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# ACTRIS non-methane hydrocarbon intercomparison experiment in Europe to support WMO-GAW and EMEP observation networks

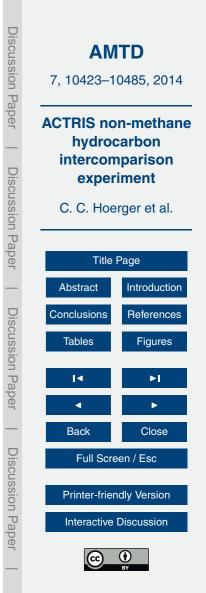
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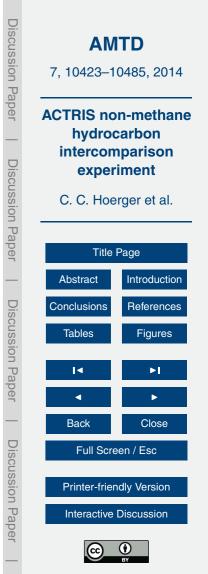


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<ul> <li><sup>21</sup>Norwegian Institute for Air Research (NILU), Kjeller, Norway</li> <li><sup>22</sup>Global Change Research Centre, Academy of Sciences of the Czech Republic, Brno, Czech Republic</li> </ul>	Discussion Paper	ConclusionsReferencesTablesFigures
Received: 17 September 2014 – Accepted: 24 September 2014 – Published: 13 October 2014	Pape	
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# Abstract

The performance of 20 European laboratories involved in long-term non-methane hydrocarbon (NMHC) measurements within the framework of Global Atmosphere Watch (GAW) and European Monitoring and Evaluation Programme (EMEP) was assessed

- with respect to the ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) and GAW data quality objectives (DQOs). Compared to previous intercomparisons the DQOs of ACTRIS are much more demanding with deviations to a reference value of less than 5% and repeatability of better than 2% for mole fractions above 0.1 nmol mol<sup>-1</sup>.
- <sup>10</sup> The participants were asked to measure both a 30 component NMHC mixture in nitrogen (NMHC\_N<sub>2</sub>) at approximately 1 nmol mol<sup>-1</sup> and whole air (NMHC\_air), following a standardised operation procedure including zero- and calibration gas measurements. Furthermore, they had to report details on their instruments and they were asked to assess measurement uncertainties.
- <sup>15</sup> The NMHCs were analysed either by gas chromatography-flame ionisation detection or gas chromatography-mass spectrometer methods. Most systems performed well for the NMHC\_N<sub>2</sub> measurements (88 % of the reported values were within the GAW DQOs and even 58 % within the ACTRIS DQOs). For NMHC\_air generally more frequent and larger deviations to the assigned values were observed compared to NMHC\_N<sub>2</sub> (77 %
- <sup>20</sup> of the reported values were within the GAW DQOs, but only 48 % within the ACTRIS DQOs). Important contributors to the poorer performance in NMHC\_air compared to NMHC\_N<sub>2</sub> were a more complex matrix and a larger span of NMHC mole fractions (0.03–2.5 nmol mol<sup>-1</sup>). Issues, which affected both NMHC mixtures, are the usage of direct vs. two-step calibration, breakthrough of C<sub>2</sub>–C<sub>3</sub> hydrocarbons, blank values in
- <sup>25</sup> zero-gas measurements (especially for those systems using a Nafion<sup>®</sup> Dryer), adsorptive losses of aromatic compounds, and insufficient chromatographic resolution. Essential for high-quality results are experienced operators, a comprehensive quality



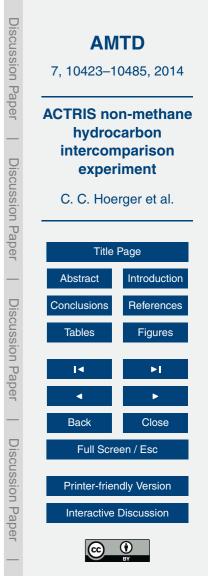
assurance and quality control, well characterised systems, and sufficient man-power to operate the systems and evaluate the data.

### 1 Introduction

Volatile organic compounds (VOCs) are important tropospheric trace gases (Koppmann, 2007; Warneck, 1988). Their sources to the atmosphere are anthro-5 pogenic as well as biogenic and include a large variety of non-methane hydrocarbons (NMHCs, mostly from C<sub>2</sub>-C<sub>16</sub>) such as alkanes, alkenes, alkynes, aromatic compounds, and terpenoids (Andreae and Merlet, 2001; Monks et al., 2009; Placet et al., 2000; Plass-Dülmer et al., 1993; Sawyer et al., 2000). The mole fractions of these compounds vary from a few pmol mol<sup>-1</sup> to tens of nmol mol<sup>-1</sup> in background and urban air, 10 respectively (e.g. Gros et al., 2007; Parrish and Fehsenfeld, 2000). Atmospheric VOCs impact on the oxidising capacity of the atmosphere through their contribution to the generation of photo-oxidants (e.g. ozone and organic radicals) and are precursors of secondary organic aerosols. For these reasons, reliable measurements of VOCs are essential and they are consequently included in the long-term monitoring programs of 15 the Global Atmosphere Watch (GAW) of the World Meteorological Organization (WMO) (WMO, 2007a), regional programs such as the European Monitoring and Evaluation

Programme (EMEP), and national air pollution monitoring networks.

Measurement capability for VOCs in Europe is widespread but no common un derstanding of quality assurance, calibration standards and scales exists. In the WMO GAW Report No. 171, 17 priority VOCs (NMHCs and oxygenated VOCs) were identified (Table 1) and general quality assurance recommendations were described (Table 2) (WMO, 2007b). Within the framework of European infrastructure project ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure
 Network) additional NMHCs beyond these priority substances are measured (Table 1). To harmonise trace gas measurements of NMHCs in Europe, measurement quidelines and a quality management system were developed under ACTRIS

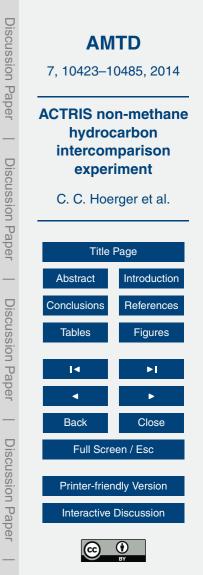


(http://www.actris.net/Project/WorkPackages/WP4/tabid/4428/Default.aspx). One aim of ACTRIS was to assess the current NMHC measurement capacity in Europe and to investigate the analytical performance of laboratories in terms of data quality objectives (DQOs) for repeatability and uncertainty. In ACTRIS more strict DQOs com-<sup>5</sup> pared to GAW were defined (Table 2), which is essential for a better quantification of background concentration trends. Whilst in the WMO GAW Report No. 171 DQOs are defined for accuracy and precision, these have been replaced in ACTRIS with uncertainty (in the sense of expanded combined uncertainty with coverage factor k = 2, JCGM, 2008) and repeatability (which characterises the short term standard variation in multiple measurements).

VOC species are normally measured with gas chromatography coupled to either a flame ionisation detector (GC-FID) or a mass spectrometer (GC-MS). Furthermore, proton transfer reaction mass spectrometry (PTR-MS) has recently been used for oxygenated VOCs, terpenoids, dialkenes, and aromatics. While for PTR-MS VOCs from

- <sup>15</sup> air samples are directly analysed, GC-based techniques need a preconcentration step. Here VOCs are analysed either immediately after sampling onto suitable adsorbents (on-line) or they are collected in specially treated steel or glass cylinders or on cartridges filled with adsorbents and analysed later in the laboratory (off-line). Problems which can occur are: chemical reactions in the samples (due to e.g. reactions with
- ozone), adsorptive losses, memory effects or leaks, losses during the preconcentration and the desorption steps, chemical reactions during thermal desorption, insufficient separation on the chromatographic column and misidentification, peak overlap, and inaccurate quantification (Helmig, 1999, 1997; Helmig and Vierling, 1995; Koppmann et al., 1995; Parrish and Fehsenfeld, 2000; Plass-Dülmer et al., 2002; Rudolph, 1999;
   Westberg and Zimmerman, 1993).

Several NMHC intercomparisons have been carried out in the past on European and global scales with less demanding quality objectives (e.g. NOMHICE (Apel et al., 1994, 2003, 1999), AMOHA (Plass-Dülmer et al., 2006; Slemr et al., 2002), GAW (Rappenglueck et al., 2006), (Bernardo-Bricker et al., 1995; De Saeger and

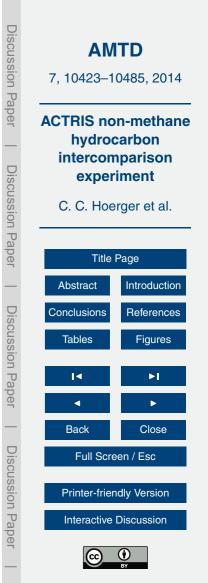


Tsani-Bazaca, 1993; Hahn, 1994; Pérez Ballesta et al., 2001; Romero, 1995; Volz-Thomas et al., 2002)). NOMHICE (Nonmethane Hydrocarbon Intercomparison Experiment) and AMOHA (Accurate Measurements of Hydrocarbons in the Atmosphere) were two systematic multistage intercomparisons for NMHCs performed in North Amer-

- <sup>5</sup> ica and Europe, where the complexity of the NMHC measurements (numbers of compounds and sample gas mixtures) increased during the experiments. While in earlier intercomparisons, the use of certified NMHC calibration standards was not common (Apel et al., 1994, 2003, 1999; De Saeger and Tsani-Bazaca, 1993; Hahn, 1994; Pérez Ballesta et al., 2001; Romero, 1995), multicomponent standards with certified
- NMHC mole fractions were circulated for analysis among the participating laboratories in more recent intercomparisons (Plass-Dülmer et al., 2006; Rappenglueck et al., 2006; Slemr et al., 2002). Thus, it could be demonstrated that calibration with multicomponent NMHC calibration standards provides significantly more accurate results than the frequently used method of calibration with just a single hydrocarbon species,
- <sup>15</sup> such as *n*-butane combined with an "internal" standard technique, i.e. relative to carbon FID-combustion signal, the so-called C-response. Therefore, in the ACTRIS intercomparison experiments all participating laboratories were asked to use certified multicomponent NMHC calibration standards, traceable to the GAW scale, for calibrating their instruments and for performing the quality checks.

<sup>20</sup> Twenty stations or laboratories from nine European countries took part in this AC-TRIS intercomparison exercise. Pressurised cylinders filled with NMHCs in nitrogen (in the following called NMHC\_N<sub>2</sub>) and NMHCs in whole air (in the following called NMHC\_air) were analysed by the different laboratories using their own certified multicomponent NMHC calibration standard. The participants performed their measure-

<sup>25</sup> ments either with GC-FID or GC-MS instrumentation. Additionally, two PTR-MS analysed both NMHC\_ N<sub>2</sub> and NMHC\_air. The performance of the different laboratories was examined with respect to compliance with the DQOs of ACTRIS and GAW (Table 2). Feedback was provided to the participants during a workshop, via analysis of technical details of each instrument, and the provision of recommendations for further



characterisations and improvements. This paper presents the results, discusses problems, and evaluates the different instrumental set-ups focusing on alkanes, alkenes, alkynes, and aromatic compounds.

# 2 Method section

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# 5 2.1 Intercomparison approach

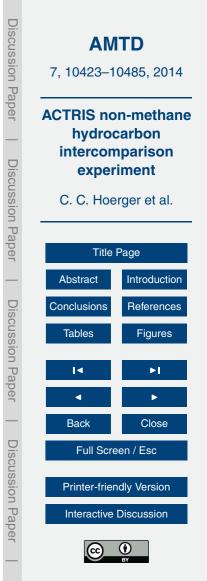
Twenty European laboratories with 23 different GC instruments participated in this NMHC intercomparison exercise in 2012 (Fig. 1, Tables 3 and 4). Additionally, two PTR-MS instrument analysed the NMHC mixtures (instruments are listed in Table 4, for more details see the Supplement). Two separate intercomparsion exercise loops were performed in order to keep the total time required for the exercise within a few months. All participants received one cylinder filled with NMHC\_N<sub>2</sub> and with NMHC\_air.

It should be pointed out that the "Perkin Elmer Online Ozone Precursor Analyser" is the only commercially available all-in-one instrument tested in this study. All other instruments use combinations of commercially available parts and custom-built units.

### 15 2.2 Preparation of NMHC mixtures

The two NMHC mixtures NMHC\_N<sub>2</sub> and NMHC\_air were prepared in 10 L "Quantum" passivated aluminium cylinders (Air Products, purchased from National Physical Laboratory (NPL)). NMHC\_N<sub>2</sub> was diluted with nitrogen (quality 5.0 from Linde AG, Germany) from a ~ 100 nmol mol<sup>-1</sup> uncertified mixture of 30 NHMCs (and several monoterpenes) in nitrogen (prepared by NPL for HPB on demand) into two cylinders by HPB.

<sup>20</sup> penes) in nitrogen (prepared by NPL for HPB on demand) into two cylinders by HPB. The resulting mole fractions in NMHC\_ N<sub>2</sub> were ~ 1 nmol mol<sup>-1</sup> (Table 5). The final pressure in the cylinders was ~ 120 bar. NMHC\_air was filled with ambient air (dew point < -30 °C, relative humidity ~ 1 %) from Dübendorf (a suburban area of Zurich, Switzerland) in two 10 L cylinders using a modified oil-free diving compressor (Model



SA-6; RIX Industries, USA) on 31 October 2011. The mole fractions in NMHC\_air ranged from 0.03 to 2.5 nmol mol<sup>-1</sup> (Table 5). The final pressure in the cylinders was  $\sim 80$  bar.

# 2.3 Determination of assigned values (error-weighted means) for NMHC mixtures

Three laboratories (WCC-VOC, HPB, and Empa) assigned values for NMHC mole fractions to the different cylinders before and after the intercomparison. Additionally, these two time-separated measurements were used to assess the stability of the NMHC mixtures. All three laboratories used certified NMHC calibration standards from the GAW Central Calibration Laboratory for NMHCs (NPL). The NMHC mole fractions were usu-

Central Calibration Laboratory for NMHCs (NPL). The NMHC mole fractions were ally assigned as error-weighted means (Barlow, 1989; Bronštejn, 2007).

The error-weighted mean uses the uncertainty *u* of the measurements as weight  $w_i = 1/u^2$  and calculates the mean value *X* as follows:

$$X_{\text{error-weighted}} = \sum (w_i \cdot x_i) / \sum (w_i)$$

where  $x_i$  = measured value.

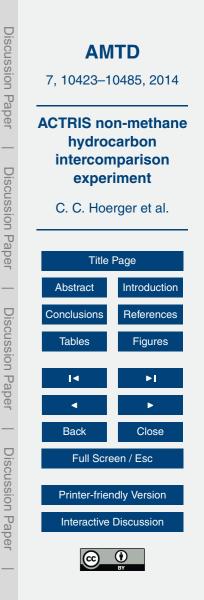
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For measurement uncertainty, it can be distinguished between internal and external uncertainty. If values with the same systematic uncertainties of a single GC instrument are compared, then the internal uncertainty  $u_{internal}$  is considered

$$u_{\text{internal}} = 1/\sqrt{\sum (w_i)}$$

<sup>20</sup> When comparing results from different GC systems with different systematic uncertainties, additionally the external uncertainty  $u_{\text{external}}$  is calculated as weighted deviation from the weighted mean value

$$u_{\text{external}} = \sqrt{\left(\sum \left(w_i \cdot (x_i - X_{\text{error-weighted}})^2\right) / \left((n-1) \cdot \sum (w_i)\right)\right)}$$
10430



(1)

(2)

(3)

where n = number of laboratories.

As with three laboratories, or for some compounds only two, the deviations from the mean may accidentally be very small. Thus, as estimate of the uncertainty the maximum value of the internal and the external uncertainty was chosen. To obtain the sepanded uncertainty of the error-weighted mean, the uncertainty value was multiplied by two (corresponding to  $2\sigma$ ) (Table 5).

For 1,3-butadiene and isoprene a mole fraction drift between the measurements before and after the intercomparison was observed in NMHC\_air. Thus, instead of the error-weighted mean, the arithmetic mean of the measurement was determined as follows:

$$X_{\text{arithmetic}} = \left(\sum (x_i)\right)/n$$

The uncertainty of the arithmetic mean is calculated as the standard deviation of the measurements  $x_i$ :

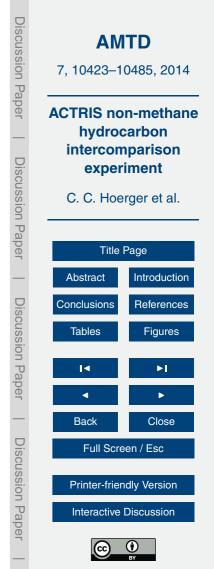
$$u_{\text{arithmetic}} = \sqrt{\frac{\sum (x_i - X_{\text{arithmetic}})^2}{n-1}}$$

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The measurements of the three laboratories agreed within 3 and 5% for NMHC\_N<sub>2</sub> and NMHC\_air, respectively. Exceptions to this were ethylbenzene (up to 8% in NMHC\_N<sub>2</sub>), o-xylene (up to 9% in NMHC\_N<sub>2</sub> and 8% in NMHC\_air), and 2,2-dimethylbutane (up to 15% in NMHC\_air). Although HPB and Empa were assigning mole fractions to the NMHC mixtures before and after the intercomparison, their data
 from determinations within the intercomparison itself are also displayed in the figures and tables together with those of other participants, although their data cannot be treated as purely blind intercomparison results.

### 2.4 Measurement approach

A detailed measurement guideline was provided to the participants to ensure consistent and comparable measurements of the NMHC mixtures. All participants used the



(4)

(5)

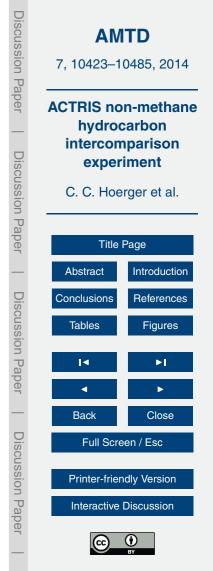
same provided pressure regulators (model 206A from Scott Specialty Gases, USA) and transfer lines (Silcosteel<sup>®</sup>, 1/16", ~ 2.5 m). At least 24 h before the measurement the pressure regulator was mounted onto the gas cylinder and connected to the transfer line. Afterwards, the regulator and the transfer line were flushed three times and an initial leak test was performed (observation of pressure during 10 min). The pressure regulator and the transfer line were kept pressurized for at least 24 h (with closed cylinder valve) for equilibration of surfaces. Additionally, this setup served as static leak test.

All participants were asked to quantify the NMHCs using their own calibration stan-<sup>10</sup> dard (Table 4). The composition and the mole fractions in the cylinders were unknown to all participants. The measurement procedure was the following: at least 3 calibration standard measurements, 5 measurements of NMHC\_N<sub>2</sub>, 5 measurements of NMHC\_air, at least 3 calibration standard measurements, and a zero-gas measurement before and after the NMHC mixture measurements. Fourteen participants per-<sup>15</sup> formed their analysis with GC-FIDs and nine with GC-MSs. More information about the instruments is given in Table 4. In this paper, results for 27 and 35 NMHCs are shown for NMHC\_N<sub>2</sub> and NMHC\_air, respectively. The 3 trimethylbenenes and the monoterpenes present in NMHC\_N<sub>2</sub> were not investigated in this intercomparison paper. The assigned NMHC mole fractions (with expanded uncertainties) are given in Table 5.

### 20 2.5 Data quality objectives (DQOs) for NHMC measurements

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In the WMO GAW Report No. 171 (WMO, 2007b) general DQOs for different priority VOCs were defined (Tables 1–2). Within the framework of ACTRIS, the list of priority compounds was expanded and more challenging DQOs (ACTRIS DQOs) were defined (Tables 1–2). Overall, ACTRIS DQOs are about a factor of two stricter as DQOs from GAW. The ACTRIS DQOs were introduced in order to better detect trends of NMHCs, which in recent years declined between 1 and 8% year<sup>-1</sup> in Europe (Solberg, 2012, 2013, and references therein). These ACTRIS DQOs were presented and discussed at the 4th WMO GAW VOC Expert Group Meeting (York, 2012) and the GAW Scientific



Advisory Group for Reactive Gases Meetings (Garmisch-Partenkirchen, 2013), and it was envisioned to implement the ACTRIS DQOs as new DQOs for GAW. The accepted repeatability of the measurements in ACTRIS is 2% for alkanes, alkenes (including isoprene), alkynes, and aromatics, and 5% for monoterpenes. For the uncer-

tainty, the accepted deviation from a reference value is set to 5 % for alkanes, alkenes (including isoprene), alkynes, and aromatics, and to 10 % for monoterpenes. For mole fraction below 0.1 nmol mol<sup>-1</sup> an absolute value of 0.005 nmol mol<sup>-1</sup> is accepted as uncertainty, 0.01 nmol mol<sup>-1</sup> for monoterpenes. In the results section the measurement performance is compared against both DQOs ACTRIS as well as GAW (Table 2).

# 10 2.6 Expanded uncertainty determination of NMHC measurements

In order to have comparable uncertainty calculations for all measurements (with coverage factor k = 2), all participants were asked to submit their results with expanded combined uncertainties, determined following the concept of the "Guide to the Expression of Uncertainty in Measurements" (JCGM, 2008).

The expanded combined uncertainty  $\Delta \chi_{unc}$  includes both the random errors described by the precision  $\Delta \chi_{prec}$  and the systematic errors  $\Delta \chi_{systematic}$  of the measurement:

$$\Delta \chi^2_{\rm unc} = \Delta \chi^2_{\rm prec} + \Delta \chi^2_{\rm systematic} \tag{6}$$

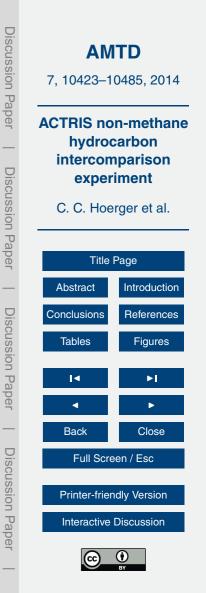
<sup>20</sup> The precision for measured mole fractions is calculated as follows:

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$$\Delta \chi_{\text{prec}} = \frac{1}{3} \text{DL} + \chi \cdot \sigma_{\chi_{\text{sample}}}^{\text{rel}}$$
(7)

where DL = detection limit,  $\chi$  = mole fraction of considered peak, and  $\sigma_{\chi_{sample}}^{rel}$  = relative standard deviation of the sample.

Briefly, systematic errors comprise the error  $\Delta \chi_{cal}$  due to uncertainty of the calibration standard's mole fractions, systematic integration errors (due to peak overlay or



poor baseline separation) in  $\Delta A_{int}$ , systematic errors due to blank correction  $\Delta \chi_{blank}$ , and potential further instrumental problems  $\Delta \chi_{instrument}$  (e.g. sampling line artefacts, possible non-linearity of the MS detector, changes of split flow rates).

Following Gaussian error propagation, the overall systematic error  $\Delta \chi_{systematic}$  is then described as

$$\Delta \chi^{2}_{\text{systematic}} = \Delta \chi^{2}_{\text{cal}} + \Delta \chi^{2}_{\text{int}} + \Delta \chi^{2}_{\text{blank}} \left( + \Delta \chi^{2}_{\text{instrument}} \right)$$
(8)

The systematic error  $\Delta \chi_{cal}$  due to the calibration gas uncertainty is calculated as follows:

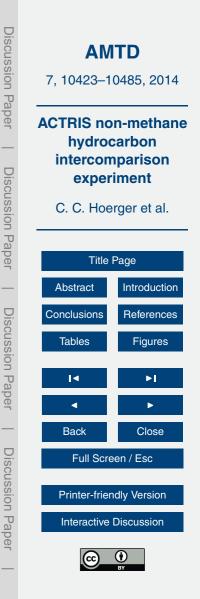
$$\Delta \chi_{\text{cal}} = \frac{A_{\text{sample}} \cdot V_{\text{cal}}}{V_{\text{sample}} \cdot A_{\text{cal}}} \cdot \delta \chi_{\text{cal}}$$
(9)

<sup>10</sup> where  $A_{\text{sample}}$  = peak area of sample measurement,  $A_{\text{cal}}$  = peak area of the calibration standard measurement,  $V_{\text{sample}}$  = sample volume of sample,  $V_{\text{cal}}$  = sample volume of calibration standard, and  $\delta \chi_{\text{cal}}$  = certified standard uncertainty of calibration standard and potential drift of the calibration standard.

The systematic integration errors include

<sup>15</sup> 
$$\Delta \chi_{int}^{2} = \left(\frac{f_{cal}}{V_{sample}} \cdot \delta A_{sample}\right)^{2} + \left(\frac{A_{sample} \cdot V_{cal} \cdot \chi_{cal}}{V_{sample} \cdot A_{cal}^{2}} \cdot \delta A_{cal}\right)^{2}$$
(10)
with  $f_{cal,i} = \frac{V_{cal} \cdot \chi_{cal}}{A_{cal} - A_{blank}}$ 

where  $A_{\text{sample}} = \text{peak}$  area of sample measurement,  $A_{\text{cal}} = \text{peak}$  area of the calibration standard measurement,  $A_{\text{blank}} = \text{peak}$  area of blank measurement,  $V_{\text{sample}} = \text{sample}$ volume of sample,  $V_{\text{cal}} = \text{sample}$  volume of calibration standard,  $\chi_{\text{cal}} = \text{mole}$  fraction of calibration standard peak,  $\delta A_{\text{cal}} = \text{integration error of calibration standard measure$  $ment, and <math>\delta A_{\text{sample}} = \text{integration error of the sample measurement.}$ 



If a blank correction has to be applied, the error of this correction is described as the deviation from the mean blank value:

$$\Delta \chi_{\text{blank}} = \sigma_{\text{blank}} \cdot \frac{1}{\sqrt{n-1}}$$

where the standard deviation  $\sigma_{\text{blank}}$  is calculated from *n* zero-gas measurements. For more details with examples for the calculation of the different errors see ACTRIS VOCs measurement guidelines (http://www.actris.net/Deliverables/tabid/4623/Default.aspx).

## 2.7 C-response for GC-FID systems

A GC-FID system can be characterized for losses or artefacts by making use of the known carbon response, the so-called C-response. When the C-responses for the various NMHC compounds are calculated, they should agree within a few percent. Deviations are often due to poor peak separation, adsorptive losses in the system, or changes at active sites in the adsorbents.

To analyse the performance of the GC-FID systems during this intercomparison, the C-response factors were investigated. The C-response  $R_i$  for each compound *i* was calculated as follows:

$$R_{i} = \frac{A_{i}^{\text{std}} - A_{i}^{\text{b}}}{m_{i}^{\text{std}} N_{i} V^{\text{std}}}$$

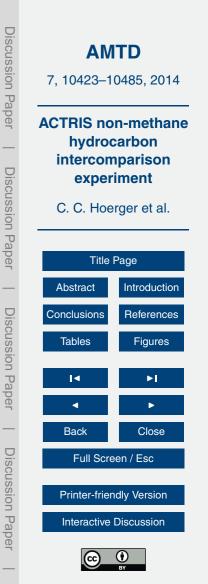
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where  $A_i^{\text{std}}$  and  $A_i^{\text{b}}$  are the peak areas of compound *i* in the calibration standard (std) and the blank (b), respectively,  $m_i^{\text{std}}$  denotes the certified mole fraction of the calibration standard,  $N_i$  the number of C atoms in compound *i* and  $V^{\text{std}}$  the sampled volume of the calibration standard.

When comparing the C-response values in the calibration standard and in  $NMHC_N_2$ , the C-responses should ideally be identical. If this is not the case this



(11)

(12)

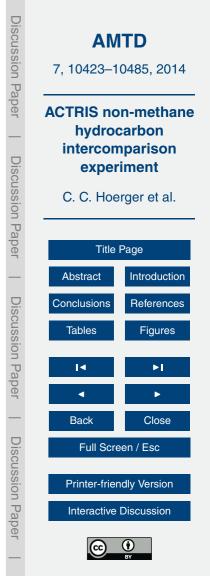
points towards either artefacts in the analytical system (e.g. breakthrough during trapping, adsorptive losses, peak overlap) or in the FID due to sample matrix effects influencing the flame. For easier comparison, the C-responses were normalised by the average C-response of the available  $C_4$ – $C_6$  alkanes (highlighted in yellow in Fig. 4). For two-column systems the average C-response of the second column was determined using  $C_7$ – $C_8$  alkenes, benzene, and toluene (highlighted in green in Fig. 4). If an individual C-response deviated by more than 10 % from the average C-response it was not considered in the normalisation process.

## 3 Results and discussion

<sup>10</sup> The compliance of the results with ACTRIS and GAW DQOs (Table 2) is shown for each participant and compound in Figs. 2 and 3 and Tables 6 and 7 for NMHC\_N<sub>2</sub> and NMHC\_air, respectively. In addition, the C-responses were calculated for GC-FID systems and are depicted in Fig. 4. The repeatability of the NMHC mixture measurements for FID- and MS-systems are summarised in Tables 8 and 9 and are compared to ACTRIS and GAW DQOs (Table 2).

Most systems performed well for the measurements of NMHC\_N<sub>2</sub>. Nearly 90% of all results were within the GAW DQOs and even nearly 60% within the ACTRIS DQOs (Fig. 2, Table 6). The best performance for this mixture with mole fractions ~ 1 nmol mol<sup>-1</sup> was achieved for alkanes. Approximately 80% of the submitted data for C<sub>2</sub>-C<sub>3</sub> and C<sub>8</sub>-alkanes were even within the ACTRIS DQOs (Fig. 2, Table 6). Since alkanes are rather stable, this result was somewhat expected. However, C<sub>4</sub>-C<sub>7</sub>-alkanes seemed to be more problematic and more deviations to the assigned mole fractions were observed (yellow and red colours in Table 6). For alkenes and aromatic compounds the percentages of results within the ACTRIS range were 58 and 47%, re-

For NMHC\_air, more frequent and larger deviations from the assigned values were observed compared to NMHC\_N<sub>2</sub>. Most of the stations reported at least one result



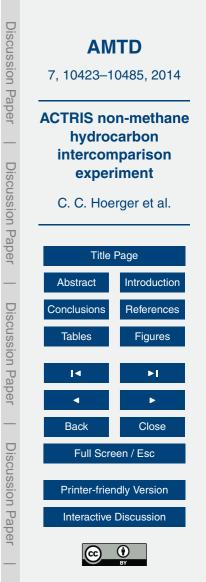
outside the GAW range in their measurements (Table 6). For NMHC\_air nearly 80 % of all results were within the DQOs of GAW, but only 48 % of all results were within ACTRIS DQOs. Compared to NMHC\_N<sub>2</sub> the mole fractions in NMHC\_air varied much more and ranged from 0.03 to 2.5 nmol mol<sup>-1</sup> (Table 5). Ethene, ethane, and toluene had the highest mole fractions (Table 5) and most stations reported these compounds in the GAW range (Table 7). The analysis of  $C_4$ - $C_8$ -alkanes seemed to be more problematic than  $C_2$ - $C_3$ -alkanes (yellow and red colours in Table 7). Except  $C_4$ -alkenes and the xylenes, all other alkenes and the aromatic compounds were mostly reported within the GAW DQOs (Table 7). For mole fractions below 0.1 nmol mol<sup>-1</sup> some good results within the GAW range were achieved for isoprene and  $C_5$ -alkenes (Table 7, Fig. 3). In the following, reasons for non-compliant results will be discussed.

# 3.1 Repeatability of NMHC measurements

The repeatability of the instruments was evaluated as the standard deviation (1*σ*) of the 5 measurements for each NMHC mixture (Tables 8 and 9). The majority of the
<sup>15</sup> participants submitted a repeatability in NMHC\_N<sub>2</sub> within the GAW range, 70% even within the ACTRIS DQOs. The repeatability in this mixture was similar for both detector types (FID and MS). But among the GC-FIDs some of the Perkin Elmer systems had poorer repeatability compared to the other systems, which was mainly related to the chromatographic resolution (see Sect. 3.9 "chromatography resolution"). The poorest repeatability in NMHC\_N<sub>2</sub> was achieved for ethyne, 2,2,4-trimethylpentane, and 2-methylbutane (Table 8) mainly due to poor chromatographic resolution.

For NMHC\_air a similar repeatability within the GAW DQO range was observed as for NMHC\_N<sub>2</sub>, but the repeatability within the ACTRIS DQOs was 10% lower compared to NMHC\_N<sub>2</sub>. As for NMHC\_N<sub>2</sub> the repeatability results were independent of the detector types. Additionally to 2.2.4 trimethylapatters and 2 methylbytens the other

<sup>25</sup> the detector types. Additionally to 2,2,4-trimethylpentane and 2-methylbutane the other  $C_6$ -alkanes had poor repeatability in NMHC\_air due to poor chromatographic resolution. The poorer repeatability was not directly related to lower mole fractions, e.g. below



0.1 nmol mol<sup>-1</sup> (see compounds marked with asterisk in Table 9). As a general feature, the level of repeatability is more related to individual systems than compounds.

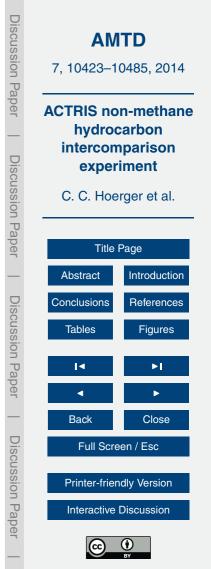
# 3.2 Uncertainty estimations of the NMHC measurements

Only the participants DOU, KOS (both systems), WCC-VOC, RIG, HPB (both systems),
JFJ, MHD, NILU, and ZSF gave a complete analysis of their uncertainties. All other participants calculated their measurement uncertainties only partially (e.g. only precision). Several participants reported smaller uncertainties in NMHC\_air compared to NMHC\_N<sub>2</sub>, e.g. YRK, where the instrument has notably poorer repeatability for dry nitrogen compared to humid air. For values outside the GAW DQOs some participants
were aware that their measurements had larger uncertainties due to e.g. co-elution with other compounds (yellow colours in Tables 6 and 7). Generally, for most stations and compounds the uncertainties were often underestimated and do not comprise the deviation from the assigned values (Fig. 5). This needs to be improved in programmes like GAW and EMEP, as realistic uncertainty estimation is essential for user, e.g. in model validation.

# 3.3 Calibration standards

The participants calibrated their NMHC measurements either against certified multicomponent NMHC calibration standards or against whole air working standards, which in turn are related to a certified multicomponent NMHC calibration standard (CMN and Medusa systems). The systems using a NPL standard for direct calibrations (Table 4) generally exhibited a good performance. The mole fraction range of the NPL mixture (e.g. 2, 4, or 10 nmol mol<sup>-1</sup>) apparently did not affect the quality of the results (Figs. 2 and 3, Tables 7 and 8). The systems FZJ\_B, FZJ\_A, and PUY, which showed slightly poorer results, used different certified NMHC calibration standards (Ta-

<sup>25</sup> ble 2). However, these results were also affected by other instrumental issues (e.g. chromatographic resolution, non-linearity of MS-detector) and therefore, the quality of



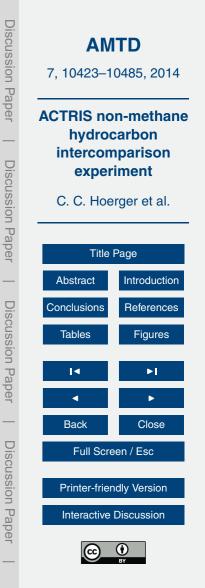
the calibration standards different from NPL (the GAW Central Calibration Laboratory for NMHCs) cannot be assessed. Nevertheless, FZJ\_B underestimated the mole fractions of some compounds mainly due to a different calibration procedure performed during the intercomparison (direct calibration instead of a dilution of a 100 nmol mol<sup>-1</sup>

 calibration standard). This is obvious from the comparison of C-responses for propene, 1,3-butadiene, and ethyne between NMHC\_N<sub>2</sub> and the Apel-Riemer standard used for calibration (Fig. 4n).

It has to be mentioned that for some stations the deviations from the assigned values observed between NMHC\_N<sub>2</sub> and the NPL calibration standard used at the sites cannot be explained in a simple way as both comprise the same mixture and manufacturer, and thus, the deviations should be the same within the repeatability of the instruments. The fact that this was not the case for some participants and compounds, points to unidentified sample transfer issues.

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- The Medusa instruments (JFJ, MHD, and NILU) tended to overestimate the NMHC <sup>15</sup> mole fractions (Figs. 2 and 3, Tables 7 and 8). However, the excellent repeatability suggests that the systems run much better than the deviations indicate. Thus, a significant issue might arise from the fact that Medusa instruments and CMN are calibrated with whole air working standards. Compared to direct calibration this has two complications: a two-stage calibration and the more complex composition of the calibration gas. Such
- <sup>20</sup> problems were reported by CMN, who indicated issues with the calibration and the stability of the whole air working standard. Due to time constrains of the intercomparison exercise timetable the NPL calibration standard and the whole air working standard were not fully characterised. Therefore, the submitted mole fractions of CMN were largely affected and numerous reported values were outside the GAW DQOs. Thus,
- <sup>25</sup> direct calibration by calibration standards with certified NMHC mole fractions appears superior to whole air working standards for NMHCs.



# 3.4 FID systems

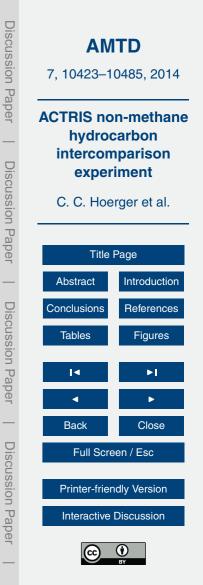
In order to better understand the characteristics of the GC-FID systems, the Cresponse factors for the calibration standards and NMHC\_N<sub>2</sub> were calculated at the different sites (Fig. 4). If an instrument runs correctly, the normalised C-responses of the various compounds will be ~ 1 (Burns et al., 1983; Dietz, 1967; Faiola et al., 2012; Gong and Demerjian, 1995; Scanlon and Willis, 1985; Sternberg et al., 1962) and the C-responses of both calibration standard and NMHC\_N<sub>2</sub> will be equal. Several GC-FID systems tend to slightly underestimate NMHC\_N<sub>2</sub> compared to the calibration

- standard. This was observed by the lower normalised C-responses for NMHC\_N<sub>2</sub> compared to the calibration standards, as well (Fig. 4). Even more surprising was the fact that in some of the systems employing two columns, a lower normalised C-response for NMHC\_N<sub>2</sub> compared to the calibration standard was observed on only one column e.g. AUC (on the PLOT column) and DOU (on the CP-Sil column) (Fig. 4a, h). The latter excluded sample transfer problems from the cylinder to the GC, but pointed towards
- systematically different carrier or detector sensitivity conditions between analyses of calibration standard and NMHC\_N<sub>2</sub>. Overall, these discrepancies cannot be explained as general features, but must be related to individual technical issues of the respective GC systems.

In general, if the normalized C-response factors from the calibration standard and the NMHC\_N<sub>2</sub> differ from each other (Fig. 4) or from the expected value of 1, the possible reasons for this are manifold. It includes losses of sample due to breakthrough, incomplete desorption of losses on walls, poor chromatographic resolution with inadequate peak separation or shape, and other artefacts (e.g. water management). These possible reasons are addressed in the sections below.

#### 25 3.5 Problems with C<sub>2</sub>–C<sub>3</sub>-hydrocarbons

Most participants reported  $C_2-C_3$ -hydrocarbons within the ACTRIS DQOs in NMHC\_N<sub>2</sub> (Table 6, Fig. 2). However, a few systems reported  $C_2-C_3$ -hydrocarbons

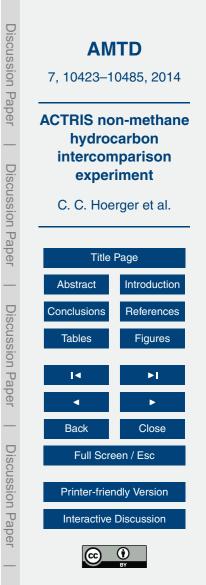


values even outside the GAW range. The systems of AUC (only for ethene and propene), HAR, PAL, SMK, and IPR showed losses of C<sub>2</sub>–C<sub>3</sub>-hydrocarbons in the normalised C-response plots, and ZSF and AUC (only for ethane) gave enhanced values (Fig. 4a-f). All these six mentioned systems used a Perkin Elmer Turbomatrix, which <sup>5</sup> contain an Air Toxics/Air Monitoring trap, apply a 2 mL min<sup>-1</sup> outlet split between trap and column, and have a two columns configuration with Deans switch (Table 4). Sample breakthrough could be a specific issue of the Perkin Elmer trap for these compounds. Badol et al. (2004) reported breakthrough for ethene and ethyne when the sampling volume exceeded 900 mL. However, no systematic influence of sample volume (up to 1360 mL) and trapping temperature (-40 or -30 °C) could be identified (Table 4). For 10 example IPR used -30°C as adsorption temperature and a very large sample volume (1360 mL) but showed only moderate loss of C<sub>2</sub>-hydrocarbons compared to e.g. SMK with 500 mL sample volume and larger losses (Fig. 4). For ZSF, the C-responses for the  $C_2-C_3$ -hydrocarbons were even enhanced (> 1) compared to all other hydrocarbons (Fig. 4e). This might be due to the displacement to 2650 m a.s.l. of the instrument 15

shortly before this intercomparison exercise (see Sect. 3.11 "other issues"). Another explanation for decreased C-responses for  $C_2-C_3$ -hydrocarbons could be a split issue during column injection. If during thermodesorption a pressure pulse builds up the split ratio might vary during the injection period causing different split ratios for high and low volatile hydrocarbons. Further this pressure pulse could influence the

Deans switch. However, it is hard to imagine that this really causes such a substantial flow change in the Deans switch. The systems of DOU and KOS\_A with Deans switches, but with different thermodesorber (Markes and Entech, respectively), did not show losses of  $C_2$ – $C_3$ -hydrocarbons. With these results it is not possible to distinguish between split and trap issues and this certainly needs further investigation.

In NMHC\_air the results of the low boiling alkanes (up to  $C_5$ ) were more scattered compared to NMHC\_N<sub>2</sub> (Figs. 2 and 3) mainly due to limited chromatographic resolution (see Sect. 3.9 "chromatographic resolution"). Despite these apparent losses in specific systems (C-response, Fig. 4), most determined mole fractions of the NMHC



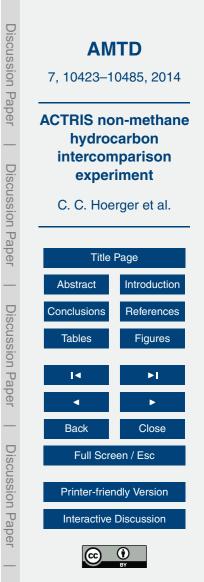
mixtures (Fig. 5) did not show deviations for the  $C_2-C_5$ -alkanes. Only WCC-VOC reported 50% reduced ethane results (Fig. 5j) in NMHC\_air, whereas C-responses did not indicate any losses (Fig. 4h), thus, indicating specific matrix problems in NMHC\_air (see PTR-MS results in the Supplement).

Low boiling alkenes (C<sub>2</sub>-C<sub>5</sub>) showed partly substantial deviations to the assigned mole fractions in the AUC, PAL, SMK, ZSF, and IPR results, especially in NMHC\_air (Figs. 3 and 4a, 4c-f). While the aforementioned problems, breakthrough and/or split-injection, definitely played a role, additionally the low alkene mole fractions in NMHC\_air and, in case of KOS\_A poor chromatography resolution contributed to these deviations from the assigned mole fractions.

#### 3.6 Ethyne

For ethyne large differences in the C-response factors (values between 0.3–1.4) were observed for the different stations (Fig. 4). Furthermore, large variations (up to 0.4) between the two C-responses (calibration standard and NMHC\_N<sub>2</sub>) were evident. Based on the literature (Dietz, 1967; Scanlon and Willis, 1985; Sternberg et al., 1962) the effective carbon number is between 2 and 2.6. Thus, in the normalised C-response figures ethyne is expected to be 1 or higher. This was actually observed for DOU, YRK, WCC-VOC, and RIG. Deviations between the laboratory standard and the AC-TRIS NMHC\_N<sub>2</sub> were observed at ZSF, DOU, HPB\_A, and FZJ\_B. Since in ZSF and

- in FZJ\_B the deviations were not specific to ethyne but a general phenomenon for many compounds both stations are not further considered here. The normalised Cresponse of ethyne in the calibration standard of IPR was substantially lower than that of other stations and may have been due to a pressure regulator inappropriate for ethyne (Fig. 4f). Finally, the instruments at DOU and HPB\_A had in common that both
- employ an Al<sub>2</sub>O<sub>3</sub>/KCI-PLOT column. However, other stations using the same type of column (YRK, RIG) did not show this feature. We currently speculate about slightly different matrices between the calibration standard and NMHC\_N<sub>2</sub> causing different



interactions with active sites of the specific PLOT column, resulting in more or less losses.

Together with ethene, ethyne is the most difficult compound to be retained in Air Toxics/Air Monitoring traps (Badol et al., 2004). As AUC, HAR, PAL, SMK, ZSF, and KOS\_A employ this type of traps, a breakthrough might be possible. However as already discussed no conclusive behaviour, e.g. higher losses for higher sample volume and higher trapping temperature, was observed.

Ethyne C-responses are highly variable and indicate losses potentially due to individual reasons or combinations of breakthrough and split injection. Despite these losses observed in the C-response factors, the difference to the assigned mole fractions were minor to moderate in the NMHC mixtures (Figs. 2 and 3, Tables 6 and 7), indicating reproducible losses in the different NMHC mixtures during this intercomparison exercise.

This shows that it is essential to have ethyne in the calibration standard for direct calibration. However, there is a need for thorough testing as i.e. real ambient air samples with higher humidity might result in higher breakthrough.

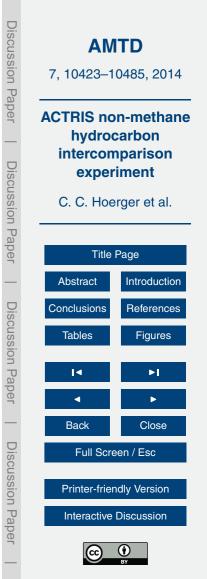
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# 3.7 Alkene artefacts

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For alkene measurements, the C-responses and the results of the measurement of NMHC\_N<sub>2</sub> indicated no substantial problems (except for the losses explained in the previous section) (Fig. 4). However, in NMHC\_air alkenes exhibited largest differences to the assigned values (Table 6, Fig. 5). Instruments using a Nafion<sup>®</sup> Dryer indicated blank values of up to 0.35 nmol mol<sup>-1</sup> for C<sub>2</sub>–C<sub>3</sub>-alkenes and up to 0.1 nmol mol<sup>-1</sup> for C<sub>4</sub>-alkenes. Combined with the fact that the mole fractions of C<sub>4</sub>–C<sub>5</sub>-alkenes were in the range between 0.02 and 0.12 nmol mol<sup>-1</sup> it is expected that substantial differences to the assigned values occur due to blank issues (Table 10). For ethene and propene,

however, due to the much larger mole fractions (up to 2.5 nmol mol<sup>-1</sup>) and the smaller blank values (up to 0.25 nmol mol<sup>-1</sup>) such effects were comparably minor.

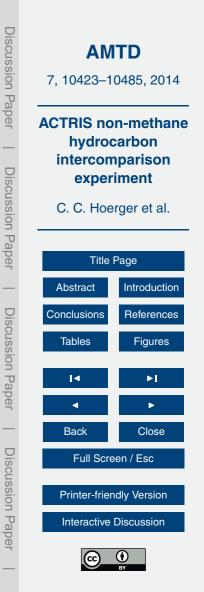


When using a Nafion<sup>®</sup> Dryer to remove humidity from the sample, potential artefacts in  $C_2-C_4$ -alkenes may occur depending on the status of the Nafion<sup>®</sup> Dryer (Gong and Demerjian, 1995; Plass-Dülmer et al., 2002, and references therein). Frequently in zero-gas measurements butene peaks (for 1-butene, *trans*-2-butene, and *cis*-butene) (Table 10) are observed due to the Nafion<sup>®</sup> Dryer and these blank values have to be subtracted in calibration or ambient air measurements. Not all participants submitted blank values, but for those who submitted blanks the values were subtracted. Most participants were aware of the effects of a Nafion<sup>®</sup> Dryer and reported larger uncertainties of their values (Tables 6 and 7).

#### 10 3.8 Losses of aromatic compounds and C<sub>6</sub>–C<sub>8</sub>-alkanes

The C-responses for the C<sub>7</sub>-C<sub>8</sub>-alkanes and for the aromatics were lower than 1 (Fig. 4) indicating losses in the analytical system. Lower C-responses were observed either in both, calibration standard and NMHC\_N<sub>2</sub> (Fig. 4; AUC, PAL, SMK, IPR YRK (except benzene), RIG, FZJ\_B, and less evident in HPB\_A), or only in NMHC\_N<sub>2</sub>
<sup>15</sup> (Fig. 4; HAR, DOU, and HPB\_B). This effect was apparent in both round-robin loops. However, this is not a C-response issue for aromatics, because in many systems not all aromatics showed a reduced C-response (Fig. 4; KOS (both systems), WCC-VOC, for benzene: AUC, HAR, HPB (both systems), RIG, YRK) and several other systems showed only a reduced C-response for NMHC\_N<sub>2</sub> (Fig. 4; HAR, DOU, and HPB\_B).

- For these systems, systematic problems like insufficient desorption from the trap or adsorptive losses in the GC-system can thus be excluded, but adsorptive losses only in NMHC\_N<sub>2</sub> might have occurred due to insufficient equilibration time and flushing procedure of the pressure regulator and transfer lines. RIG reported lower C-responses compared to the calibration standard for  $C_6-C_8$ -alkanes and aromatics (Fig. 4k). This
- was related to insufficient desorption temperature due to ice on the outer side of the Peltier cooled trap which has built up during trapping.



In general, too low desorption temperature from the trap can be excluded for the glass beads traps (70–130 °C, Table 2). For the Air Toxics traps no losses of aromatics were observed for HAR (trap at 320 °C) (Fig. 4a). By contrast, losses prevailed at up to 380 °C (IPR), which were consequently not due to too low desorption temperature

 <sup>5</sup> (Fig. 4f). The YRK results indicated losses, which were not due to desorption temperature (Carbopack B and Carboxen 1000 at 350 °C), but were ascribed to adsorption on newly installed stainless steel transfer lines. In the slightly more humid NMHC\_air, YRK achieved relatively higher aromatic mole fractions compared to the assigned values (Figs. 2 and 3) indicating humidity passivation of active surface sites. Thus, losses
 were only apparent in dry calibration standards (Fig. 4g).

Different hypotheses to explain losses of aromatics and  $C_6-C_8$ -alkanes did not result in simple and conclusive explanations. Losses were observed in individual systems when desorption was not sufficient, when adsorptive losses on inappropriate surfaces like newly installed stainless steel lines (heated or not) occurred, or when dry sample gases were analysed. As long as a decrease in the C-response is evident in both the calibration and NMHC\_N<sub>2</sub> the submitted mole fractions did not differ much from the assigned values (e.g. YRK and AUC) (Fig. 4, Table 7).

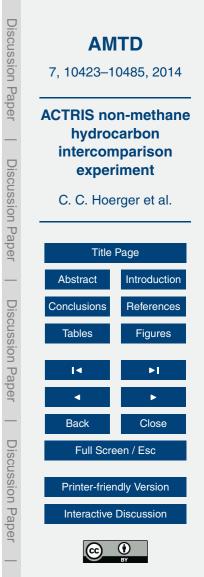
# 3.9 Chromatographic resolution

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Poor peak separation or peak shape (tailing) can influence the peak integration and the results. Both effects can mask other problems if the sample matrix is rather complex, such as in NMHC\_air, where peak overlap is likely to occur in FID-systems. Due to difference in humidity compared to NMHC\_N<sub>2</sub> and to substantially different peak sizes in ambient air, the chromatographic resolution, e.g. peak overlap, for NMHC\_air differed considerably from the characteristics seen in NMHC\_ N<sub>2</sub> (Figs. 2 and 3, Tables 6 and

<sup>25</sup> 7). For some stations this led for example to the overestimation of alkanes in NMHC\_air in comparison with NMHC\_N<sub>2</sub>.

A good example is the comparison between AUC and HAR, which have an identical set-up of their instruments. The chromatogram for the PLOT-column of AUC showed

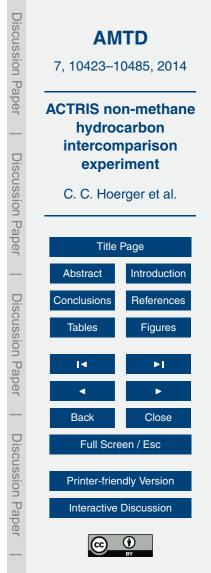


no baseline separation and many peak tailings for  $C_2-C_6$ -hydrocarbons (alkanes and alkenes) (Fig. 6a). In contrast, HAR has a good chromatographic resolution of these compounds on the PLOT-column (Fig. 6b). The main reason for these substantial differences in the chromatography could be attributed to column degradation. KOS\_A had

- <sup>5</sup> no baseline resolution for methane, ethane, and ethene in NMHC\_air. This led to an overestimated ethane mole fraction due to peak overlap (Fig. 6c). This effect was accelerated by a shorter initial hold time of only 5 min compared to the similar system of PAL with a hold time of 15 min (Table 4). The chromatogram of PAL showed a nice baseline separation of methane, ethane, and ethene (Fig. 6c). Results by FZJ\_B also showed authorities deviation from the application of for the C\_\_C\_\_ elkapse in both NMHC.
- <sup>10</sup> substantial deviations from the assigned values for the C<sub>2</sub>–C<sub>4</sub>-alkanes in both NMHC mixtures due to non-baseline separation especially (DB1 column of 120 m length, start at -60 °C for 8 min). Further investigations following this ACTRIS intercomparison exercise related these problems to aging effects of the column. After using a new column, the peaks were baseline-separated and the deviations were not observed anymore.
- Insufficient C<sub>4</sub>-C<sub>6</sub> peak separation often contributed to results outside the GAW DQOs in NMHC\_air, especially for 2-, 3-methylpentane, 2,2-, 2,3-methylpentane, and 2-methyl-2-butene (Figs. 2 and 6, Tables 6 and 7). Similar results were reported in the AMOHA intercomparsion: some participants had problems in separating 1-butene from 1,3-butadiene, *cis*-2-butene from 2-methylbutane, and isoprene from the methyl pen tanes (Plass-Dülmer et al., 2006; Slemr et al., 2002). Overall, good chromatography is
- tanes (Plass-Dülmer et al., 2006; Slemr et al., 2002). Overall, good chromatography is the basis for good measurement results.

### 3.10 MS systems

Compared to FID systems, MS systems allow a better compound identification and peak separation at the cost of detector stability. With few exceptions, HPB\_B (MS) reported the NMHCs within the ACTRIS DQOs. The instrument is operated with a FID running in parallel to the MS detector. While the FID revealed a stable behaviour of the instrument, in the MS signal drifts were observed by HPB. Thus, in routine measurements the MS is tuned weekly and every air sample is accompanied by a calibration



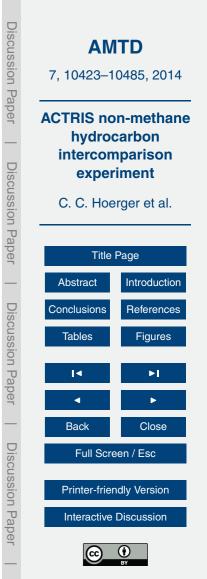
measurement. In fact the HPB\_B (MS) system was the best performing MS system in this intercomparison indicating that NMHC measurements within the ACTRIS DQOs are reliably achievable by MS systems.

The comparably larger deviations to the assigned values seen in NMHC\_N<sub>2</sub> and NMHC\_air by CMN and the Medusa systems were mainly due to calibration issues (the use of whole air working standards instead of certifies multicomponent NMHC calibration standards, see Sect. 3.3 "calibration standards"). Nevertheless, the very good repeatability of the Medusa systems indicates the potential to perform high quality NMHC measurements (Fig. 5v–x).

- <sup>10</sup> FZJ\_A (MS) was optimized to perform fast chromatography as the instrument is employed in aircraft measurements. The sample volume is kept small in order to reduce the sampling time. With a chromatography time of 3 min, the peak resolution can hardly be compared to the other GC systems. Nevertheless, FZJ\_A performed fairly well for normal alkanes and aromatics, whereas branched alkanes and alkenes showed larger
- <sup>15</sup> deviations from the assigned values. Whether this was due to problems in the rather complex 74 components standard in the 0.1 to 10 nmol mol<sup>-1</sup> range (Apel Riemer Environmental Inc.) cannot be judged from the available data. Further, breakthrough of C<sub>4</sub>-compounds was reported by FZJ\_A. In general, the blank chromatogram revealed many peaks (chromatogram not shown), which possibly affected the results, especially
   <sup>20</sup> in NMHC air.

For NMHC\_N<sub>2</sub> the MS systems of PUY and SIR reported most values within the GAW or ACTRIS DQOs, whereas for NMHC\_air some more reported values were outside the GAW range (Tables 6 and 7). For PUY this was probably due to drifting calibration standard measurements (up to 20%) and poor repeatability (Tables 8 and

9); for SIR it was probably connected to blank value measurements (relatively high blank values compared to assigned values, Table 10) and poor stability of the calibration measurements. The MS of SMR clearly underestimated the mole fractions in NMHC\_N<sub>2</sub> (Table 6), except for isoprene. In contrast, for NMHC\_air SMR reported all values within the GAW or ACTRIS range (Table 6). SMR reported that their calibration



measurements were not linear and they corrected for their calibration for non-linearity. Furthermore, the submitted data of the calibration measurements were not reproducible, whereas the two NMHC mixtures were. In summary, as shown for the MS systems, the calibration and non-linearity are important issues, which have to be handled with most care when using a GC-MS system for the measurements of NMHCs.

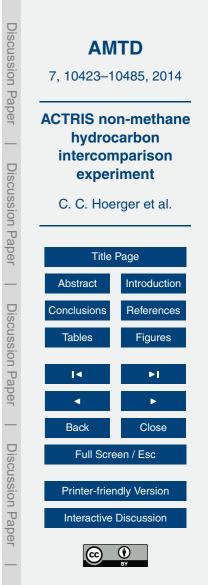
## 3.11 Other issues

During the ACTRIS intercomparison only very dry NMHC mixtures were analysed and therefore a full performance assessment of water management systems cannot be made, but some basic conclusions can be drawn. Water removal from the NMHC mixture was either achieved by Nafion<sup>®</sup> Dryers, cold traps, or hydrophobic adsorbents at room temperature. The cold trap systems (YRK, WCC-VOC, HPB\_A) exhibited a very good performance and no artefacts in these three systems were observed. Such systems sometimes have a large internal volume for water removal and whilst very suitable for online measurements, they are not so well suited for conditions where limited

- flushing volume is an issue e.g. when analysing limited sample volumes. Overall however, this method appeared superior compared to Nafion<sup>®</sup> Dryers which had significant reported alkene artefacts (see Sect. 3.7 "alkene artefacts"). The use of comparably weaker hydrophobic adsorbents at room temperature indicated no problems for HPB\_ B. However, the weak adsorbents used in HPB\_B are not appropriate for adsorption
- of low boiling NMHCs. Ozone management was not in the scope of this ACTRIS intercomparison study. One specific issue was associated with the ZSF system, which had been brought to 2650 m a.s.l. shortly before this intercomparison. Pressure and flow rates were not properly adjusted and caused some of the deviations.

# 3.12 PTR-MS results

<sup>25</sup> The two NMHC mixtures were analysed with the PTR-MS of SMR II and WCC-VOC. Isoprene in NMHC\_N<sub>2</sub> fitted well inside the ACTRIS DQOs, whereas isoprene in



NMHC\_ air, toluene and benzene in both NMHC mixtures were reported outside the GAW range. The detailed results and some explanation are given in the Supplement.

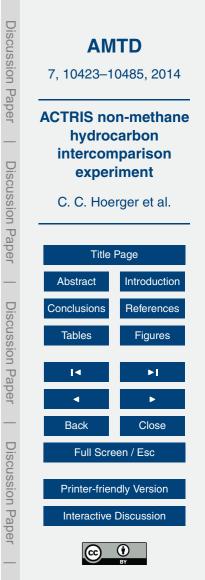
# 4 Conclusions

In the NMHC intercomparison exercise performed in the European infrastructure project ACTRIS a significant number of instruments were capable of measuring NMHC in nitrogen (NMHC\_N<sub>2</sub>) within the ACTRIS quality objectives. 88% of the submitted NMHC values were within the DQOs of GAW and 58% even in the DQOs of ACTRIS with respect to the deviation to assigned values. It should be noted that NMHC\_N<sub>2</sub> was almost identical to the NPL calibration standards used at the stations and a substan-

tial number of deviations was not expected. Participants generally achieved very good repeatability in their measurements in line with the objectives.

In whole air (NMHC\_air) more frequent and larger deviations to the assigned values compared to NMHC\_N<sub>2</sub> were observed (77% of the reported values were within the GAW DQOs, but only 48% were within the ACTRIS DQOs). Considering the complex-

- <sup>15</sup> ity of the matrix and the partly low mole fractions, this is a good result. An important contributor to poor results in NMHC\_air was blank values observed in zero-gas measurements in some of the systems, especially those using a Nafion<sup>®</sup> Dryer. Systems with cold traps did have fewer problems with blank values. The study highlights the importance of good zero-gas measurements to determine realistic blank values to be sub-
- <sup>20</sup> tracted from measurement results. Another factor contributing to the poorer NMHC\_air results is the reduced chromatographic resolution, particularly in the range of C<sub>4</sub>–C<sub>6</sub>compounds. Generally, those systems using direct calibrations in the nmol mol<sup>-1</sup>-range achieved better results than those using whole air working standards. This confirms and emphasises the results found in the AMOHA and GAW intercomparisons (Plass-
- Dülmer et al., 2006; Rappenglueck et al., 2006; Slemr et al., 2002). The two-stagecalibration and more complex matrix in whole air standards introduce additional potential errors. For ethyne losses may occur due to breakthrough in the adsorption trap.

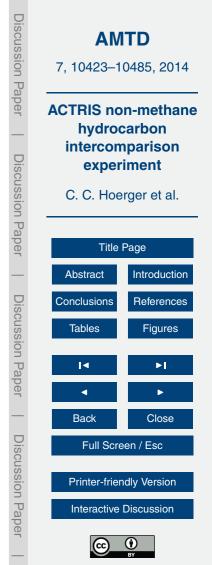


Additionally, ethyne had a specific C-response (1 or higher). Therefore, it is essential to calibrate ethyne directly and carefully characterise the response of the system in dry calibration standard and humid ambient air sample matrices.

- The use of FID C-responses for comparing the quality of the NMHC measurements <sup>5</sup> proved to be a powerful tool. It helped to identify problems in a number of analytical systems. However, as long as a system behaves similarly with different sample gas matrices, deviations in the C-response may cancel, resulting in a correct observation. But this requires thorough testing of the respective GC-systems. Breakthrough is generally an issue for C<sub>2</sub>–C<sub>3</sub>-hydrocarbons in adsorptive traps. Deviations from the expected <sup>10</sup> C-responses for low boiling hydrocarbons were mainly observed in systems using the
- Perkin Elmer Thermodesorber with Air Toxics/Air Monitoring traps. Whether these deviations were due to breakthrough or split injection issues could not be resolved. Many of the participating instruments indicated losses of C<sub>7</sub>–C<sub>8</sub> aromatic compounds, most probably due to adsorptive losses. Despite such losses, many participants achieved
- good results for aromatics, but deviations were slightly larger than in other compound groups. Although generally FID systems achieved better results, good measurements were seen to be possible with GC-MS systems, however, since the MS is less stable than FID more frequent calibrations are required.

An important result of this intercomparison is that most participants substantially <sup>20</sup> underestimated their uncertainties and some participants did not cover the major uncertainty contributions. The results of this intercomparison will help to reassess and better understand the quality of the measurements. Another issue was the occasionally inattentive data submission, with mistakes and incomplete information, which partially yielded erroneous results. While these problems were detected and resolved in the <sup>25</sup> relatively small dataset of this intercomparison, it is still an issue with submission of insufficiently controlled datasets provided to data centres and users.

The "Perkin Elmer Online Ozone Precursor Analyser" is the only commercially available instrument used by five participants in this intercomparison. Although these were not among the best performing in this study, reasonable results can be achieved. We



believe that the ACTRIS DQOs whilst demanding are essential for trend analysis and can be achieved with state-of-the-art measurement performance. Essential for high quality results are experienced operators, comprehensive quality assurance and quality control, well characterised systems, and sufficient man-power to operate the systems and evaluate the data.

# The Supplement related to this article is available online at doi:10.5194/amtd-7-10423-2014-supplement.

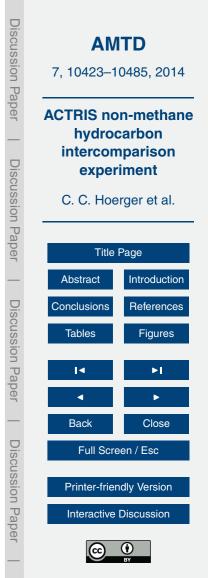
Acknowledgement. The research leading to these results was performed under the ACTRIS Research Infrastructure Project supported by the European Union Seventh Framework Pro gramme (FP7/2007-2013) under grant agreement n. 262254. We acknowledge the Swiss National Air Pollution Monitoring Network (NABEL), the Swiss Federal Office for the Environment (FOEN), Empa, HALCIM (funded by FOEN), and the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG) for their support. The Department of Environment, Food and Rural Affairs (DEFRA) is acknowledged for the funding of the VOC
 measurements in the UK. The Umweltbundesamt Deutschland (Federal Environment Agency, Germany) is acknowledged for their support to the WCC-VOC. J. Jäger and R. Wegener like to thank Deutsche Forschungsgemeinschaft for funding within the priority program HALO (WE-4384/2-2). The LSCE team acknowledges the support from CEA, CNRS and IPSL. The Academy of Finland Centre of Excellence (grant no. 1118615) and the Nordic Centre of Excellence (RAICC are acknowledged for their support.

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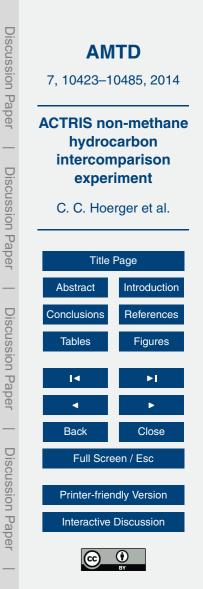
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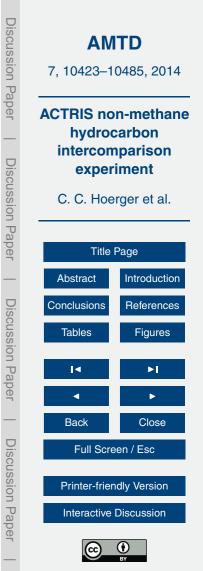
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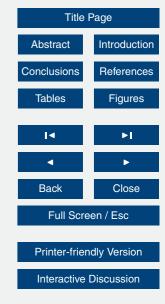
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Table 1. List of priority VOCs as defined in the WMO GAW Report No. 171 (WMO, 2007b) and the list of NMHCs investigated in this paper.

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ethane propane <i>n</i> -butane methylpropane <i>n</i> -pentane 2-methylbutane	opane propane butane <i>n</i> -butane ethylpropane methylpropane pentane <i>n</i> -pentane	Paper   Disci	ACTRIS non-metha hydrocarbon intercomparison experiment		
	2,2-dimethylbutane 2,3-dimethylbutane cyclohexane <i>n</i> -heptane <i>n</i> -octane		Discussion Paper	C. C. Hoe	
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	GAW uncertainty	GAW repeatability	ACTRIS uncertainty	ACTRIS repeatability
alkanes	10%	5%	5%	2%
alkenes incl. isoprene	20 %	15 %	5%	2%
alkynes	15%	5%	5%	2%
aromatics	15 %	10 %	5%	2%
mole fraction $< 0.1$ nmol mol <sup>-1</sup> (ppb)	0.02 ppb	0.015 ppb	0.005 ppb	0.002 ppb

Table 2. GAW and ACTRIS data quality objectives (DQOs).

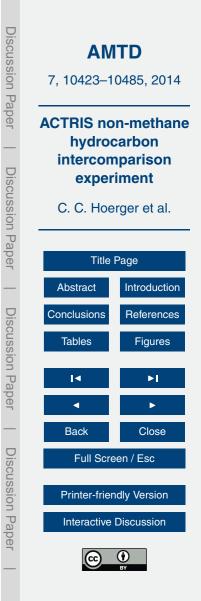


Table 3. Participants of the ACTRIS NMHC intercomparison listed by institution and station site (with acronym). For monitoring networks, it is differentiated between GAW and EMEP (VOC) and their status in the respective network is listed.

Institution	Station site	Acronym	Monitoring n GAW	etworks EMEP (VOC)
Czech Hydrometeorological Institute (Czech Republic)	Kosetice	KOS	regional	×
Finnish Meteorological Institute (Finland)	Pallas	PAL	global	-
	SMEAR II, Hyytiälä	SMR	regional	_
University of Helsinki (Finland)	SMEAR II, Hyytiälä	SMR II	regional	×
Ecole des Mines de Douai (France)	Mines des Douai	DOU	regional*	×
National center for scientific research, Gif-sur-Yvette Cedex (France)	Sirta	SIR	_	-
National center for scientific research, Aubière Cedex (France)	Puy-de-Dôme	PUY	regional*	_
German Weather Service (DWD), Hohenpeissenberg (Germany)	Hohenpeissenberg	HPB	global	_
Research Center Jülich (Germany)	Jülich	FZJ	-	_
Technische Universität München (Germany)	Zugspitze- Schneefernerhaus	ZSF	global	-
Karlsruhe Institute of Technology, Garmisch-Partenkirchen (Germany)	Garmisch- Partenkirchen	WCC- VOC	WCC	-
Umweltbundesamt Station Schmücke (Germany)	Schmücke	SMK	contributing	×
University of Urbino (Italy)	Monte Cimone	CMN	global	-
European Commission Joint Research Centre, Ispra (Italy)	Ispra	IPR	regional	×
National University of Ireland/ University of Bristol (UK)	Mace Head	MHD	global	-
Norwegian Institute for Air Research, Kjeller (Norway)	NILU	NILU	-	-
Swiss Federal Laboratories for Materials Science and Technology	Rigi	RIG	regional	×
(Empa), Dübendorf (Switzerland)	Jungfraujoch	JFJ	global	-
Ricardo-AEA, Harwell/Centre for Ecology & Hydrology (UK)	Auchencorth	AUC	regional	×
	Harwell	HAR	contributing	×
National Centre for Atmospheric Science, University of York (UK)	York	YRK	global	_

WCC: World Calibration Centre; \* in progress, stations are assessed for GAW regional.

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 $\smile$ BY **Table 4.** Analysis methods used in the ACTRIS NMHC intercomparison exercise (stations acronym, instrument, ozone  $(O_3)$  trap, water  $(H_2O)$  trap, preconcentration unit, sample volume, trap adsorbents, re-focus/cryofocus). For acronyms see Table 3.

Acronym	Instrument	O <sub>3</sub> trap	H <sub>2</sub> O trap	Preconcentration unit	Sample vol- ume (mL)	Adsorbents and ad- sorption (ads.) and desorption (des.) temperature	Re-focus/cryofocus and temperatures
GC-FIDs							
Perkin Elme	er systems with l	Deans s	witch				
AUC	Perkin Elmer GC-FID/FID	no	Nafion <sup>®</sup> - Dryer	Perkin Elmer Turbomatrix with online accessory <sup>a</sup>	600	Air Toxics Analyser Trap <sup>b</sup> (ads. at -30 °C, des. at 320 °C)	no
HAR	Perkin Elmer GC-FID/FID	no	Nafion <sup>®</sup> - Dryer	Perkin Elmer Turbomatrix with online accessory <sup>a</sup>	600	Air Toxics Analyser Trap <sup>b</sup> (ads. at -30 °C, des. at 320 °C)	no
PAL	Perkin Elmer GC-FID/FID	no	Nafion <sup>®</sup> - Dryer	Perkin Elmer Turbo- matrix 300 with online accessory <sup>a</sup>	1200	Air Toxics Analyser Trap <sup>b</sup> , mixed bed car- bon (ads. at -40°C, des. at 325°C)	no
SMK	Perkin Elmer GC-FID/FID	no	Nafion <sup>®</sup> - Dryer	Perkin Elmer Turbo- matrix 300 with online accessory <sup>a</sup>	500	TD/ATD Air Monitoring Trap (ads. at -30 °C, des. at 325 °C)	no
ZSF	Perkin Elmer GC-FID/FID	no	Nafion <sup>®</sup> - Dryer	Perkin Elmer Turbo- matrix 650 with online accessory <sup>a</sup>	600	Air Toxics Analyser Trap <sup>b</sup> (ads. at -30 °C, des. at 325 °C)	no
Other system	ms with Deans :	switch					
IPR	Agilent GC- FID/FID	no	Nafion <sup>®</sup> - Dryer	Perkin Elmer Turbomatrix with online accessory <sup>a</sup>	1360	Air Toxics Analyser Trap <sup>b</sup> (ads. at -30 °C, des. at 380 °C)	no
KOS_A	Agilent 7890 GC-FID/FID	no	Nafion <sup>®</sup> - Dryer	Markes UNITY- Thermal Desorber	400	Air Toxics Analyser Trap <sup>b</sup> (ads. at -20°C, des. at 310°C)	no
DOU	Chrompak GC-FID/FID	no	Nafion <sup>®</sup> - Dryer	Entech	360	glass beads (ads. at -120°C, des. at 70°C)	
Two column	systems with s	plit injec	tion				
YRK	Agilent GC- FID/FID	no	Glass volume at –27°C	Markes UNITY-Thermal Desorber	1000	Carbopack <sup>®</sup> B, Carboxen <sup>®</sup> 1000 (ads. at -20°C, des. at 350°C)	no
WCC-VOC	Varian 3800 GC-FID/FID	no	Silcosteel <sup>®</sup> at -30 °C	custom made	400	Carbopack <sup>®</sup> BHT (ads. at -120°C, des. at 200°C)	no

AMTD 7, 10423-10485, 2014 **ACTRIS** non-methane hydrocarbon intercomparison experiment C. C. Hoerger et al. **Title Page** Introduction Abstract Conclusions References Tables Figures < Close Back Full Screen / Esc Printer-friendly Version Interactive Discussion

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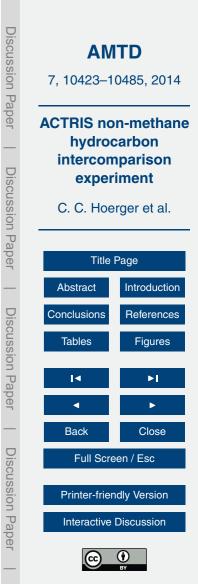
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Acronym	Instrument	O <sub>3</sub> trap	H <sub>2</sub> O trap	Preconcentration unit	Sample vol- ume (mL)	Adsorbents and adsorption (ads.) and desorption (des.) temperature	Re-focus/cryofocus and temperatures
One column s	/stems						
RIG	Agilent GC- FID	no	Nafion <sup>®</sup> - Dryer	custom-made (Adsorp- tion Desorption Unit)	600	Stainless steel tube with fused silica beads, Carboxen <sup>®</sup> 1003, Carboxen <sup>®</sup> 1016, Carbosieve <sup>®</sup> S-III (ads. at -45°C, des. at 235°C)	no
HPB_A	Varian 3800 GC-FID	YES but not used in this exercise	1/8" sulfin- ert U-tube (Restek) at -40°C	custom-made	750	glass beads (ads. at -180°C, des. at 130°C)	no
HPB_B (FID)	Agilent 6890 GC-FID/MS	YES but not used in this exercise	no	custom-made	400 (for nitrogen); 1500 (ambi- ent air)	fritted glass tube with Tenax <sup>®</sup> TA, Carbopack <sup>®</sup> X, Carboxen <sup>®</sup> 569 (ads. at 30°C, des. at 200°C)	Cryofocus on methyl silicone capillary at -180°C, des. at 60°C
FZJ_B	Agilent 6890 GC-FID	if necessary $O_3$ was removed by a SS cap- illary heated to 120 °C prior to sampling in the canister		custom-made (valve unit and cryotrap)	800	glass beads (ads. at -180°C des. at 130°C)	partly re-focussing on column-head at -60 °C
KOS_B	Agilent 6890 GC-FID	no	Nafion <sup>®</sup> - Dryer	Markes UNITY-Thermal Desorber	400	Air Toxics Analyser Trap <sup>b</sup> (ads. at -20 °C, des. at 310 °C)	no
GC-MSs							
CMN	Agilent GC- MS	no	Nafion <sup>®</sup> - Dryer	Markes UNITY-Thermal Desorber	1000	Carbograph <sup>®</sup> 1, Carboxen <sup>®</sup> 1003, Carbosieve <sup>®</sup> SIII (ads. at -30 °C, des. at 310 °C)	no
FZJ_A	Custom- made GC with 5975C inert MSD	42.5 cm Silcosteel <sup>®</sup> , 0.25 mm i.d., 120 °C	no	custom-made (Gerstel)	150	Glas liner with Carbotrap <sup>®</sup> C, Carbotrap <sup>®</sup> B, Carbosieve <sup>®</sup> SIII (adsorption at 30 °C, desorption at 225 °C	focus trap (Carbopack <sup>®</sup> X) (adsorption at 35 °C, desorption at 225 °C)
HPB_B (MS)	Agilent 6890 GC-FID/MS	YES but not used in this exercise	no	custom-made	400 (for nitrogen); 1500 (ambi- ent air)	fritted glass tube with Tenax <sup>®</sup> TA, Carbopack <sup>®</sup> X, Carboxen <sup>®</sup> 569 (ads. at 30°C, des. at 200°C)	cryofocus on methyl sili- cone capillary at -180 to 60°C



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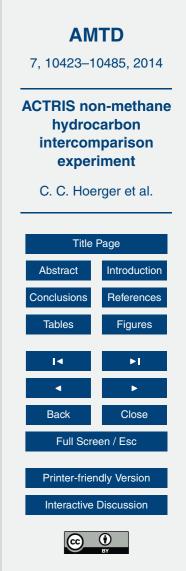
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Acronym	Instrument	0 <sub>3</sub>	H <sub>2</sub> O trap	Preconcentration unit	Sample vol-	Adsorbents and adsorption	Re-focus/cryofocus and
		trap			ume (mL)	(ads.) and desorption (des.) temperature	temperatures
PUY	Perkin Elmer GC-MS	no	no	Perkin Elmer ATD	800 and 1500	Tenax <sup>®</sup> TA, Carbosieve <sup>®</sup> S-III (ads. at 20°C, des. at 280°C)	Tenax <sup>®</sup> TA, Carbosieve <sup>®</sup> (adsorption at -10°C, desorption at 280°C)
SIR	Varian 3800 GC-MS (ion trap)	no	no	Perkin Elmer Turbomatrix	700	Tenax <sup>®</sup> TA (ads. at room temper- ature, des. at 225 °C)	cold trap with Air Toxics (Carbosieve <sup>®</sup> SIII, Carpopack <sup>®</sup> B), (adsorption at 0°C, desorption at 325°C)
SMR	Agilent GC- MS	no	no	Markes UNITY- Thermal Desorber	1800	Tenax <sup>®</sup> TA, Carbopack <sup>®</sup> B, molecular sieve (ads. at 25°C, des. at 300°C)	no
Medusa sys	tems						
JFJ	Agilent GC- MS	no	2× Nafion <sup>®</sup> - Dryer	custom-made	2000	HaySepD <sup>®</sup> (ads. at -160°C, des. at 100°C)	cryofocussing on sec- ond trap with HaySepD <sup>®</sup> (adsorption at -160 °C, desorption at 100 °C)
MHD	Agilent GC- MS	no	2× Nafion <sup>®</sup> - Dryer	custom-made	2000	HaySepD <sup>®</sup> (ads. at -165°C, des. at 100°C)	cryofocussing on sec- ond trap with HaySepD <sup>®</sup> (adsorption at -165°C, desorption at 100°C)
NILU	Agilent GC- MS	no	2× Nafion <sup>®</sup> - Dryer	custom-made	2000	HaySepD <sup>®</sup> (ads. at -165°C, des. at 100°C)	cryofocussing on sec- ond trap with HaysepD <sup>®</sup> (adsorption at -165°C, desorption at 100°C)
PTR-MS							
SMR II	Ionicon Ana- Iytik	no	no	no	continuous flow 0.1 L min <sup>-1</sup>	no	no
WCC-VOC	Ionicon Ana- lytik	no	no	no	continuous flow 0.1 L min <sup>-1</sup>	no	no

SS = stainless steel;

<sup>a</sup> standard online accessory (see Perkin Elmer http://www.perkinelmer.co.uk/content/applicationnotes/app\_gaschromaozoneprecursoranalysis.pdf) including unheated SS lines and valves;

<sup>b</sup> Carbopack<sup>®</sup>B, Carbosieve<sup>®</sup>SIII are the adsorbents of the Air Toxics Analyser Trap (personal communication: M. Dinse, 2014 (Perkin Elmer)).



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**Table 4.** Continued: Analysis methods used in the ACTRIS intercomparison exercise (stations acronym, pre-column, column, column temperature, sample path, injector type, and calibration gas). For acronyms see Table 3.

Acronym	Pre-column (length × inner diam- eter × film thickness)	Column (length × inner diameter × film thickness)	Column temperature	Sample path	Injection type	Laboratory standard
GC-FIDs						
Perkin Eli	mer systems w	ith Deans switch				
AUC	no	$\begin{array}{l} \text{SGE BP-1} \ (50\ \text{m}\ \times\ 0.22\ \text{mm} \\ \times \ 1\ \mu\text{m}), \ Al_2O_3/Na_2SO_4 \\ \text{PLOT} \ (50\ \text{m}\ \times\ 0.32\ \text{mm}), \\ \text{Deans switch} \end{array}$	$\begin{array}{ccc} 45^\circ C & \text{for} & 15\text{min},\\ 5^\circ C\text{min}^{-1} & \text{to} & 170^\circ C,\\ 15^\circ C\text{min}^{-1} & \text{to} & 200^\circ C,\\ \text{hold for } 6\text{min} \end{array}$	SS not heated	outlet split, when trap is heated, set to $2 \text{ mLmin}^{-1}$ , split ratio ~ 1 : 1	30 NMHCs, 4 nmol mol <sup>-</sup> NPL
HAR	no	$\begin{array}{l} \text{SGE BP-1} \ (50\ \text{m}\ \times\ 0.22\ \text{mm} \\ \times \ 1\ \mu\text{m}), \ Al_2O_3/Na_2SO_4 \\ \text{PLOT} \ (50\ \text{m}\ \times\ 0.32\ \text{mm}), \\ \text{Deans switch} \end{array}$	$\begin{array}{ccc} 45^\circ C & \text{for} & 15\text{min},\\ 5^\circ C\text{min}^{-1} & \text{to} & 170^\circ C,\\ 15^\circ C\text{min}^{-1} & \text{to} & 200^\circ C,\\ \text{hold for } 6\text{min} \end{array}$	SS not heated	outlet split, when trap is heated, set to $2 \text{ mLmin}^{-1}$ , split ratio ~ 1 : 1	30 NMHCs, 4 nmol mol <sup>-</sup> NPL
PAL	no	$\begin{array}{l} \text{SGE BP-1 (50 m \times 0.22 mm} \\ \times  1  \mu\text{m}),  \text{Agilent}  \text{GS-} \\ \text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4  \text{PLOT}  (50 \text{ m} \\ \times  0.32 \text{ mm}), \text{ Deans switch} \end{array}$	46 °C for 15 min, 5 °C min <sup>−1</sup> to 170 °C, 15 °C min <sup>−1</sup> to 200 °C	SS	split injection	30 NMHCs, 4 nmol mol <sup>−</sup> NPL
SMK	no	$\begin{array}{l} \text{SGE BP-1 (50 m \times 0.22 mm} \\ \times 1 \ \mu\text{m}),  \text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4 \\ \text{PLOT (50 m \times 0.32 mm \times 5 \ \mu\text{m}), Deans switch} \end{array}$	$\begin{array}{rrrr} 46^\circ C & \text{for} & 15\text{min},\\ 5^\circ C\text{min}^{-1} & \text{to} & 170^\circ C,\\ 15^\circ C\text{min}^{-1} & \text{to} & 200^\circ, \text{ hold}\\ \text{until 50\text{min}} \end{array}$	SS	outlet split, when trap is heated, set to $2 \text{ mLmin}^{-1}$ , split ratio ~ 1 : 1	30 NMHCs, 4 nmol mol <sup>-</sup> NPL
ZSF	no	$\begin{array}{llllllllllllllllllllllllllllllllllll$	5°C min <sup>-1</sup> to 170°C,	SS (transfer line at 230 °C)	outlet split, when trap is heated, set to $2 \text{ mLmin}^{-1}$ , split ratio ~ 1 : 1	30 NMHCs, 4 nmol mol <sup>−</sup> NPL
other sys	tems with Dear	ns switch				
IPR	no	J&W DB-1 (50 m $\times$ 0.318 mm $\times$ 1.2 $\mu m), HP-Al_2O_3/KCl PLOT (50 m \times 0.321 mm \times 8 \mu m), Deans switch$	40 °C for 5 min, 6 °C min <sup>-1</sup> to 200 °C, hold for 15 min	teflon at room temperature, SS and Silcosteel <sup>®</sup> at 250 °C	outlet split, when trap is heated, set to $2 \text{ mL min}^{-1}$ , split ratio ~1:1 (controlled with needle valve)	30 NMHCs, 4 nmol mol <sup>−</sup> NPL
KOS_A	no	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$45 ^{\circ}$ C for 5 min, 6 $^{\circ}$ C min <sup>-1</sup> to 160 $^{\circ}$ C, 9 $^{\circ}$ C min <sup>-1</sup> to 200 $^{\circ}$ C, hold for 14 min	SS not heated (transfer line >200 °C	split, trap flow $40 \text{ mLmin}^{-1}$ , split $20 \text{ mLmin}^{-1}$	30 NMHCs, 10 nmol mo NPL
DOU	no	Varian CP Sil-5 CB (50 m $\times$ 0.32 mm 1.2 $\mu$ m), Al <sub>2</sub> O <sub>3</sub> /KCl PLOT (50 m $\times$ 0.25 mm $\times$ 1 $\mu$ m), Deans switch	35°C for 10 min, 7.5°C min <sup>-1</sup> to 200°C, hold for 15 mins	SS heated and Silcosteel <sup>®</sup>	split less	33 NMHCs, 2 nmol mol <sup>-</sup> NPL

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Acronym	Pre-column (length × inner diam- eter × film thickness)	Column (length × inner diameter × film thickness)	Column temperature	Sample path	Injection type	Laboratory stan- dard
Two colui	mn systems wi	th split injection				
YRK	no	$\begin{array}{lll} \mbox{Varian} & \mbox{Al}_2 O_3/KCl & \mbox{PLOT} \\ (50 \mbox{ m } \times & 0.53 \mbox{ mm}), & \mbox{2} \times \\ \mbox{Chromopack-LOWOX} & (each \\ 10 \mbox{ m } \times & 0.53 \mbox{ mm } \times & 10 \mbox{ µm}) \end{array}$	$\begin{array}{rrrr} 40^{\circ}\text{C} & \text{for} & 15.5\text{min}, \\ 13^{\circ}\text{C}\text{min}^{-1} & \text{to} & 110^{\circ}\text{C}, \\ 8^{\circ}\text{C}\text{min}^{-1} & \text{to} & 200^{\circ}\text{C} \end{array}$	SS heated	split 70 % PLOT/30 % LOWOX	30 NMHCs, 4 nmol mol <sup>-1</sup> , NPL
WCC- VOC	no	Varian CP-Silica PLOT (30 m $\times$ 0.32 mm $\times$ 4 $\mu$ m), Varian VF 1 MS (60 m $\times$ 0.25 mm $\times$ 1 $\mu$ m), parallel	$\begin{array}{cccc} -30^{\circ}\mathrm{C} & \mathrm{for} & 8.7\mathrm{min},\\ 40^{\circ}\mathrm{C}\mathrm{min}^{-1} & \mathrm{to} & 20^{\circ}\mathrm{C},\\ 5^{\circ}\mathrm{C}\mathrm{min}^{-1} & \mathrm{to} & 120^{\circ}\mathrm{C},\\ 20^{\circ}\mathrm{C}\mathrm{min}^{-1} & \mathrm{to} & 220^{\circ}\mathrm{C},\\ 43^{\circ}\mathrm{C}\mathrm{min}^{-1} & \mathrm{to} & 40^{\circ}\mathrm{C} \end{array}$	Silcosteel <sup>®</sup> , sulfinert at room tempera- ture, SS at 100 °C	split on two parallel columns 1 : 1 (flow re- strictor)	26 NMHCs, 1.3 nmol mol <sup>-1</sup> , NPL
One colu	mn systems					
RIG	no	Varian $Al_2O_3/KCI$ PLOT (50 m × 0.53 mm)	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	SS not heated	splitless	30 NMHCs, 4 nmol mol <sup>-1</sup> , NPL
HPB_A	no	Varian $Al_2O_3/KCI$ PLOT (50 m × 0.53 mm)	40 °C for 2 min, 4 °C min <sup>-1</sup> to 72 °C, 6 °C min <sup>-1</sup> to 200 °C, isothermal at 200 °C for 33.67 min	Silcosteel <sup>®</sup> at room tempera- ture and 120°C; SS at 150°C	splitless	30 NMHCs, 2 nmol mol <sup>-1</sup> , NPL
HPB_B (FID)	no	SGE BPX-5 (50 m × 0.22 mm × 1 μm)	$10^\circ\text{C}$ for 5 min, 6 $^\circ\text{C}$ min $^{-1}$ to 240 $^\circ\text{C}$	Silcosteel <sup>®</sup> , ul- timetal at room temperature or at 150°C; SS and VALCO valves at 150°C	splitless, column out- flow is split 1 : 1.5 to MS : FID	
FZJ_B	no	Agilent DB-1 (120 m × 320 μm × 3 μm)	-60 °C for 8 min, 4 °C min <sup>-1</sup> to 180 °C, 20 °C min <sup>-1</sup> to 220 °C, isothermal at 220 °C for 10 mi	SS silanised, ACTRIS sam- ples additionally 75 cm PFA- tubing	splitless	74 VOCs, 0.16– 10.8 nmol mol <sup>-1</sup> , Apel Riemer En- vironmental, Inc. 54 VOCs, 0.16– 10.8 nmol mol <sup>-1</sup> , Apel Riemer Envi- ronmental, Inc.

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Acronym	Pre-column (length × inner diam- eter × film thickness)	Column (length × inner diameter × film thickness)	Column temperature	Sample path	Injection type	Laboratory standard
KOS_B	no	J&W DB-1 (50 m × 0.32 mm)	$45 \degree C$ for 5 min, 6 $\degree C$ min <sup>-1</sup> to 160 $\degree C$ , 9 $\degree C$ min <sup>-1</sup> to 200 $\degree C$ , hold for 14 min	SS not heated (transfer line >200 °C)	splitless	30 NMHCs, 10 nmol mol <sup>-1</sup> , NPL
GC-MSs						
CMN	no	J&W GasPro PLOT (30 m × 0.35 mm)	$\begin{array}{cccc} 49^{\circ}\text{C} & \text{for} & 6\text{min}, \\ 9.5^{\circ}\text{C}\text{min}^{-1} & \text{to} & 145^{\circ}\text{C}, \\ \text{hold for 2 min, 10}^{\circ}\text{C}\text{min}^{-1} \\ \text{to 250}^{\circ}\text{C}, \text{ hold for 20 min} \end{array}$	SS (working std); Silcosteel <sup>®</sup> (NPL) and PTFE	splitless	30 NMHCs, 4 nmol mol <sup>-1</sup> , NPL
FZJ_A	no	Agilent DB 624 (20m × 0.18mm)	35 °C for 0.3 min, 120 °C min-1 to 220 °C, isothermal at 220 °C for 1.46 min	PFA tubing and Silcosteel <sup>®</sup> tubing (Restek), valve seal- ing (Valcon E rotor material by VICI, 493 K); GERSTEL Graphpack fittings, Silcosteel <sup>®</sup> liner with adsorption material	splittess	74 VOCs, 0.16- 10.8 nmol mol <sup>-1</sup> , Apel Riemer Environmental, Inc. 54 VOCs, 0.16- 10.8 nmol mol <sup>-1</sup> , Apel Riemer Environmental, Inc.
HPB_B (MS)	no	SGE BPX-5 (50 m $\times$ 0.22 mm $\times$ 1 $\mu m)$	$10\degree C$ for 5 min, 6 $\degree C$ min $^{-1}$ to 240 $\degree C$	Silcosteel <sup>®</sup> , sulfin- ert, ultimetal at room temperature or at 150°C. SS, VALCO valves at 150°C	splitless, column out- flow is split 1 : 1.5 to MS : FID	30 NMHCs, 2 nmol mol <sup>-1</sup> , NPL
PUY	no	OPTIMA-5MS (60 m × 0.25 mm, 0.25 μm)	35 °C for 5 min, 5 °C min <sup>-1</sup> to 250 °C, hold 2 min	SS not heated	outlet split: $30 \text{ mL min}^{-1}$ , $1.5 \text{ mL min}^{-1}$ on column; inlet split: $50 \text{ mL min}^{-1}$ , $20 \text{ mL min}^{-1}$ on trap	29 NMHCs, 1– 10 nmol mol <sup>-1</sup> , Air Products, 2 nmol mol <sup>-1</sup> , Restek
SIR	no	CP PoraBOND Q (25 m × 0.25 mm × 3.00 µm)	100°C to 250°C (Run time: 30 min)	SS and fused silica at 220 °C	split 1/5 between pre- concentration unit and column (5 mL min <sup>-1</sup> , 1.4 mL min <sup>-1</sup> on col- umn)	30 NMHCs, 4 nmol mol <sup>-1</sup> , NPL
SMR	no	Agilent DB-5 (60 m × 0.235 mm × 1 μm)	50 °C, 4 °C min <sup>-1</sup> to 150 °C, 8 °C min <sup>-1</sup> to 290 °C	For this excercise: Silcosteel <sup>®</sup> lines	splitless	7 NMHCs, 2 nmol mol <sup>-1</sup> , NPL

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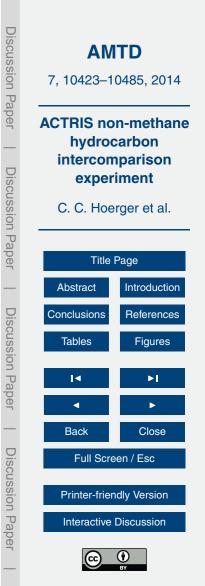
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Acronym	Pre-column (length × inner diam- eter × film thickness)	Column (length × inner diameter × film thickness)	Column temperature	Sample path	Injection type	Laboratory standard
Medusa s	systems					
JFJ	no	Varian CP 7351 CP- CP PoraBOND Q (25 m × 0.32 mm × 5 μm)	$40^{\circ}$ C for 16.6 min, 23°C min <sup>-1</sup> for 7 min, 200°C for 6.6 min	SS 40°C	splitless	30 NMHCs, 4 nmol mol <sup>-1</sup> , NPL
MHD	MS-4 and HiSiv-3000 in 80 cm × 0.75 mm SS (Restek)	Varian CP7351 CP-CP PoraBOND Q (25 m × 0.32 mm × 5 µm)	40°C, 10°C min <sup>-1</sup> to 200°C	SS	splitless	45 VOCs, 0.4–1.3 nmol mol <sup>-1</sup> , Apel- Riemer Environmental Inc.
NILU	Molecular sieve 4 Å, mesh HISIV-3000 at 40 °C	Varian CP PoraBOND Q (25 m × 0.32 mm × 5 μm)	40°C, 22.9°C min <sup>-1</sup> to 200°C, 40°C	SS, PEEK, KNF pump (neoprene diaphragm), flowmeter, pressure gauge	splitless	30 NMHCs, 2.7 nmol mol <sup>-1</sup> , NPL
PTR-MS						
SMR II	no	no	no	no	no	16 VOCs, 0.84–1.14 nmol mol <sup>-1</sup> , Apel-Riemer Environ- mental, Inc.
WCC- VOC	no	no	no	no	no	3 different NPL calibra- tion standards (see Sup- plement)

SS = stainless steel, NPL = National Physical Laboratory, UK

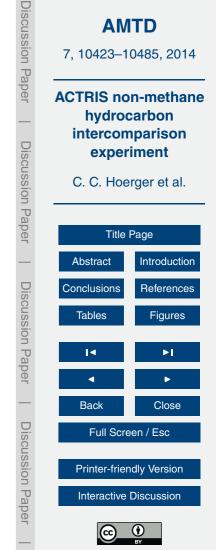


**Table 5.** Assigned mole fractions (error-weighted means with expanded uncertainties) for NMHC\_N<sub>2</sub> and NMHC\_air (nmol mol<sup>-1</sup>).

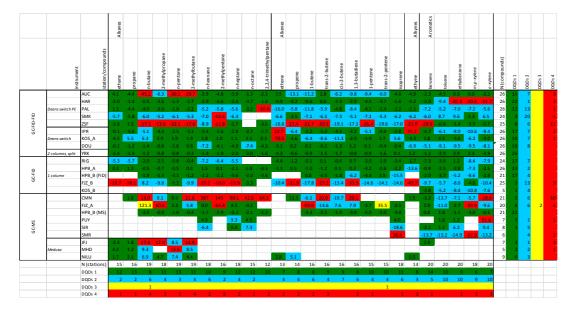
	Error-weight NMH		anded uncertainty NMH	(nmol mol <sup>-1</sup> ) Cair
	cylinder 1	cylinder 2	cylinder 1	cylinder 2
Alkanes				
ethane	$1.071 \pm 0.016$	$1.118 \pm 0.016$	$1.871 \pm 0.037$	$1.904 \pm 0.041$
propane	$1.061 \pm 0.014$	$1.104 \pm 0.015$	$1.608 \pm 0.025$	$1.611 \pm 0.023$
<i>n</i> -butane	$1.025 \pm 0.028$	$1.076 \pm 0.015$	$1.407 \pm 0.019$	$1.407 \pm 0.015$
methylpropane	$1.051 \pm 0.011$	$1.114 \pm 0.013$	$0.778 \pm 0.026$	$0.765 \pm 0.024$
<i>n</i> -pentane	$1.031 \pm 0.012$	$1.092 \pm 0.017$	$0.834 \pm 0.012$	$0.834 \pm 0.014$
2-methylbutane	$1.011 \pm 0.011$	$1.075 \pm 0.014$	$1.669 \pm 0.029$	$1.654 \pm 0.028$
<i>n</i> -hexane	$1.019 \pm 0.013$	$1.083 \pm 0.014$	$0.157 \pm 0.006$	$0.151 \pm 0.006$
2-methylpentane	$1.025 \pm 0.014$	$1.089 \pm 0.014$	$0.343 \pm 0.025$	$0.348 \pm 0.021$
3-methylpentane			$0.195 \pm 0.009$	$0.194 \pm 0.008$
2,2-dimethylbutane			$0.257 \pm 0.038$	$0.256 \pm 0.033$
2,3-dimethylbutane			$0.070 \pm 0.020$	$0.072 \pm 0.020$
cyclohexane			$0.140 \pm 0.005^{a}$	0.141 ± 0.009 <sup>a</sup>
<i>n</i> -heptane	$1.011 \pm 0.011$	$1.077 \pm 0.012$	$0.443 \pm 0.008$	$0.463 \pm 0.010$
<i>n</i> -octane	$1.011 \pm 0.021$	$1.076 \pm 0.023$	$0.443 \pm 0.008^{a}$	$0.463 \pm 0.010^{a}$
2,2,4-trimethylpentane	$1.028\pm0.012$	$1.095 \pm 0.012$	$0.145 \pm 0.008^{a}$	$0.144 \pm 0.008^{a}$
Alkenes				
ethene	$1.065 \pm 0.015$	$1.127 \pm 0.015$	$2.531 \pm 0.034$	$2.532 \pm 0.035$
propene	$1.030 \pm 0.013$	$1.091 \pm 0.016$	$0.571 \pm 0.020$	$0.552 \pm 0.014$
1-butene	$1.007 \pm 0.031$	$1.070 \pm 0.033$	$0.114 \pm 0.006^{a}$	$0.109 \pm 0.006^{a}$
2-methylpropene			$0.858 \pm 0.039^{a}$	1.081 ± 0.049 <sup>a</sup>
trans-2-butene	$1.024 \pm 0.018$	$1.088 \pm 0.019$	$0.074 \pm 0.003^{a}$	$0.075 \pm 0.003^{a}$
cis-2-butene	$1.008 \pm 0.011$	$1.069 \pm 0.013$	$0.066 \pm 0.002$	$0.067 \pm 0.002$
1,3-butadiene <sup>b</sup>	$1.024 \pm 0.025$	$1.087 \pm 0.024$	$0.066 \pm 0.011$	$0.062 \pm 0.014$
1-pentene	$1.001 \pm 0.012$	$1.086 \pm 0.036$	$0.048 \pm 0.014^{a}$	$0.044 \pm 0.013^{a}$
trans-2-pentene	$0.984 \pm 0.015$	$1.042 \pm 0.018$	$0.057 \pm 0.004$	$0.058 \pm 0.004$
cis-2-penten			$0.033 \pm 0.003$	$0.032 \pm 0.003$
2-methyl-2-butene			$0.125 \pm 0.020$	$0.121 \pm 0.006$
isoprene <sup>b</sup>	$2.039 \pm 0.038$	$2.178 \pm 0.034$	$0.021 \pm 0.008$	$0.022\pm0.006$
Alkynes				
ethyne	$1.020 \pm 0.026$	$1.118 \pm 0.024$	$1.467 \pm 0.032$	$1.485 \pm 0.039$
propyne			$0.065 \pm 0.019^{a}$	$0.065 \pm 0.017^{a}$
Aromatic compounds				
benzene	$1.022 \pm 0.012$	$1.091 \pm 0.013$	$0.460 \pm 0.006$	$0.458 \pm 0.007$
toluene	$1.021 \pm 0.048$	$1.222 \pm 0.039$	$1.709 \pm 0.059$	$1.737 \pm 0.055$
ethylbenzene	$1.017 \pm 0.057$	$1.182 \pm 0.057$	$0.245 \pm 0.010$	$0.247 \pm 0.008$
m,p-xylene	$2.035 \pm 0.117$	$2.569 \pm 0.108$	$0.884 \pm 0.038$	$0.882 \pm 0.036$
o-xylene	$1.047 \pm 0.097$	$1.180 \pm 0.095$	$0.279 \pm 0.019$	$0.282 \pm 0.023$

<sup>a</sup> assigned mole fractions were determined only with results from HPB;

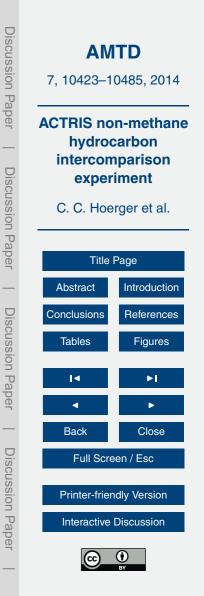
<sup>b</sup> arithmetic mean of measurements instead of error-weighted mean



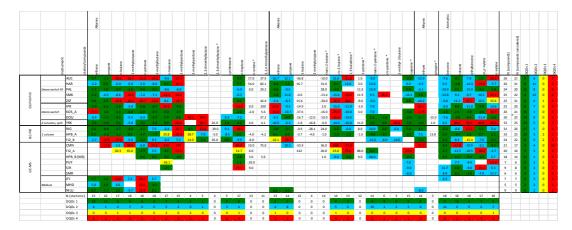
**Table 6.** Overview of NMHC measurement performance in NMHC\_N<sub>2</sub>. Colour code: green: value within ACTRIS DQOs (DQOs 1, see Table 2); blue: value within GAW DQOs (DQOs 2); yellow: values outside GAW DQOs, but error bars of measured mole fraction and assigned value overlap (DQOs 3); red: value outside GAW DQOs (DQOs 4). Numbers in coloured boxes report the difference (%) between the measurement and the assigned value (positive value: higher value than assigned; negative value: lower value than assigned). *N* (compounds) indicates the number of compounds reported by the respective station; *N* (stations) indicates the number of stations reporting the respective compound.



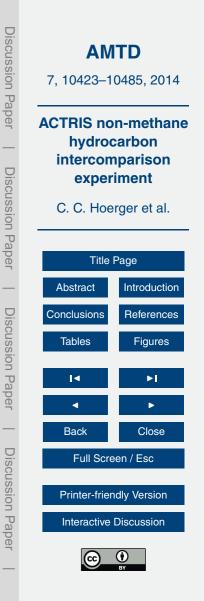
PE: Perkin Elmer

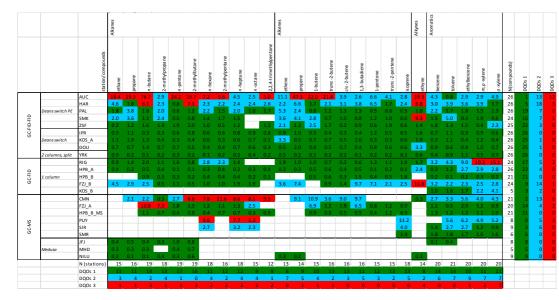


**Table 7.** Overview of NMHC measurement performance in NMHC\_air. Colour code: green: value within ACTRIS DQOs (DQOs 1, see Table 2); blue: value within GAW DQOs (DQOs 2); yellow: values outside GAW DQOs, but error bars of measured mole fraction and assigned value overlap (DQOs 3); red: value outside GAW DQOs (DQOs 4). Columns without colours: assigned values were determined with only HPB values. Numbers in coloured boxes report the difference (%) between the measurement and the assigned value (positive value: higher value than assigned; negative value: lower value than assigned). *N* (compounds) indicates the number of compounds reported by the respective station; *N* (stations) indicates the number of stations reporting the respective compound. \*: mole fractions < 0.1 nmol mol<sup>-1</sup>.



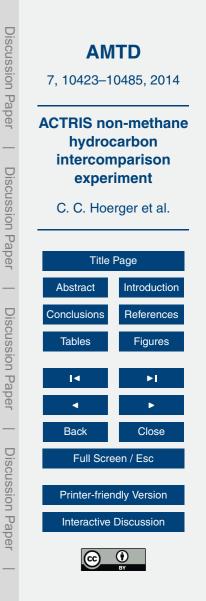
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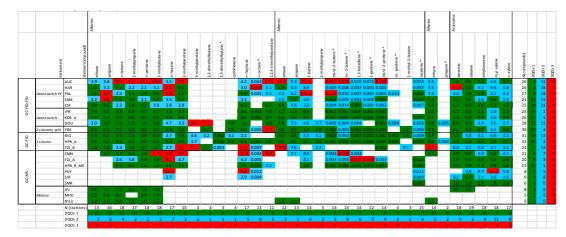


**Table 8.** Repeatability in NMHC\_N<sub>2</sub> (%). Green colour indicates values within ACTRIS DQOs (DQOs 1, see Table 2), blue values within GAW DQOs (DQOs 2), and red values outside GAW DQOs (DQOs 3).

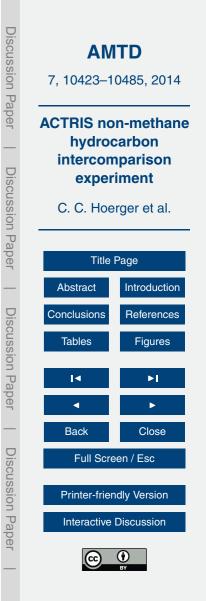
PE: Perkin Elmer



**Table 9.** Repeatability in NMHC\_air (%). Green colour indicates values within ACTRIS DQOs (DQOs 1, see Table 2), blue values within GAW DQOs (DQOs 2), and red values outside GAW DQOs (DQOs 3). \* mole fractions <  $0.1 \text{ nmol mol}^{-1}$ .



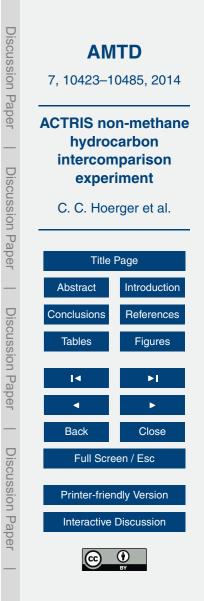
PE: Perkin Elmer

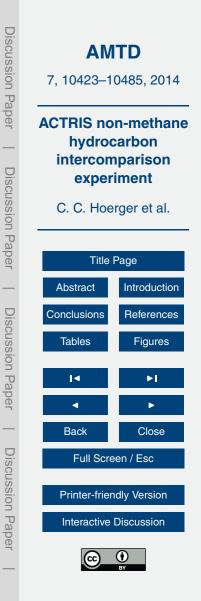


**Table 10.** Blank values  $(pmol mol^{-1})$  for different compounds submitted from the participants. Empty cells indicate no blank values measured and/or reported. \* mole fractions < 100 pmol mol^{-1}.

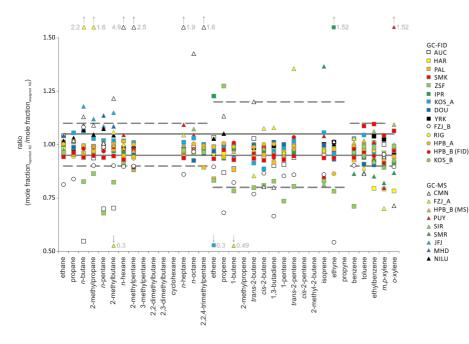
			Alammes																		Alkynes		Aromatics													
		station/compounds	ethane	propane	<i>n</i> -butane	2-methylpropane	<i>n</i> -pentane	2-methylbutane	<i>n</i> -hexane	2-methylpentane	3-methylpentane	2,2-dimethylbutane	2,3-dimethylbutane *	cyclohexane	<i>n</i> -heptane	<i>n</i> -octane *	2,2,4-trimethylpentane	ethene	propene	1-butene	2-methylpropene	trans -2-butene *	cis -2-butene *	1,3-butadiene *	1-pentene *	trans -2-pentene *	cis -pentene *	2-methyl-2-butene	isoprene *	ethyne	propyne *	penzene	toluene	ethylbenzene	m,p-xylene	o-xylene
		AUC																																		
		HAR																																		
	Deans switch PE			38	22	13		5										210		172		71	41	113		1				13		24	13			
GC-FID-FID		SMK								4					3				68	28		15	7	7	5	4			7			17	3	16	29	10
문		ZSF	15	15			6	8	4	6							11	118		132			41	59	13	6			11			22	78	4	25	25
00		IPR			3	2	1								4			35	26	10			2		9							10	2	4		8
	Deans switch	KOS_A					4	9										359	55	30		45	12							79		15			6	
		DOU	35	13	5	11	3	3	1	2					1		3	57	22	5		3	3	3		2				11		4	3	1	1	1
		YRK		_				_					_					_								6						4			_	
		RIG																	15					5								17				
₽		HPB_A																10	2	2	74									12		7				
GC-FID	1 column	HPB_B			36										2					9				144					171			45	18			
Ŭ		FZJ_B																																		
		KOS_B																_														10	5	2	2	2
		CMN		2															2				2									1	1			
		FZJ_A			7											2																27	10	10		9
		HPB_B_MS			57															19				9		16						43	25			
\$		PUY							4							13													5				48	25	60	36
GC-MS		SIR							5							2													3			20	33	35	138	24
Ĭ		SMR																_														5	1		_	
		JFJ																																		
	Medusa	MHD						5																												
		NILU	1															_	1																	

PE: Perkin Elmer

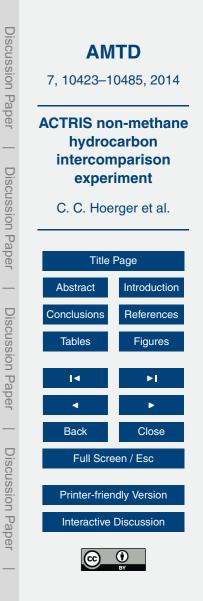


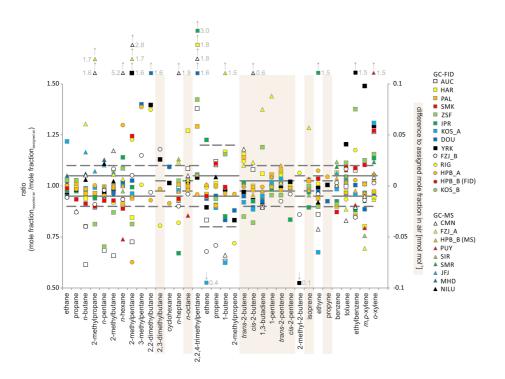


**Figure 1.** The participants of the ACTRIS NMHC intercomparison in Europe. Left: Western, Central and Southern Europe; right: Northern Europe. For abbreviations and further details see Table 3.

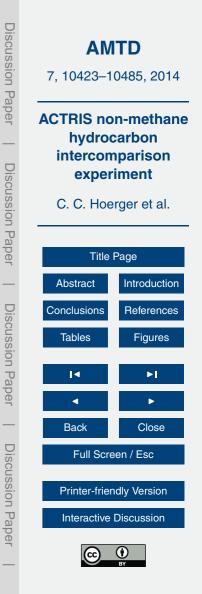


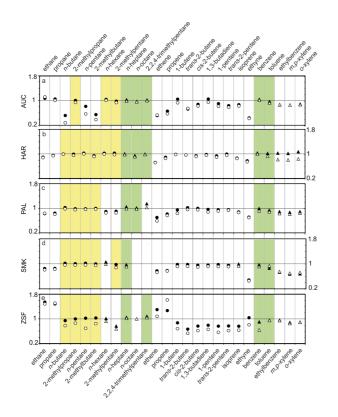
**Figure 2.** NMHC results for each site (colour coded symbols) are presented relative to the assigned values in NMHC\_N<sub>2</sub>. Solid and dashed grey lines indicate ACTRIS and GAW DQOs, respectively (Table 2). For abbreviations see Table 3.



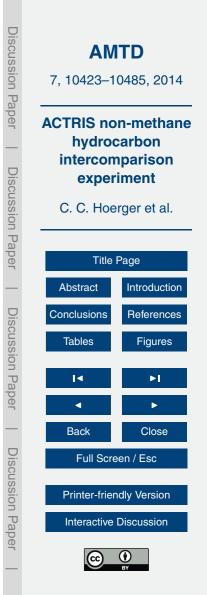


**Figure 3.** NMHC results for each site (colour coded symbols) are depicted for NMHC\_air. On the left scale the values are presented relative to the assigned values and on the right scale the values are presented as difference to assigned mole fractions (in nmol mol<sup>-1</sup>) for compounds below 0.1 ppb (brownish highlighted). Solid and dashed grey lines indicate ACTRIS and GAW DQOs, respectively (Table 2). For abbreviations see Table 3.





**Figure 4.** C-responses of FIDs. Circles ( $\bigcirc$ ) indicate column one, triangles ( $\triangle$ ) column two. Filled symbols indicate the C-responses in the calibration standard, open symbols the C-responses in NMHC\_N<sub>2</sub>. The C-responses for column one were normalised by the average C-response of the available C<sub>4</sub>-C<sub>6</sub>-alkanes (highlighted in yellow), column two by the average C-response of the available C<sub>7</sub>-C<sub>8</sub>-alkanes, benzene, and toluene (highlighted in green). If an individual C-response deviated by more than 10 % from the average C-response, the value was not considered in the normalisation process. Ideally, both C-responses should behave identically, and have a value around 1.



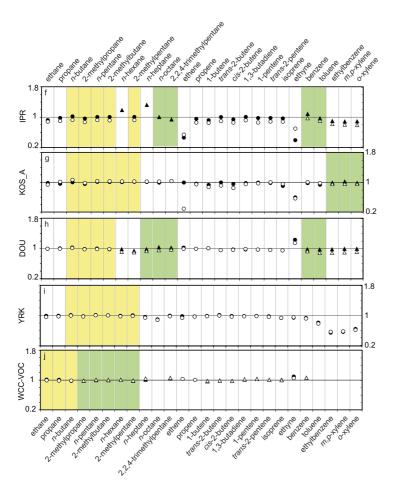
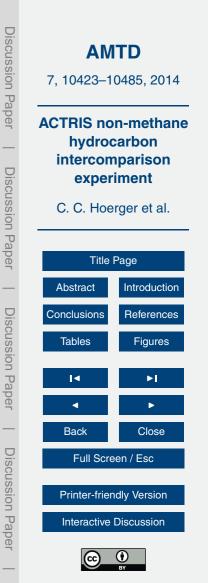
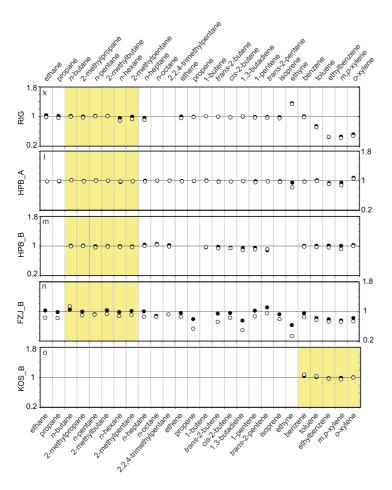


Figure 4. Continued.





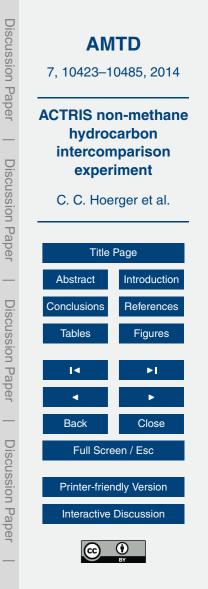
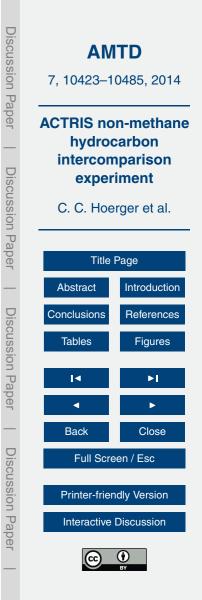


Figure 4. Continued.



**Figure 5.** Normalised mole fractions for NMHC\_N<sub>2</sub> and NMHC\_air. Circles ( $\bigcirc$ ) indicate column one, triangles ( $\triangle$ ) column two. Open symbols indicate NMHC\_N<sub>2</sub>, filled symbols NMHC\_air. For NMHC > 0.1 nmol mol<sup>-1</sup> use left *y* axis with normalised mole fraction to assigned values. Blue symbols indicate values in NMHC\_air < 0.1 nmol mol<sup>-1</sup>. Right *y* axis (in blue) shows difference to assigned mole fraction (nmol mol<sup>-1</sup>) in NMHC\_air < 0.1 nmol mol<sup>-1</sup>.

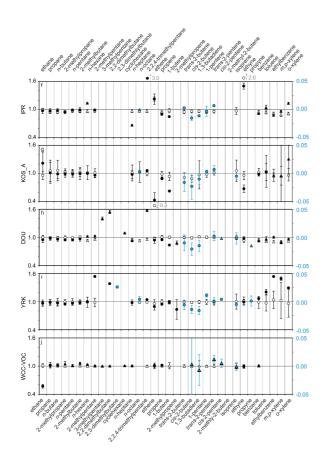
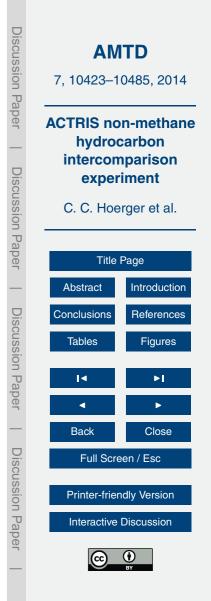
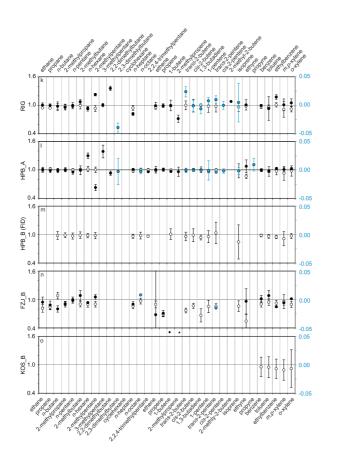
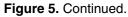
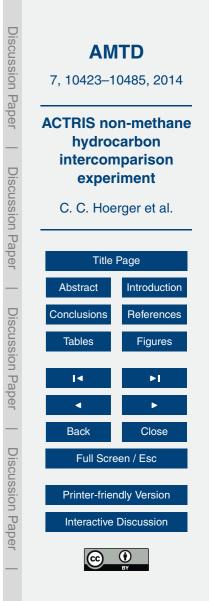


Figure 5. Continued.









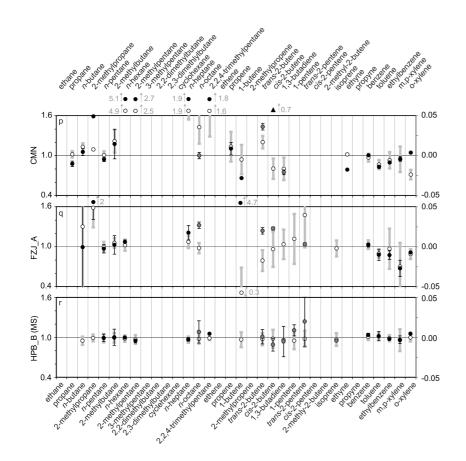
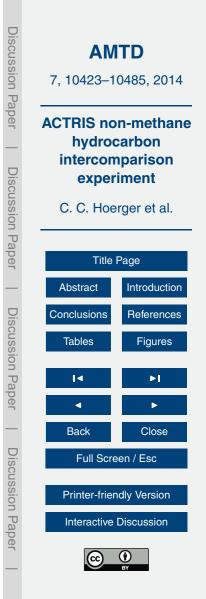


Figure 5. Continued.



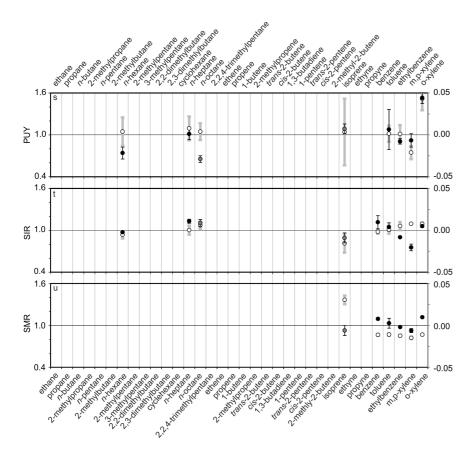
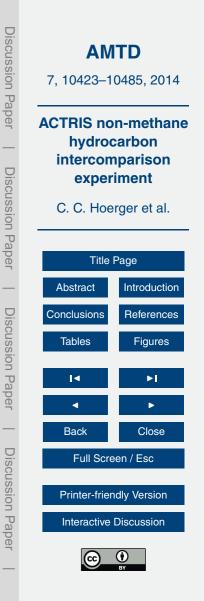


Figure 5. Continued.



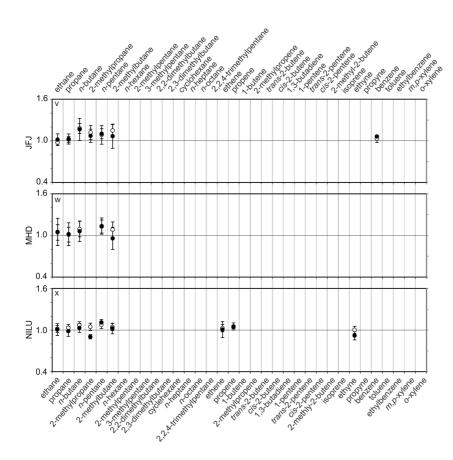
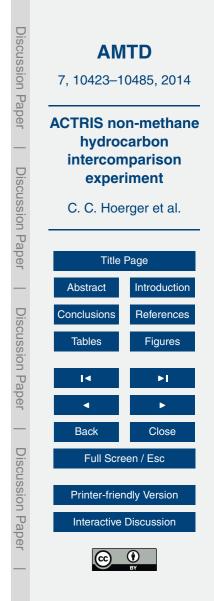
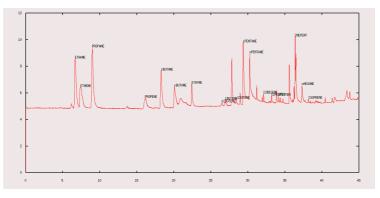


Figure 5. Continued.



a) Chromatogram in NMHC\_air for AUC (PLOT-column).



b) Chromatogram in NMHC\_air for HAR (PLOT-column).

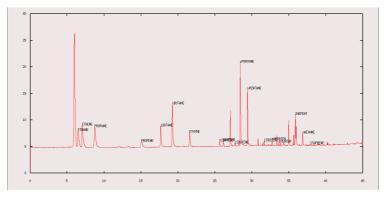
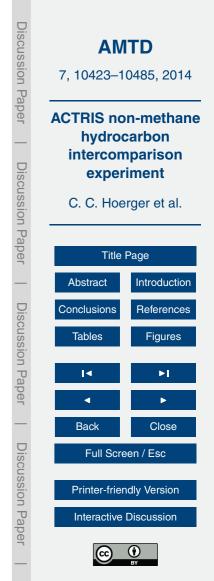
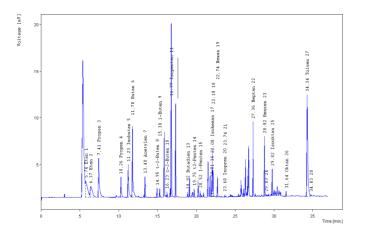


Figure 6. Examples of chromatograms. (a) Chromatogram in NMHC\_air for AUC (PLOT-column). (b) Chromatogram in NMHC\_air for HAR (PLOT-column). (c) Chromatogram in NMHC\_air for KOS\_A (PLOT-column). (d) Chromatogram in NMHC\_air for PAL (PLOT-column).



#### c) Chromatogram in NMHC\_air for KOS\_A (PLOT-column).



d) Chromatogram in NMHC\_air for PAL (PLOT-column).

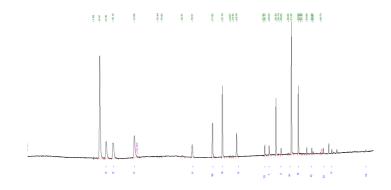


Figure 6. Continued.

