hitherto reported uncertainty range for compound specific isotopic measurement” Reply: This is correct. However, there is only a small number of published tests that would allow a true evaluation of the accuracy (and not only reproducibility and linearity) of measurements of carbon isotope ratios of VOC. We added a short paragraph to Summary and Conclusion (Page 13, Line 23-33 in revised manuscript) explaining this: “Tests of the accuracy of carbon isotope ratio measurements of n-alkanes showed a bias of approximately 2 ‰ between the isotope ratios of test mixtures prepared in-house and GC-IRMS measurements. It was not possible to identify whether this is due to uncertainty in the isotope ratio of the test mixture or bias of GC-IRMS mea-

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surements. Nevertheless, this demonstrates the importance of testing the accuracy of GC-IRMS measurements of atmospheric VOC. Unfortunately the number of published comparisons between artificial VOC mixtures with known isotope ratios and GC-IRMS measurements is limited, a consequence of the substantial resources and effort required to prepare test mixtures with known isotope ratios and the lack of certified or otherwise well characterised reference mixtures suitable for such tests. This supports the necessity for creating reference materials for isotope ratio analysis of organic compounds in the atmosphere as pointed out by Gensch et al. (2014). “ Other comments by Referee 1 Comment: -Page33Figure6: Additionally to the discussion above, the chromatogram of the test mixture shows at a glance two different discrimination trends for the alkane separation, given that the mixture contains, as usual, similar concentration of all components: the peak areas seem to first increase for compounds 2 to 4, then decrease from 4 to 6, 10 and 11. If that is the case, the authors may consider revising the GC oven temperature program. Losing the ‘lighter’ alkanes from the mixture due to too high GC starting temperature might incidentally explain their 13C enrichment in the on-line data. As it is now, the method is excellent for ambient measurements of aromatics, yet unsuitable for alkanes. Reply: Overall, we think that a problem in the initial temperature program cannot be completely ruled out, but also is not a very likely explanation for the observed discrepancy between GC-IRMS and off-line isotope ratios. We included this possibility in the modified discussion (see above), but do not think that this is a more convincing explanation than any of the other possibilities. We changed the discussion (see above), but overall it has to be accepted that this is just one of several possible explanations.

Comment: - Page4Line8 and Page6Line10: revise the different furnace temperature values. – Reply: We see no reason why the temperatures given should be revised. No changes made. Comment: Page21Figure1: insert ‘VOC sample’ between furnace and valve. – Reply: Depending on valve position and stage of the operation of the TSPS, either sample or pure helium can flow through the transfer lines and other parts of the TSPS. Labeling one part specifically with “VOC sample” may cause more irrita-

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tion than clarity for the reader. The procedure of sample transfer is explained in the text. No changes made. Comment: Pages33-34Figure6: revise the different retention time values for benzene (compound 3), given that the same GC temperature program was used for test and ambient samples. Reply: The sample chromatogram was run after the heart-cut timing was changed substantially compared to the reference gas measurement. Since the heart-cut procedure is based on changing pressure differentials, the overall pressure differential across the separation column changes (the electronic pressure control only controls the column head pressure, not the pressure difference). Under these circumstances an exact match of retention times cannot be expected. We added an explanation on Page 1378, Line 8 (Page 10, Line 20-25 in revised manuscript): "It should be noted that the change in the time window for transfer of the column effluent to the combustion interface changes the retention times, especially for peaks eluting early in the time window which is monitored by the IRMS. This is the result of the change in pressure at the end of the separation column which is caused by the He gas-flow that is used to prevent the column effluent from entering the combustion interface. The resulting change in pressure difference between the head and the end of the separation column results in a change of the carrier gas flow velocity." Comment: Editorial revisions: - Page7Line19: replace 'd' by ' δ '(=delta) Reply: The paper in AMTD on page 1374, line 19 correctly shows δ .

Referee 2. Comment: Page 1370, Line 10: "Selective VOC sampling from volumes between 20 and 80 L of ambient air was done on adsorbent filled cartridges." Please clarify how the ambient air sample volume was determined. Is there a known capacity limit for these cartridges? Would reaching or exceeding the capacity of the cartridge cause sampling bias? Reply: Ambient air sample volume was measured using a flow totalizer as mentioned on Page 1370, Line 25. Based on our tests, no breakthrough was observed for the sample volumes tested as explained in the paper on Page 1377, Lines 15-18. We mention that it might be possible to use larger sample volumes on Page 1382 with the caveat that this has not been tested. We think no further discussion or explanation of sample breakthrough is needed. No change made.

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Comment: -Page 1376, Lines 8-11: I would not expect n-alkanes to be more reactive than aromatics inside of the stainless steel canister. Please elaborate on why this is a viable explanation for the bias in n-alkane measurements. Reply: When conducting stability tests for calibration mixtures several years ago we observed that in some canisters the concentration of the heavier n-alkanes at ppbV levels in dry gases decrease with time. However, for none of the canisters used here such tests were conducted and we modified our discussion (see reply to Referee 1 above) to avoid the impression that we have firm evidence that this actually happened here. Comment: -Figure 4: Can you comment on the apparent positive artifacts for n-hexane and benzene recovery with storage? Reply: The estimated overall relative uncertainty of concentration measurements is, as given in the paper, approximately 10%. The values given in Figure 4 are ratios of two measurements and the number of repeat measurements is small, therefore the deviations from 100 % are statistically not significant. Recoveries and artifacts (blank values) have been discussed in detail in other parts of the paper. The reference point (no storage) is the same for both types of storage tests; therefore the agreement between the different storage tests is better than the actual uncertainty of the recoveries. We clarified this by revising the captions for Figure 4 and 5: "Fig. 4. Impact of storage on sample recovery for storage of 1 to 2 weeks at ambient temperatures (diamonds) and 6 to 7 months in a freezer (circles). The recovered masses are given relative to samples analysed immediately after sampling. Both storage tests used the same reference values. Values used are the average of 3 to 4 measurements and the error bars show the variability of results for analysis after storage. Masses loaded range from 25 ng to 75 ng. Values were not corrected for blanks. Fig. 5. Change in $\delta^{13}\text{C}$ of VOC collected on cartridges during storage for 1 to 2 weeks at ambient temperatures (diamonds) and 6 to 7 months in a freezer (circles). The differences are given relative to the $\delta^{13}\text{C}$ values of samples analysed without storage. Both storage tests used the same reference values. Values used are the average of 3 to 4 measurements and the error bars show the variability of results for analysis after storage. Masses loaded range from 25 ng

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to 75 ng. Values were not corrected for blanks." Comment: Technical Corrections: -Page 1366, Line 18: Replace "Volatile Organic Compounds" with "Volatile organic compounds". Reply: Done, Page 1 Line 25 Comment: -Section 2.3.2: Including a reference for the origin of the two-stage pre-concentration technique would be preferable; for example, Rudolph, J., Lowe, D. C., Martin, R. J., & Clarkson, T. S. (1997), Geophysical Research Letters, 4(6), 659–662 (which is also referenced in the companion field study paper, Kornilova et al., 2013). Reply: Done, Page 5, Line 10-11. -Figure 3 contains two identical plots for p,m-xylene. The final figure is likely meant to be for o-xylene, based upon the content of other figures and tables. Reply: Correct figure in revised manuscript Comment: -Table 2: Provide some type of separation between Duration/Temperature/Flow Rate rows and recovery percent results of the listed compounds. Reply: Separation was there in the original submitted table, omitting or including a separation is a journal style decision we leave to the editor. Comment: -Table 3: Why is hexane omitted, when it is present in Figures 4 and 5? The results in Table 3 and Figures 4 and 5 are from different tests. For the tests summarized in Table 3 there was an interference (possibly due to a He contaminant) that did not allow reliable, quantitative analysis of n-hexane. We do not think that this is of sufficient interest for the reader to justify a specific explanation in the paper. No change made. Comment: -Figures 4 and 5: Please note the difference between white circles and black diamonds. Which represents ambient/freezer storage? Reply: Explanation added to figure caption. Comment: -Figure 6: Labeling the chromatograms "A" and "B" (or similar) may expedite identification of test mixture and ambient sample for the reader. Reply: Figures changed in revised manuscript. Comment: -Figure 6: Are peaks 2 and 3 correctly labeled? The difference in retention time from test mixture to ambient is substantial. Reply: See reply to referee 1 and added explanation on Page 1378, Line 8 (Page 10, Line 20-25 in revised manuscript).

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/8/C762/2015/amtd-8-C762-2015->

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