**Atmospheric
Measurement
Techniques**
Discussions

Interactive comment on "ACTRIS non-methane hydrocarbon intercomparison experiment in Europe to support WMO-GAW and EMEP observation networks" *by* C. C. Hoerger et al.

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Anonymous Referee #1 Received and published: 20 November 2014 This is another comprehensive and interesting intercomparison of techniques to determine non-methane hydrocarbons. This has been a challenging and ongoing task for many years. It is good to see the establishment of ambitious Data Quality Objectives (DQOs). Unfortunately, it seems it is still hard to comply with these DQOs and there seems to remain various, sometimes poorly understood reasons for that. Netherthe- less, it is very encouraging to see joint efforts to tackle all these challenges. Overall, the paper shows some valuable material and associated discussion. It also mentions various

limitations. After addressing the issues lined out below, I would recommend the publication of this manuscript in AMT. Major issues: 1) One limitation of this study is that only dry samples were used in the intercomparison. Also, I assume these samples did not contain O3. As a consequence the performance of important instrumental parts critical in removal of H2O and O3 and their potential impact on the samples could not be compared. This limitation should be mentioned explicitly in the abstract and the conclusion. The reviewer is right in this important comment. The authors already mentioned this fact in the results section "other issues". We now additionally addressed this in the abstract as follows: "The participants were asked to measure analyse two dry gas mixtures in pressurised cylinders, a 30-component NMHC mixture in nitrogen (NMHC_N2) at approximately 1 nmol/mol and whole air (NMHC_air), following a standardised operation procedure including zero- and calibration gas measurements." We wish to point out, however, that devices for ozone or water removal were installed in the analytical systems of the participants and thus the round robin test gases passed these sections and they were included in this intercomparsion, however, as correctly mentioned not in routine operation of ambient air samples with varying amounts of water vapour and ozone. Nevertheless, we also included a sentence in the conclusion: "It should be noted that this comparison uses test gases which do only partly reflect the complexity of ambient air, e.g. no ozone and low water content."

2) Page 10431, lines 18-22: If I understand it correctly, it seems HPB and Empa assigned values to NMHC_N2 and NMHC_air and at the same time participated in the intercomparison. This an unusual approach and contradicts the statement on page 10432, lines 10-11, that "The composition and the mole fraction in the cylinders were unknown to all participants". The authors should comment on this and justify why no external entity performed this task. The reviewer is right, however, originally it was not planned that the reference laboratories' results would be included in the intercompari- son evaluation. Later, we decided to add the results of the mid-term analyses by Empa and HPB as these were not used for the determination of the reference values. Furthermore, at that time the reference values had not been determined yet. The authors

pointed out on page 10431, lines 18-22 that "Empa and HPB data cannot be treated as purely blind intercomparison results". The sentence on page 10432 lines 10-11 was changed to "The composition and the mole fractions in the cylinders were unknown to all participants, except for the reference laboratories HPB and Empa (see above)."(line 233 of the revision)

3) One interesting point the authors especially make is that the "Perkin Elmer Online Ozone Precursor Analyser" is the only commercially available all-in-one instrument tested in this study. Still, table 4 lists some different configurations among these instruments and the results vary to some extent. This provides some unique opportunity to discuss the different performance results and potentially ïňṆnd some recommendation for standard approaches, at least for these instruments. It would be valuable to include another separate chapter which would include this kind of discussion. The authors were actually in favour of this, however, the results show overall limited results achieved by Perkin Elmer instruments. Partly this is due to their use in automated operation at remote stations, which attained less maintenance, partly it is due to QA/QC at most stations not being optimal. Thus, these instruments seem to have better potential for reliable NMHC measurements than what was obtained in this intercomparison. A section specifically discussing the PE instruments thus would set them into a light worse than their potential is assumed to be, and the authors decided to not further emphasize this issue.

4) Page10432, lines 25-27: It seems that the references to Solberg (2012; 2013) serve as a justiïňĄcation for introducing the ACTRIS DQOs. It would be valuable to brieïňĆy describe the measurement system used in the Solberg references, as this measurement system seems to be suitable to determine these annual trends. Solberg (2012, 2013) refer to EMEP reports on VOC measurements at European EMEP sites and thus do not refer to specific measurements.

4) Page 10436, line 10 - page 10437, line 11: The authors should also discuss that some laboratories show more accurate determination of selected NMHC in NMHC_air

compared with NMHC_N2, e.g. SMR for isoprene and FZJ_B for acetylene (just to name two examples). This is something one would not expect in the ïňĄrst place. The number of such occasions is low, only 7% of NMHC_air determinations were better than NMHC_N2. This is considered an accidentally better result for the more complex mixture. This is further supported by the fact that NMHC_N2 is most similar to the laboratory standards used, mostly NPL, and thus there is no reason to expect worse determinations for NMHC_N2 than NMHC_air.

Other comments: Page 10425, line 1: According to table 3 I am counting 18 laboratories. Also, it seems some of the laboratories are not associated with either GAW or EMEP (SIR, FZJ, NILU). This should be clariïňĄed. We added a corresponding clarification in Table 3. Actually, there are 18 institutions, measuring at 20 sites with a total number of 25 instruments (23 GC and 2 PTR-MS). We changed in the abstract to "18 European institutions. . ."

Page 10425, lines 10-14: It needs to be mentioned that both, NMHC_N2 and NMHC_air, were dry samples and most likely did not contain O3. For a mixture NMHC in N2 nobody expects other constituents than NMHC and N2 and trace level impurities. Compressed ambient air in cylinders do only contain water according to the respective vapour pressure which is at room temperature at most 20 hPa, and compared to the filling pressure of the cylinder of on average (during the intercomparison) 70 10^3hPa, corresponding to an absolute humidity of less than 300 ppm. Furthermore, ozone is rapidly destroyed on metal surfaces, thus no ozone is present in the cylinders. In this section we added the following sentence to clarify: "Ozone management was not in the scope of this ACTRIS intercomparison study and, furthermore, ozone is rapidly destroyed on metal surfaces, thus no ozone is present in the cylinders."

Page 10427, line 8: "Coverage factor" needs to be explained. Also it needs to be explained why the value k=2 was chosen. Because this roughly corresponds to a 95% confidence interval and this is generally used in gas metrics (e.g. Grenfell et al., 2010, NMI certificates for reference gases, climate gases references, GAW glossary, ACTRIS

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Page 10427, line 13: The term "recently" needs to be removed as the PTR-MS technique has been around for some time. The reviewer is right and the sentence was changed to: Furthermore, proton transfer reaction mass spectrometry (PTR-MS) is also used for the measurement of oxygenated VOCs, terpenoids, dialkenes, and aromatics.

Page10429, lines22-23: It looks like ambient air of Dubendorf had 1 % relative humidity, which I doubt which is what the authors wanted to say. The authors should mention the reason why they used a very dry NMHC_air sample and how they dried the sample. As mentioned above, due to the compression by roughly factor 100 with Rix compressors most water vapour condensed and the air actually had 1 % relative humidity.

Page 10431, lines 7-8: How much was the mole fraction drift for 1,3-butadiene and isoprene? The sentence was changed as follows: "For 1,3-butadiene and isoprene the mole fractions in NMHC_air declined from the start to the end of the intercomparison by on average 21% and 41%, respectively."

Page 10431, lines 7-14: This is a bit confusing. I assume that the values shown in table 5 refer to the cylinders prior to the intercomparison exercise. It is not clear why some mole fraction drift before and after the intercomparisons needs to be considered. The authors verified by measurements before and after the intercomparison that the composition in the cylinders did not drift during the intercomparison within the stated uncertainties except for the aforementioned dienes. The values in table 5 correspond to the mean of the determinations of the reference labs before and after the intercomparison.

Page 10432, lines 17-18: Please add a justiïňĄcation why the trimethylbenzenes and monoterpenes were excluded from the intercomparison. Minor item: it should read "trimethylbenzene" instead of "trimethylbenene". During the intercomparison, only few laboratories reported results of these compounds. Further labs were asked to mea-

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sure and report values also for these compounds and some more results have been received meanwhile and are still expected. If the data base is sufficient the trimethylbenzenes will be evaluated as well as terpene results in a second paper. "trimethylbenenes" was changed to "trimethylbenzenes". (Line 239-241 of the revision)

Section 2.6 Please clarify, if equations 7, 9, and 10 are also taken from JCGM (2008) or any other source. For equation 10 it would be good to include the derivation in the supplemental material. No, the equations were derived in this paper. The derivation has been added to the supplementary material.

Page 10433, lines 11-12: What is the justiïňĄcation to use k=2, since k may range between 2 and 3? See explanation above, Page 10427, line 8.

Page 10434, line 1: I think it should be $\Delta\chi$int instead of ΔAint. The reviewer is right; we corrected the equation to $\Delta\chi$int2.

Page 10435, line 6: This reference is not helpful, as it seems that login credentials are required. We mistakenly gave the wrong link and corrected this to an unprotected website: http://www.actris.net/Portals/97/Publications/quality%20standards/WP4_D4.9_M42_300920

Page 10436, line 4: Why were in particular C4-C6 alkanes chosen? Some stations did not report C2-C3 alkanes (e.g. HPB_B, FZJ_A) and additionally breakthrough in C2 compounds can occur. Therefore we decided to take only C4 to C6 alkanes into account.

Page 10436, line 6: I assume the authors mean C7-C8 alkanes (not alkenes). Correct, has been changed. Page 10436, lines 10-11: The authors should justify why they use ïňĄgures and tables to show the same information. Some of the redundancy could be removed. The intention was to show the spread of the data in the figures. However, it is hard to identify the results of individual labs from these figures, thus, for clear presentation of the results of the participating laboratories, also the figures are given. But

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as also Reviewer 2 suggested shortening the paper, we removed the above mentioned Figures into the Supplemental and added frequency plot (new Figure 3) to summarize the results. Page 10436, line 10 - page 10437, line 11: I guess this section needs a separate individual header. We added "Introduction to results" as header.

Page 10437, line 1: I think the authors mean table 7. Changed Page 10439, line 21: Replace "constrains" by "constraints". Changed.

Page 10441, lines 13-16: Unclear. The authors should explain why this would have a speciïñÄc impact on C2-C3 hydrocarbons only. The explanation is given in the section "other issues". Pressure and flow rates were not properly adjusted to these changed conditions, e.g. lower ambient pressure, and caused some of the deviations which were also visible in C2 and C3 hydrocarbons. This part was rephrased in the revised manuscript as follows: "The reduced atmospheric pressure might have caused changes in the chromatographic conditions which had not been adjusted at the time of the measurements.

Page 10442, lines 1-4: Section is unclear. Did the WCC-VOC measure ethane with PTR-MS? No, WCC-VOC measured ethane with the GC-FID/FID. We changed the sentences as follows: Only WCC-VOC reported 50% reduced ethane results (Figure 5j) in NMHC_air, whereas C-responses of NMHC_N2 did not indicate any losses (Figure 4h). However, WCC-VOC observed specific matrix problems in NMHC_air in their GC-FID/FID system which they attributed to extraordinary high OVOC levels causing unusual artefacts in their trapping and desorption system. The high OVOC mole fractions ($\sim$200 nmol/mol) were analysed by their PTR-MS system (see PTR-MS results in Supplementary Material).

Page 10442, lines 8-9: Unclear. I assume alkene mole fractions were low in the samples for all participants, not only for AUC, PAL, SMK, ZSF, and IPR. So why was it a speciïñÄc challenge for these participants? These participants had issues with breakthrough, split-injection, and chromatography. All other participants did not have these

issues.

Page10442,lines23-24: Unclear. What are the speciïñÄcs of a pressure regulator which is in particular inappropriate for ethyne? This was the comment of the respective participant, who noted that ethyne was not compatible with the pressure regulator as specified by the manufacturer (Alphagaz, HBSI 2). But we deleted the reference to the regulator, as it was confirmed by the producer that this should not be an issue at all.

Page 10444, lines 1-2: It should be elaborated what the authors exactly mean by the term "status of NaïñÄon", in particular if this status depends on humidity. This may be of relevance, as this intercomparison exclusively refers to dry samples. Based on the sparse information gathered during the intercomparison, we were unable to discern which aspect of the Nafion dryer was responsible, e.g. humidity exposure or age of the Nafion dryer. The Nafion dryers were not changed before the intercomparison and it is assumed that they were regularly in use and accordingly good conditioned. As obviously blanks in zero-air occurred (e.g. C4-alkenes) in several systems (see Supplemental), these had to be subtracted from the measurement results and thus had an impact on the results in dry air too.

Page 10448, lines 7-17: These statements are a bit awkward, as only extremely dry samples were analysed. As a consequence it cannot be stated that cold trap systems exhibited a "very good performance" as they were actually not exposed to water. Also the sentence "overall however, this method appeared superior compared to NaïñÄon dryers...." is awkward, since no "overall" statement can be made at all and the verb "appeared" is very weak. The reviewer is right in the sense, that the ability of the water removal systems was not tested for wet samples. But we think that it is important to report on observed problems even though only dry samples were used. Thus, it was decided to leave this passage but re-formulated it: The cold trap systems used by YRK, WCC-VOC, HPB_A (Table 4a) exhibited no artefacts. Overall however, this method appeared to be superior compared to Nafion[®] Dryers where alkene artefacts are observed (see 'alkene artefacts').

Page 10448, lines 22-23: Unclear. How can pressure and ïñĆow rates only cause some of the deviations? What deviations in particular? We changed the sentence to "The reduced atmospheric pressure might have caused changes in the chromatographic conditions which had not been adjusted at the time of the measurements."

Page 10450, lines 1-2: Unclear. I thought all participants calibrated ethyne directly. Also, based on this paper no statement can be made about humid air samples as all samples analyzed in this study were extremely dry. The reviewer is right. But based on earlier intercomparison studies (e.g. NOMHICE) where ethyne was not calibrated directly, ethyne was always an issue. Therefore we wanted to point out that good ethyne results need a direct calibration and thorough testing of matrix effects: Though not investigated here, ethyne artefacts may occur on active sites of the Al2O3 columns and consequently calibration may differ in dry and wet matrices and need corresponding check as recommended in the results and conclusion. Page 10450, lines 12-13: Actually, not "many", but almost all participating instruments indicated losses of C7-C8 aromatics according to ïñĄgure 4. Changed to: "Almost all of the participating instruments indicated losses of C7-C8 aromatic compounds, most probably due to adsorptive losses."

Page 10450, lines 19-20: "substantially underestimated" requires some quantiïñĄcation. Some quantification is added to the results section. We changed to: "An important result of this intercomparison is that in more than 25% of the reported results uncertainties were substantially underestimated and major uncertainty contributions were not correctly assessed".

Page 10450, lines 20-21: "...some participants did not cover the major uncertainty contributions." does not really sound like a result, but rather a complaint. Would recommend to reword this a bit. The authors reworded the sentence as follows: "Another important result of this intercomparison is that in more than 25% of the reported results uncertainties were substantially underestimated and major uncertainty contributions were not correctly assessed. Last but not least erroneous results were also

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caused by the occasionally inattentive data submission, with mistakes and incomplete information. While these problems were detected and resolved in the relatively small dataset of this intercomparison, it is an issue with submission of insufficiently controlled datasets to public data centres and end-users."

Table 4: Obviously, this table has two parts. I recommend to have Table 4a and 4b. We changed Table 4 to Table 4a and 4b.

Table 5: Replace "cis-2-penten" by "cis-2-pentene". Changed as suggested.

Table 7: Some columns are not colored, although it seems the mixing ratios for these NMHCs are more than 100 pptv (2,2,4-trimethylpentane, 1-butene, and 2- methylpropene). As we wrote in the header of Table 7, the columns without colours indicate that the values were determined by HPB only.

Table 9: Why do some columns contain extremely precise repeatabilities (around 0.001%)? For compounds with mole fraction below 0.1 nmol/mol (those marked by an asterix), no percentage value, but the absolute repeatability in nmol/mol is given. We added an explanation to Table S4. "For compounds < 0.1 nmol/mol the values are given in nmol/mol. They are indicating the repeatability in absolute values."

Figure 5, Figure caption: "Normalised mole fractions...", normalised to what? Mention what the additional information provided by this ïñĄgure is which is beyond what is already shown in tables 6 and 7. We change the figure caption to: "Mole fractions for NMHC_N2 and NMHC_air normalised to the assigned values." The Tables 6 and 7 were moved into the supplementary material to shorten the paper. Figure 5, now Figure 2 is kept in the main paper as it clearly shows the individual results and includes the uncertainty (error bars).