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

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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 inter-comparisons 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⁻¹.

The participants were asked to measure both a 30 component NMHC mixture in nitrogen (NMHC_N₂) at approximately 1 nmol mol⁻¹ 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.

The NMHCs were analysed either by gas chromatography-flame ionisation detection or gas chromatography-mass spectrometer methods. Most systems performed well for the NMHC_N₂ 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_N₂ (77% 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_N₂ were a more complex matrix and a larger span of NMHC mole fractions (0.03–2.5 nmol mol⁻¹). Issues, which affected both NMHC mixtures, are the usage of direct vs. two-step calibration, breakthrough of C₂–C₃ hydrocarbons, blank values in zero-gas measurements (especially for those systems using a Nafion[®] Dryer), adsorptive losses of aromatic compounds, and insufficient chromatographic resolution. Essential for high-quality results are experienced operators, a comprehensive quality

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SA-6; RIX Industries, USA) on 31 October 2011. The mole fractions in NMHC_{air} ranged from 0.03 to 2.5 nmol mol⁻¹ (Table 5). The final pressure in the cylinders was ~ 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 usually 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:

$$X_{\text{error-weighted}} = \frac{\sum (w_i \cdot x_i)}{\sum (w_i)} \quad (1)$$

where x_i = measured value.

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

$$u_{\text{internal}} = 1/\sqrt{\sum (w_i)} \quad (2)$$

When comparing results from different GC systems with different systematic uncertainties, additionally the external uncertainty u_{external} is calculated as weighted deviation from the weighted mean value

$$u_{\text{external}} = \sqrt{\left(\frac{\sum (w_i \cdot (x_i - X_{\text{error-weighted}})^2)}{(n - 1) \cdot \sum (w_i)}\right)} \quad (3)$$

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poor baseline separation) in ΔA_{int} , systematic errors due to blank correction $\Delta \chi_{\text{blank}}$, and potential further instrumental problems $\Delta \chi_{\text{instrument}}$ (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 $\Delta \chi_{\text{systematic}}$ is then described as

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

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

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

where A_{sample} = peak area of sample measurement, A_{cal} = peak area of the calibration standard measurement, V_{sample} = sample volume of sample, V_{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

$$\Delta \chi_{\text{int}}^2 = \left(\frac{f_{\text{cal}}}{V_{\text{sample}}} \cdot \delta A_{\text{sample}} \right)^2 + \left(\frac{A_{\text{sample}} \cdot V_{\text{cal}} \cdot \chi_{\text{cal}}}{V_{\text{sample}} \cdot A_{\text{cal}}^2} \cdot \delta A_{\text{cal}} \right)^2 \quad (10)$$

$$\text{with } f_{\text{cal},i} = \frac{V_{\text{cal}} \cdot \chi_{\text{cal}}}{A_{\text{cal}} - A_{\text{blank}}}$$

where A_{sample} = peak area of sample measurement, A_{cal} = peak area of the calibration standard measurement, A_{blank} = peak area of blank measurement, V_{sample} = sample volume of sample, V_{cal} = sample volume of calibration standard, χ_{cal} = mole fraction of calibration standard peak, δA_{cal} = integration error of calibration standard measurement, and δA_{sample} = integration error of the sample measurement.

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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_{N₂} the mole fractions in NMHC_{air} varied much more and ranged from 0.03 to 2.5 nmol mol⁻¹ (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 C₄–C₈-alkanes seemed to be more problematic than C₂–C₃-alkanes (yellow and red colours in Table 7). Except C₄-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⁻¹ some good results within the GAW range were achieved for isoprene and C₅-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 (1σ) of the 5 measurements for each NMHC mixture (Tables 8 and 9). The majority of the participants submitted a repeatability in NMHC_{N₂} 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_{N₂} 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_{N₂}, but the repeatability within the ACTRIS DQOs was 10 % lower compared to NMHC_{N₂}. As for NMHC_{N₂} the repeatability results were independent of the detector types. Additionally to 2,2,4-trimethylpentane and 2-methylbutane the other C₆-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

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0.1 nmol mol⁻¹ (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_{N₂}, 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 multi-component 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⁻¹) 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 (Table 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

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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⁻¹ calibration standard). This is obvious from the comparison of C-responses for propene, 1,3-butadiene, and ethyne between NMHC_N₂ 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_N₂ 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.

The Medusa instruments (JFJ, MHD, and NILU) tended to overestimate the NMHC 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 problems were reported by CMN, who indicated issues with the calibration and the stability of the whole air working standard. Due to time constraints 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, 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 C-response factors for the calibration standards and NMHC_N₂ 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_N₂ will be equal. Several GC-FID systems tend to slightly underestimate NMHC_N₂ compared to the calibration standard. This was observed by the lower normalised C-responses for NMHC_N₂ 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_N₂ 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_N₂. 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_N₂ 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.

3.5 Problems with C₂–C₃-hydrocarbons

Most participants reported C₂–C₃-hydrocarbons within the ACTRIS DQOs in NMHC_N₂ (Table 6, Fig. 2). However, a few systems reported C₂–C₃-hydrocarbons

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mixtures (Fig. 5) did not show deviations for the C₂–C₅-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 (C₂–C₅) 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_{N₂}) 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 ACTRIS NMHC_{N₂} 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 C-response 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 Al₂O₃/KCl-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_{N₂} causing different

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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.

3.7 Alkene artefacts

For alkene measurements, the C-responses and the results of the measurement of NMHC_N₂ 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[®] Dryer indicated blank values of up to 0.35 nmol mol⁻¹ for C₂-C₃-alkenes and up to 0.1 nmol mol⁻¹ for C₄-alkenes. Combined with the fact that the mole fractions of C₄-C₅-alkenes were in the range between 0.02 and 0.12 nmol mol⁻¹ 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⁻¹) and the smaller blank values (up to 0.25 nmol mol⁻¹) such effects were comparably minor.

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When using a Nafion[®] Dryer to remove humidity from the sample, potential artefacts in C₂–C₄-alkenes may occur depending on the status of the Nafion[®] 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[®] 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[®] Dryer and reported larger uncertainties of their values (Tables 6 and 7).

3.8 Losses of aromatic compounds and C₆–C₈-alkanes

The C-responses for the C₇–C₈-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_N₂ (Fig. 4; AUC, PAL, SMK, IPR YRK (except benzene), RIG, FZJ_B, and less evident in HPB_A), or only in NMHC_N₂ (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_N₂ (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_N₂ 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 C₆–C₈-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.

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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_N₂ and NMHC_air by CMN and the Medusa systems were mainly due to calibration issues (the use of whole air working standards instead of certified 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).

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 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⁻¹ range (Apel Riemer Environmental Inc.) cannot be judged from the available data. Further, breakthrough of C₄-compounds was reported by FZJ_A. In general, the blank chromatogram revealed many peaks (chromatogram not shown), which possibly affected the results, especially in NMHC_air.

For NMHC_N₂ 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_N₂ (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

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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[®] 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[®] 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

The two NMHC mixtures were analysed with the PTR-MS of SMR II and WCC-VOC. Isoprene in NMHC_N₂ fitted well inside the ACTRIS DQOs, whereas isoprene in

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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 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 C₂–C₃-hydrocarbons in adsorptive traps. Deviations from the expected 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 C₇–C₈ 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 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 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

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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.

GAW	ACTRIS
ethane	ethane
propane	propane
<i>n</i> -butane	<i>n</i> -butane
methylpropane	methylpropane
<i>n</i> -pentane	<i>n</i> -pentane
2-methylbutane	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
	<i>trans</i> -2-butene
	<i>cis</i> -2-butene
	1,3-butadiene
	1-pentene
	<i>trans</i> -2-pentene
	<i>cis</i> -2-pentene
	2-methyl-2-butene
isoprene	isoprene
ethyne	ethyne
	propyne
benzene	benzene
toluene	toluene
	ethylbenzene
	<i>m,p</i> -xylene
	<i>o</i> -xylene
monoterpenes	
dimethylsulfide	
formaldehyde	
methanol	
ethanol	
acetone	
acetonitrile	

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

	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 ⁻¹ (ppb)	0.02 ppb	0.015 ppb	0.005 ppb	0.002 ppb

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Table 4. Analysis methods used in the ACTRIS NMHC intercomparison exercise (stations acronym, instrument, ozone (O₃) trap, water (H₂O) trap, preconcentration unit, sample volume, adsorbents, re-focus/cryofocus). For acronyms see Table 3.

Acronym	Instrument	O ₃ trap	H ₂ O trap	Preconcentration unit	Sample volume (mL)	Adsorbents and adsorption (ads.) and desorption (des.) temperature	Re-focus/cryofocus and temperatures
GC-FIDs							
<i>Perkin Elmer systems with Deans switch</i>							
AUC	Perkin Elmer GC-FID/FID	no	Nafion [®] -Dryer	Perkin Elmer Turbomatrix with online accessory ^a	600	Air Toxics Analyser Trap ^b (ads. at -30 °C, des. at 320 °C)	no
HAR	Perkin Elmer GC-FID/FID	no	Nafion [®] -Dryer	Perkin Elmer Turbomatrix with online accessory ^a	600	Air Toxics Analyser Trap ^b (ads. at -30 °C, des. at 320 °C)	no
PAL	Perkin Elmer GC-FID/FID	no	Nafion [®] -Dryer	Perkin Elmer Turbomatrix 300 with online accessory ^a	1200	Air Toxics Analyser Trap ^b , mixed bed carbon (ads. at -40 °C, des. at 325 °C)	no
SMK	Perkin Elmer GC-FID/FID	no	Nafion [®] -Dryer	Perkin Elmer Turbomatrix 300 with online accessory ^a	500	TD/ATD Air Monitoring Trap (ads. at -30 °C, des. at 325 °C)	no
ZSF	Perkin Elmer GC-FID/FID	no	Nafion [®] -Dryer	Perkin Elmer Turbomatrix 650 with online accessory ^a	600	Air Toxics Analyser Trap ^b (ads. at -30 °C, des. at 325 °C)	no
<i>Other systems with Deans switch</i>							
IPR	Agilent GC-FID/FID	no	Nafion [®] -Dryer	Perkin Elmer Turbomatrix with online accessory ^a	1360	Air Toxics Analyser Trap ^b (ads. at -30 °C, des. at 380 °C)	no
KOS_A	Agilent 7890 GC-FID/FID	no	Nafion [®] -Dryer	Markes UNITY-Thermal Desorber	400	Air Toxics Analyser Trap ^b (ads. at -20 °C, des. at 310 °C)	no
DOU	Chrompak GC-FID/FID	no	Nafion [®] -Dryer	Entech	360	glass beads (ads. at -120 °C, des. at 70 °C)	glass beads, Tenax [®] (-50 to 220 °C)
<i>Two column systems with split injection</i>							
YRK	Agilent GC-FID/FID	no	Glass volume at -27 °C	Markes UNITY-Thermal Desorber	1000	Carbopack [®] B, Carboxen [®] 1000 (ads. at -20 °C, des. at 350 °C)	no
WCC-VOC	Varian 3800 GC-FID/FID	no	Silcosteel [®] at -30 °C	custom made	400	Carbopack [®] BHT (ads. at -120 °C, des. at 200 °C)	no

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Table 4. Continued.

Acronym	Instrument	O ₃ trap	H ₂ O trap	Preconcentration unit	Sample volume (mL)	Adsorbents and adsorption (ads.) and desorption (des.) temperature	Re-focus/cryofocus and temperatures
<i>One column systems</i>							
RIG	Agilent GC-FID	no	Nafion [®] -Dryer	custom-made (Adsorption Desorption Unit)	600	Stainless steel tube with fused silica beads, Carboxen [®] 1003, Carboxen [®] 1016, Carbosieve [®] 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" sulfonated 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 (ambient air)	fritted glass tube with Tenax [®] TA, Carbo-pack [®] X, Carboxen [®] 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 capillary heated to 120 °C prior to sampling in the canister	no	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 [®] -Dryer	Markes UNITY-Thermal Desorber	400	Air Toxics Analyser Trap [†] (ads. at -20 °C, des. at 310 °C)	no
GC-MSs							
CMN	Agilent GC-MS	no	Nafion [®] -Dryer	Markes UNITY-Thermal Desorber	1000	Carbograph [®] 1, Carboxen [®] 1003, Carbosieve [®] SIII (ads. at -30 °C, des. at 310 °C)	no
FZJ_A	Custom-made GC with 5975C inert MSD	42.5 cm Silcosteel [®] , 0.25 mm i.d., 120 °C	no	custom-made (Gerstel)	150	Glas liner with Carbotrap [®] C, Carbotrap [®] B, Carbosieve [®] SIII (adsorption at 30 °C, desorption at 225 °C)	focus trap (Carbo-pack [®] 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 (ambient air)	fritted glass tube with Tenax [®] TA, Carbo-pack [®] X, Carboxen [®] 569 (ads. at 30 °C, des. at 200 °C)	cryofocus on methyl silicone capillary at -180 to 60 °C

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Table 4. Continued.

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

SS = stainless steel;

^a standard online accessory (see Perkin Elmer http://www.perkinelmer.co.uk/content/applicationnotes/app_gaschromozoneprecursoranalysis.pdf) including unheated SS lines and valves;

^b Carpopack[®]B, Carbosieve[®]SIII are the adsorbents of the Air Toxics Analyser Trap (personal communication: M. Dinse, 2014 (Perkin Elmer)).

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 diameter × film thickness)	Column (length × inner diameter × film thickness)	Column temperature	Sample path	Injection type	Laboratory standard
GC-FIDs						
<i>Perkin Elmer systems with Deans switch</i>						
AUC	no	SGE BP-1 (50 m × 0.22 mm × 1 μm), Al ₂ O ₃ /Na ₂ SO ₄ PLOT (50 m × 0.32 mm), Deans switch	45°C for 15 min, 5°C min ⁻¹ to 170°C, 15°C min ⁻¹ to 200°C, hold for 6 min	SS not heated	outlet split, when trap is heated, set to 2 mL min ⁻¹ , split ratio ~ 1 : 1	30 NMHCs, 4 nmol mol ⁻¹ , NPL
HAR	no	SGE BP-1 (50 m × 0.22 mm × 1 μm), Al ₂ O ₃ /Na ₂ SO ₄ PLOT (50 m × 0.32 mm), Deans switch	45°C for 15 min, 5°C min ⁻¹ to 170°C, 15°C min ⁻¹ to 200°C, hold for 6 min	SS not heated	outlet split, when trap is heated, set to 2 mL min ⁻¹ , split ratio ~ 1 : 1	30 NMHCs, 4 nmol mol ⁻¹ , NPL
PAL	no	SGE BP-1 (50 m × 0.22 mm × 1 μm), Agilent GS-Al ₂ O ₃ /Na ₂ SO ₄ PLOT (50 m × 0.32 mm), Deans switch	46°C for 15 min, 5°C min ⁻¹ to 170°C, 15°C min ⁻¹ to 200°C	SS	split injection	30 NMHCs, 4 nmol mol ⁻¹ , NPL
SMK	no	SGE BP-1 (50 m × 0.22 mm × 1 μm), Al ₂ O ₃ /Na ₂ SO ₄ PLOT (50 m × 0.32 mm × 5 μm), Deans switch	46°C for 15 min, 5°C min ⁻¹ to 170°C, 15°C min ⁻¹ to 200°, hold until 50 min	SS	outlet split, when trap is heated, set to 2 mL min ⁻¹ , split ratio ~ 1 : 1	30 NMHCs, 4 nmol mol ⁻¹ , NPL
ZSF	no	SGE BP-1 (50 m × 0.22 mm × 1 μm) Varian Al ₂ O ₃ /Na ₂ SO ₄ PLOT (50 m × 0.32 mm × 5 μm), Deans switch	46°C for 15 min, 5°C min ⁻¹ to 170°C, 15°C min ⁻¹ to 200°C, hold for 8 min	SS (transfer line at 230°C)	outlet split, when trap is heated, set to 2 mL min ⁻¹ , split ratio ~ 1 : 1	30 NMHCs, 4 nmol mol ⁻¹ , NPL
<i>other systems with Deans switch</i>						
IPR	no	J&W DB-1 (50 m × 0.318 mm × 1.2 μm), HP-Al ₂ O ₃ /KCl PLOT (50 m × 0.321 mm × 8 μm), Deans switch	40°C for 5 min, 6°C min ⁻¹ to 200°C, hold for 15 min	teflon at room temperature, SS and Silcosteel® at 250°C	outlet split, when trap is heated, set to 2 mL min ⁻¹ , split ratio ~ 1 : 1 (controlled with needle valve)	30 NMHCs, 4 nmol mol ⁻¹ , NPL
KOS_A	no	Varian CP Al ₂ O ₃ /Na ₂ SO ₄ PLOT (50 m × 0.32 mm), J&W DB-1 (50 m × 0.32 mm), Deans switch	45°C for 5 min, 6°C min ⁻¹ to 160°C, 9°C min ⁻¹ to 200°C, hold for 14 min	SS not heated (transfer line >200°C)	split, trap flow 40 mL min ⁻¹ , split 20 mL min ⁻¹	30 NMHCs, 10 nmol mol ⁻¹ , NPL
DOU	no	Varian CP Sil-5 CB (50 m × 0.32 mm 1.2 μm), Al ₂ O ₃ /KCl PLOT (50 m × 0.25 mm × 1 μm), Deans switch	35°C for 10 min, 7.5°C min ⁻¹ to 200°C, hold for 15 mins	SS heated and Silcosteel®	split less	33 NMHCs, 2 nmol mol ⁻¹ , NPL

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Table 4. Continued.

Acronym	Pre-column (length × inner diam- eter × film thickness)	Column (length × inner diameter × film thickness)	Column temperature	Sample path	Injection type	Laboratory stan- dard
<i>Two column systems with split injection</i>						
YRK	no	Varian Al ₂ O ₃ /KCl PLOT (50 m × 0.53 mm), 2× Chromopack-LOWOX (each 10 m × 0.53 mm × 10 μm)	40 °C for 15.5 min, 13 °C min ⁻¹ to 110 °C, 8 °C min ⁻¹ to 200 °C	SS heated	split 70% PLOT/30% LOWOX	30 NMHCs, 4 nmol mol ⁻¹ , NPL
WCC- VOC	no	Varian CP-Silica PLOT (30 m × 0.32 mm × 4 μm), Varian VF 1 MS (60 m × 0.25 mm × 1 μm), parallel	-30 °C for 8.7 min, 40 °C min ⁻¹ to 20 °C, 5 °C min ⁻¹ to 120 °C, 20 °C min ⁻¹ to 220 °C, 43 °C min ⁻¹ to 40 °C	Silcosteel [®] , sulfurnert at room tempera- ture, SS at 100 °C	split on two parallel columns 1 : 1 (flow re- strictor)	26 NMHCs, 1.3 nmol mol ⁻¹ , NPL
<i>One column systems</i>						
RIG	no	Varian Al ₂ O ₃ /KCl PLOT (50 m × 0.53 mm)	37 °C for 11 min, 6.5 °C min ⁻¹ to 180 °C, 10 °C min ⁻¹ to 200 °C, hold for 9.5 min, 50 °C min ⁻¹ to 210 °C, hold for 20 min	SS not heated	splitless	30 NMHCs, 4 nmol mol ⁻¹ , NPL
HPB_A	no	Varian Al ₂ O ₃ /KCl PLOT (50 m × 0.53 mm)	40 °C for 2 min, 4 °C min ⁻¹ to 72 °C, 6 °C min ⁻¹ to 200 °C, isothermal at 200 °C for 33.67 min	Silcosteel [®] at room tempera- ture and 120 °C; SS at 150 °C	splitless	30 NMHCs, 2 nmol mol ⁻¹ , NPL
HPB_B (FID)	no	SGE BPX-5 (50 m × 0.22 mm × 1 μm)	10 °C for 5 min, 6 °C min ⁻¹ to 240 °C	Silcosteel [®] , ul- timal 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	30 NMHCs, 2 nmol mol ⁻¹ , NPL
FZJ_B	no	Agilent DB-1 (120 m × 320 μm × 3 μm)	-60 °C for 8 min, 4 °C min ⁻¹ to 180 °C, 20 °C min ⁻¹ 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 ⁻¹ , Apel Riemer En- vironmental, Inc. 54 VOCs, 0.16– 10.8 nmol mol ⁻¹ , Apel Riemer Envi- ronmental, Inc.

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Table 4. Continued.

Acronym	Pre-column (length × inner diameter × 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 °C for 5 min, 6 °C min ⁻¹ to 160 °C, 9 °C min ⁻¹ to 200 °C, hold for 14 min	SS not heated (transfer line >200 °C)	splitless	30 NMHCs, 10 nmol mol ⁻¹ , NPL
GC-MSs						
CMN	no	J&W GasPro PLOT (30 m × 0.35 mm)	49 °C for 6 min, 9.5 °C min ⁻¹ to 145 °C, hold for 2 min, 10 °C min ⁻¹ to 250 °C, hold for 20 min	SS (working std); Silcosteel®(NPL) and PTFE	splitless	30 NMHCs, 4 nmol mol ⁻¹ , NPL
FZJ_A	no	Agilent DB 624 (20 m × 0.18 mm)	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®tubing (Restek), valve sealing (Valcon E rotor material by VICI, 493 K); GERSTEL Graphpack fittings, Silcosteel®liner with adsorption material	splitless	74 VOCs, 0.16–10.8 nmol mol ⁻¹ , Apel Riemer Environmental, Inc. 54 VOCs, 0.16–10.8 nmol mol ⁻¹ , Apel Riemer Environmental, Inc.
HPB_B (MS)	no	SGE BPX-5 (50 m × 0.22 mm × 1 μm)	10 °C for 5 min, 6 °C min ⁻¹ to 240 °C	Silcosteel®, sulfonert, ultimet at room temperature or at 150 °C. SS, VALCO valves at 150 °C	splitless, column outflow is split 1 : 1.5 to MS : FID	30 NMHCs, 2 nmol mol ⁻¹ , NPL
PUY	no	OPTIMA-5MS (60 m × 0.25 mm, 0.25 μm)	35 °C for 5 min, 5 °C min ⁻¹ to 250 °C, hold 2 min	SS not heated	outlet split: 30 mL min ⁻¹ on 1.5 mL min ⁻¹ on column; inlet split: 50 mL min ⁻¹ , 20 mL min ⁻¹ on trap	29 NMHCs, 1–10 nmol mol ⁻¹ , Air Products, 2 nmol mol ⁻¹ , 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 ⁻¹ , 1.4 mL min ⁻¹ on column)	30 NMHCs, 4 nmol mol ⁻¹ , NPL
SMR	no	Agilent DB-5 (60 m × 0.235 mm × 1 μm)	50 °C, 4 °C min ⁻¹ to 150 °C, 8 °C min ⁻¹ to 290 °C	For this exercise: Silcosteel®lines	splitless	7 NMHCs, 2 nmol mol ⁻¹ , NPL

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Table 4. Continued.

Acronym	Pre-column (length × inner diam- eter × film thickness)	Column (length × inner diameter × film thickness)	Column temperature	Sample path	Injection type	Laboratory standard
<i>Medusa systems</i>						
JFJ	no	Varian CP 7351 CP-CP PoraBOND Q (25 m × 0.32 mm × 5 μm)	40 °C for 16.6 min, 23 °C min ⁻¹ for 7 min, 200 °C for 6.6 min	SS 40 °C	splitless	30 NMHCs, 4 nmol mol ⁻¹ , 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 ⁻¹ to 200 °C	SS	splitless	45 VOCs, 0.4–1.3 nmol mol ⁻¹ , 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 ⁻¹ to 200 °C, 40 °C	SS, PEEK, KNF pump (neoprene diaphragm), flowmeter, pressure gauge	splitless	30 NMHCs, 2.7 nmol mol ⁻¹ , NPL
<i>PTR-MS</i>						
SMR II	no	no	no	no	no	16 VOCs, 0.84–1.14 nmol mol ⁻¹ , 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_N₂ and NMHC_air (nmol mol⁻¹).

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

^a assigned mole fractions were determined only with results from HPB;

^b arithmetic mean of measurements instead of error-weighted mean.

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Table 8. Repeatability in NMHC_N₂ (%). 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).

	station/compounds	Alkanes										Alkenes										Alkynes										Aromatics										N(Compounds)									
		ethane	propane	n-butane	2-methylpropane	n-pentane	2-methylbutane	n-hexane	2-methylpentane	n-heptane	n-octane	2,2,4-trimethylpentane	ethene	propene	1-butene	trans-2-butene	cis-2-butene	1,3-butadiene	1-pentene	trans-2-pentene	isoprene	ethyne	benzene	toluene	ethylbenzene	m,p-xylene	p-xylene	DQOs 1	DQOs 2	DQOs 3																					
GC-FID	AUC	15.4	29.3	76.7	2.9	24.2	26.7	7.2	5.6	4.5	2.5	5.0	11.1	47.3	22.0	21.3	3.9	2.6	6.6	4.1	2.8	19.3	4.3	0.3	2.9	2.9	4.9	26	13	12																					
	HAR	4.6	1.6	6.1	2.3	0.8	7.1	2.3	2.2	2.4	2.4	2.6	2.2	6.6	1.7	2.1	3.1	3.8	6.5	1.7	2.4	6.8	3.0	3.9	3.6	3.9	1.7	26	18	3																					
	Deans switch PE	1.8	3.8	1.6	2.0	0.6	1.2	2.2	1.5	2.0	1.0	1.7	5.3	2.4	0.4	1.2	1.3	1.3	0.5	0.6	0.5	1.8	2.2	1.7	1.8	1.5	1.3	26	19	3																					
	SMK	2.0	3.6	1.1	2.4	0.6	0.8	1.4	1.7	1.5			3.6	4.1	2.8	0.7	1.0	0.8	1.2	1.0	0.6	1.8	2.2	1.5	0.4	1.9	0.6	24	16	3																					
	ZSF	0.2	1.2	1.6	1.3	1.9	2.0	1.0	0.5	1.2			1.8	2.1	1.7	2.5	1.7	0.2	0.9	0.6	1.9	0.6	1.4	1.8	1.3	1.5	0.4	2.3	25	22	3																				
	IPR	0.9	1.1	0.3	0.3	0.6	0.8	0.6	0.6	0.8	0.9	0.8	2.9	1.0	0.3	0.4	0.3	0.4	1.2	0.5	0.5	1.6	0.7	1.1	0.9	0.9	0.8	26	17	6																					
Deans switch	KOS_A	1.1	1.9	1.3	0.4	0.3	0.4	0.6	0.3	0.6	0.7	0.1	3.3	0.5	0.7	0.7	0.5	2.0	0.3	0.3	0.6	1.8	0.3	1.1	0.4	1.2	0.4	26	17	3																					
	DQU	0.7	0.7	1.4	0.7	0.7	0.5	0.4	0.4	0.7	0.6	0.3	3.6	2.0	0.8	0.5	0.7	0.4	0.8	0.6	0.6	3.3	0.9	0.6	0.9	1.0	0.7	26	17	3																					
	2 columns, split	YHK	0.9	0.2	0.1	0.2	0.3	0.2	0.1	0.2	0.2	0.4	0.2	0.5	0.2	0.1	0.2	0.2	0.1	0.2	0.2	3.2	0.4	0.9	1.1	0.5	0.7	26	18	0																					
	1 column	RIG	0.8	1.4	2.0	1.1	1.6	0.8	2.8	2.3	1.4		1.9	1.0	1.0	0.7	0.2	0.6	1.3	1.1	1.9	1.7	3.2	4.3	9.0	10.3	15.1	24	17	5																					
GC-FID	HPB_A	0.4	0.2	0.5	0.4	0.1	0.1	0.1	0.4	0.2	0.3	0.1	0.3	0.3	0.5	0.6	0.4	0.5	0.1	0.2	0.1	2.4	0.2	1.2	2.7	2.9	2.8	26	21	4																					
	HPB_B				0.9	0.3	0.3	0.2	0.4	0.4	0.4	0.2	0.1			0.5	0.6	0.3	1.5	0.4	0.5	1.8	0.2	0.1	0.2	0.3	0.2	21	21	0																					
	FEJ_B	4.5	2.9	2.5	0.5	1.1	0.5	1.0	1.0	1.9	1.9		3.6	7.4		0.9	1.4	9.7	7.1	2.1	2.5	11.8	3.2	2.2	2.3	2.5	2.8	24	14	1																					
	KOS_B																						1.0	1.6	1.7	2.2	4.1	5	9	2																					
GC-MS	CMN	2.1	2.2	0.3	2.7	6.6	7.8	11.6	8.8	9.1	9.9		9.1	10.9	3.6	9.0	9.7				0.3	2.7	3.3	5.6	4.0	4.3	21	7	13	6																					
	FEJ_A	10.8	7.3	1.8	1.5	1.2	1.1	1.3	2.5			6.9	1.2	1.9	6.5	0.8	1.2	0.9				1.2	0.5	2.0	1.2	0.9	20	14	4	2																					
	HPB_B_MS	1.1	0.7	0.4	0.8	0.4	0.7	0.7	0.3	0.3		0.9	0.4	0.7	0.5	0.4	1.3	0.5				1.3	1.2	1.2	1.1	1.0	21	21	0	0																					
	PUY					9.6		7.7	5.3													11.2		5.6	6.2	4.9	5.2	8	0	5	3																				
	SIR					2.7		3.2	2.3													4.0		1.4	2.7	2.7	1.2	0.9	9	3	6	0																			
	SMR																					1.3		1.3	1.7	1.6	1.6	9	3	6	0																				
	Medusa	FEJ	0.4	0.5	0.4	0.3	1.0	0.8															0.3	0.2	0.4			8	0	0	0																				
		MHD	0.3	0.3	0.3	0.4	0.4	0.7															0.3	0.2	0.4			8	0	0	0																				
		NILU	0.2	0.1	0.1	0.1	0.6																0.3	0.2	0.4			8	0	0	0																				
	N (stations)	15	16	19	18	19	19	18	16	18	18	15	12	13	14	15	16	16	16	16	15	15	18	14	20	21	20	20	20	20	20																				
DQOs 1	11	11	14	13	17	18	13	12	12	9	9	6	9	10	13	13	13	13	13	13	13	13	13	13	13	10	11	11	1	1																					
DQOs 2	3	4	2	4	1	0	4	2	4	4	1	7	5	4	2	3	5	3	2	5	2	6	2	6	7	9	7	7	7	7																					
DQOs 3	1	1	3	1	1	3	2	2	2	2	2	2	0	1	1	1	0	0	0	0	0	0	4	0	0	1	2	3	3	3																					

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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 nmol mol⁻¹.

Instrument	Station/Compound	Alkanes															Alkenes															Aromatics															N (stations)		
		ethane	propane	n-butane	2-methylpropane	n-pentane	2-methylbutane	n-hexane	2-methylpentane	3-methylpentane	2,2-dimethylbutane	2,3-dimethylbutane*	cyclohexane	n-heptane	n-octane*	1,2,4-trimethylbenzene	ethene	propene	1-butene	2-methylpropane	trans-2-butene*	cis-2-butene*	1,3-butadiene*	isoprene*	trans-2-pentene*	cis-pentene*	2-methyl-2-butene	styrene*	toluene*	methylstyrene	ethylstyrene	propylstyrene	naphthalene	anthracene	fluorene	10 (stations)	11	12											
GC-FID/TO	Decons switch R	3.9	3.8	0.2	7.4	27.1	4.4	3.5	0.7				4.2	0.004	0.7	4.1	5.3	2.4		0.007	0.007	0.010	0.015	0.016	0.012	3.5	0.6	0.7	0.5	4.6	0.6		26	11	21														
	HAR	3.0	3.1	0.1	2.2	2.1	3.1	8.5	0.4				3.0	0.004	4.1	3.4	4.3	8.8		0.009	0.008	0.007	0.005	0.005	0.007	3.6	3.7	1.1	6.1	6.6	4.8	26	18	4															
	PAL	4.6	6.1	2.5	1.8	0.9	0.6	0.0					0.005	2.1	4.2	2.2	0.6			0.015	0.010	0.007	0.004	0.010	0.010	2.4	4.2	1.0	2.7	4.2	2.7	14	4	4															
	SMK	4.2	4.7	1.8	2.1	3.5	6.3						3.1	0.004	2.3	2.3	4.8	4.9		0.003	0.003	0.005	0.004	0.004	0.003	1.4	1.4	4.6	6.1	2.3	24	11	0																
	ZSF	0.4	2.3	1.4	1.5	3.0	3.8	2.8						0.4	0.4	4.8	3.3			0.004	0.014	0.003	0.003	0.003	0.007	1.0	1.2	0.8	1.6	1.7	1.1	25	11	0															
Decons switch	TPR	0.8	0.9	0.8	0.9	0.7	0.7	1.1	1.2				1.8	0.000	0.4	1.1	1.9	0.4		0.01	0.004	0.000	0.003	0.003	0.003	0.3	0.7	0.6	1.6	2.0	1.0	25	1	0															
	KOS_A	0.8	0.8	0.4	0.4	0.4	0.4	0.8	0.8				1.5	0.000	0.9	2.1	0.8	0.9		0.003	0.003	0.003	0.003	0.003	0.003	0.3	0.4	0.4	0.8	3.0	0.8	26	5	0															
GC-FID	2 column, split	2.0	1.8	1.8	1.4	1.4	1.8	4.7	3.5	0.9	1.3		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.005	0.004	0.004	0.003	0.004	0.003	0.005	0.1	0.005	0.1	4.4	3.5	2.7	28	11	0														
	YRK	2.1	0.1	0.1	0.1	0.2	1.2	1.2					0.4	0.004	0.4	0.1	0.2	1.5	0.1		0.003	0.002	0.002	0.002	0.002	0.006	0.1	0.2	0.2	3.5	3.7	3.0	30	4	1														
GC-MS	RIG	0.3	0.2	1.8	1.8	0.4	0.4	4.7	1.6	4.6	3.2	3.1	2.1			0.4	1.6	3.3	3.1	0.003	0.003	0.003	0.002	0.002	0.003	1.1	0.009	1.4	1.1	1.8	4.1	6.9	3.2	31	13	0													
	HPB_A	0.1	0.1	0.1	0.1	0.2	0.1	0.4	0.3	3.7						0.4	0.4	0.4	0.4	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.4	0.4	0.4	0.4	0.4	0.4	32	2	0														
	FZJ_B	0.4	2.3	0.1	0.1	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	24	11	0													
	CMN	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	21	7	6												
	FZJ_A	2.6	3.8	1.9	1.0	8.6	4.7							4.2	0.005			2.1		0.003	0.003	0.002	0.010	0.003		1.8	0.7	1.5	1.0	0.4	0.1	20	8	4															
Medusa	HPB_B_MS	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	21	1	0													
	PLK	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	6	3	0													
	SIR																																		9	8	0												
	SMR																																		6	0	0												
	FFJ	0.8	1.8	1.8	1.8	1.8	1.8	1.8																											6	0	0												
DQOs	1	15	16	18	17	18	18	17	15	4	4	3	4	17	13	11	11	12	13	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14													
	2	12	13	14	15	16	16	17	15	4	4	3	4	17	13	11	11	12	13	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14												
	3	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2												

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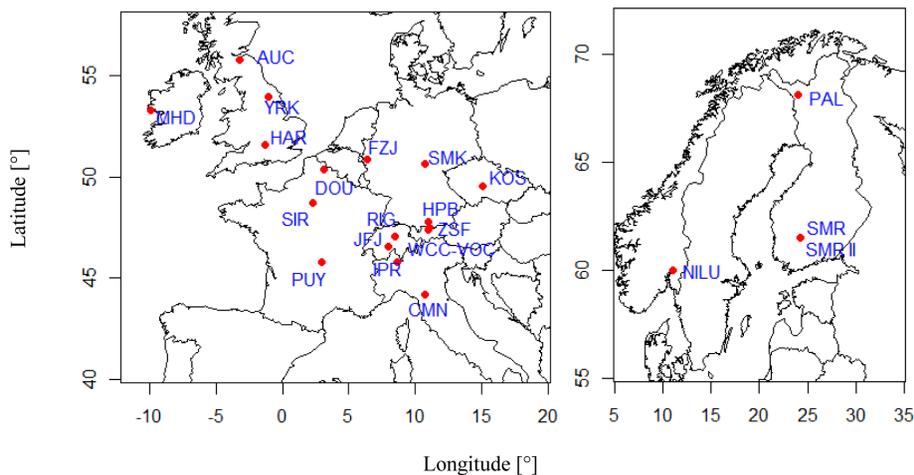


Figure 1. The participants of the ACTRIS NMHC intercomparison in Europe. Left: Western, Central and Southern Europe; right: Northern Europe. For abbreviations and further details see Table 3.

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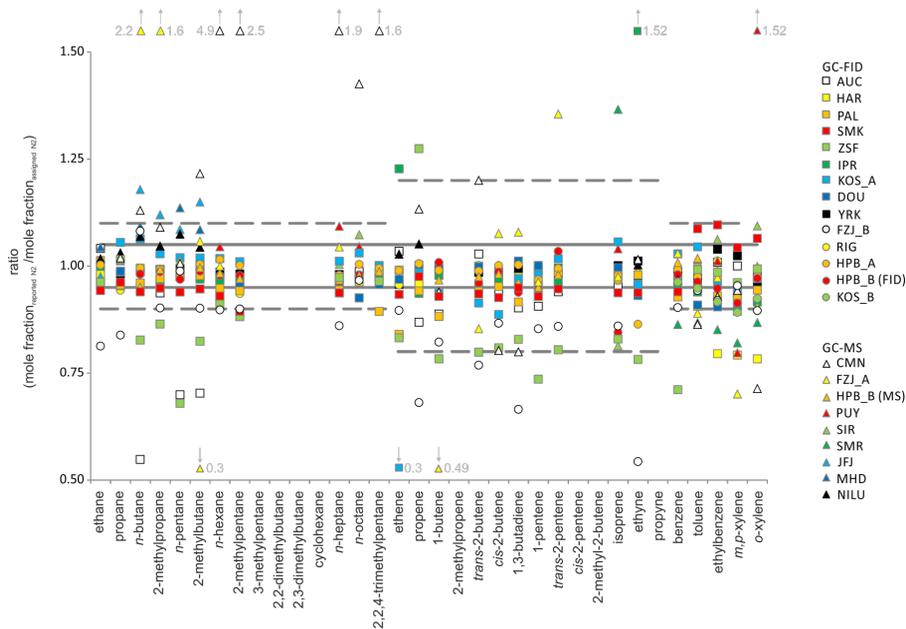


Figure 2. NMHC results for each site (colour coded symbols) are presented relative to the assigned values in NMHC_{N₂}. Solid and dashed grey lines indicate ACTRIS and GAW DQOs, respectively (Table 2). For abbreviations see Table 3.

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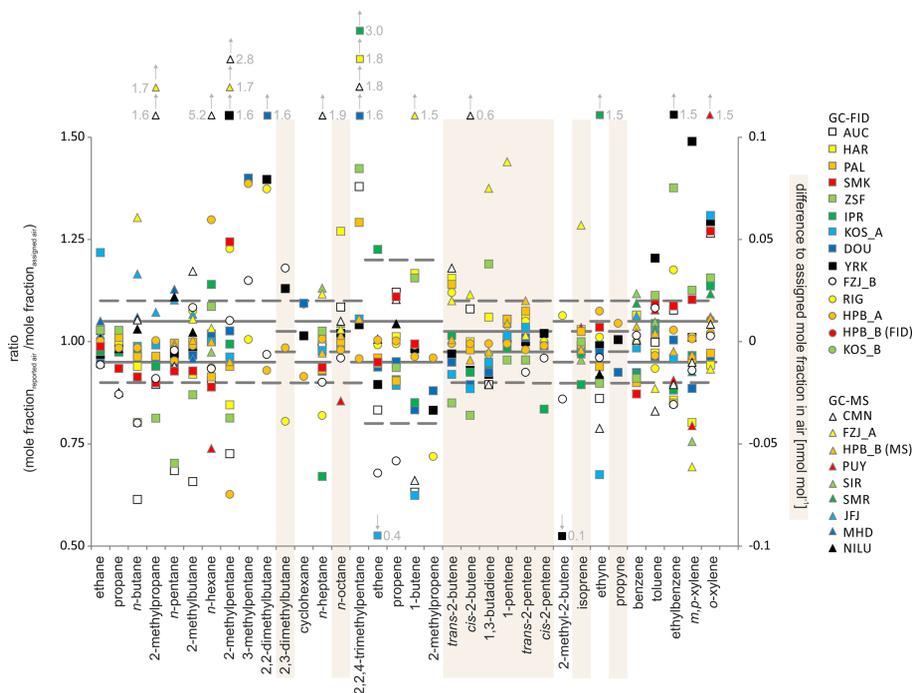


Figure 3. NMHC results for each site (colour coded symbols) are depicted for NMHC_{air}. On the left scale the values are presented relative to the assigned values and on the right scale the values are presented as difference to assigned mole fractions (in nmol mol^{-1}) for compounds below 0.1 ppb (brownish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

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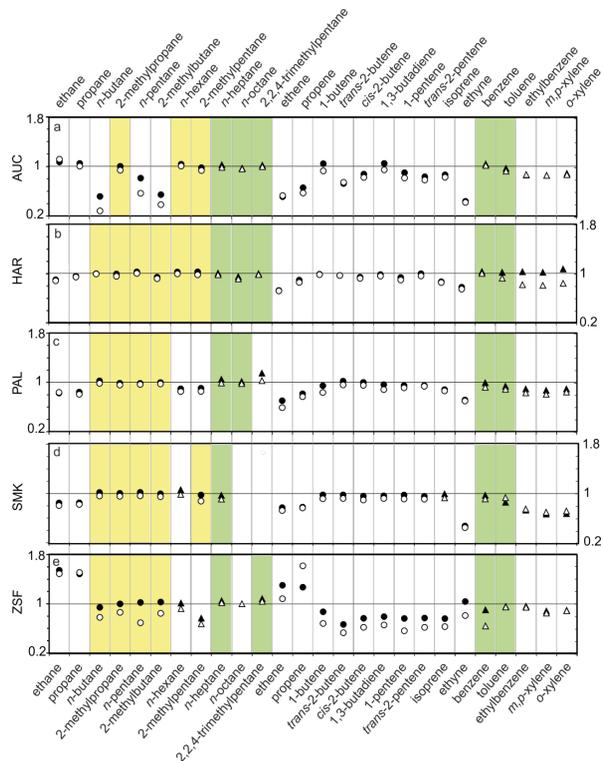


Figure 4. C-responses of FIDs. Circles (O) indicate column one, triangles (Δ) column two. Filled symbols indicate the C-responses in the calibration standard, open symbols the C-responses in NMHC_N₂. The C-responses for column one were normalised by the average C-response of the available C₄–C₆-alkanes (highlighted in yellow), column two by the average C-response of the available C₇–C₈-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.

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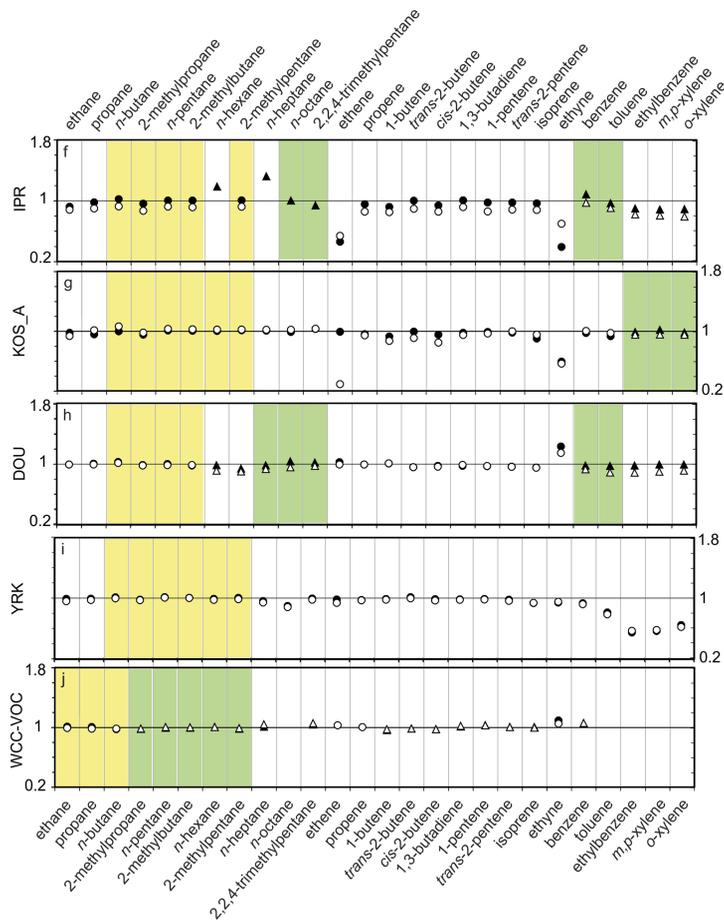


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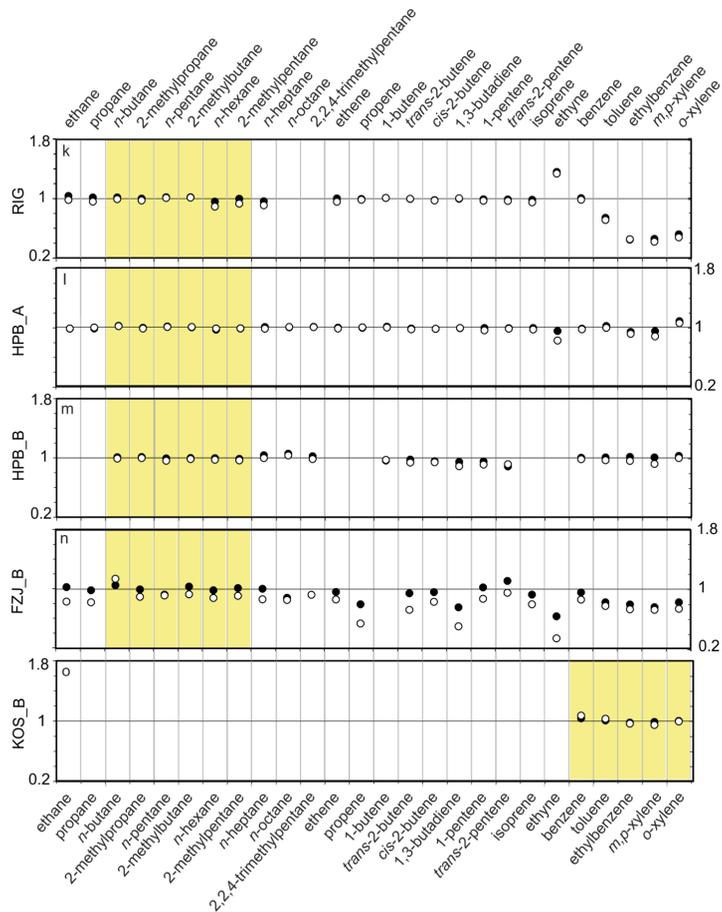


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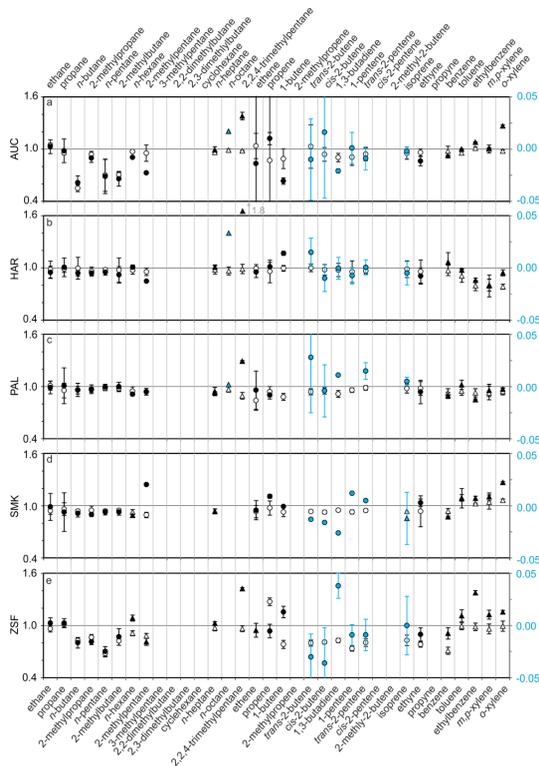


Figure 5. Normalised mole fractions for NMHC_{N₂} and NMHC_{air}. Circles (○) indicate column one, triangles (△) column two. Open symbols indicate NMHC_{N₂}, filled symbols NMHC_{air}. For NMHC > 0.1 nmol mol⁻¹ use left y axis with normalised mole fraction to assigned values. Blue symbols indicate values in NMHC_{air} < 0.1 nmol mol⁻¹. Right y axis (in blue) shows difference to assigned mole fraction (nmol mol⁻¹) in NMHC_{air} < 0.1 nmol mol⁻¹.

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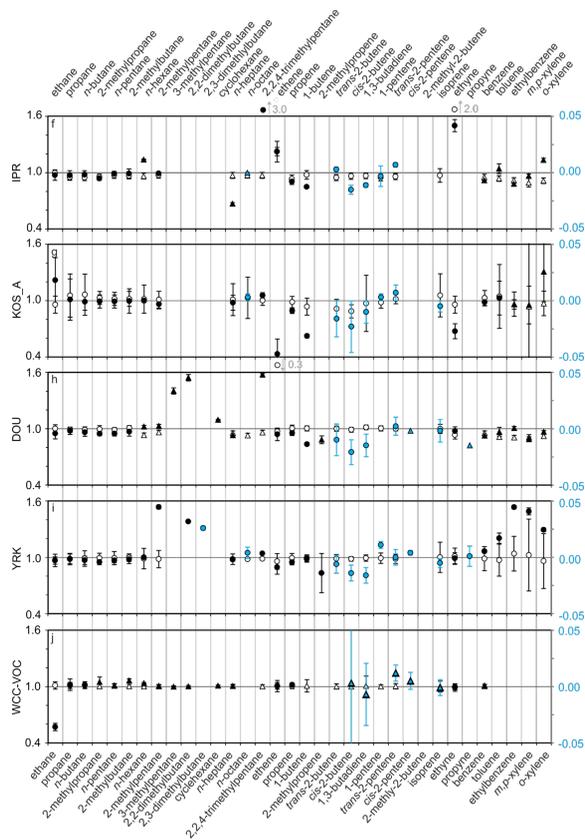


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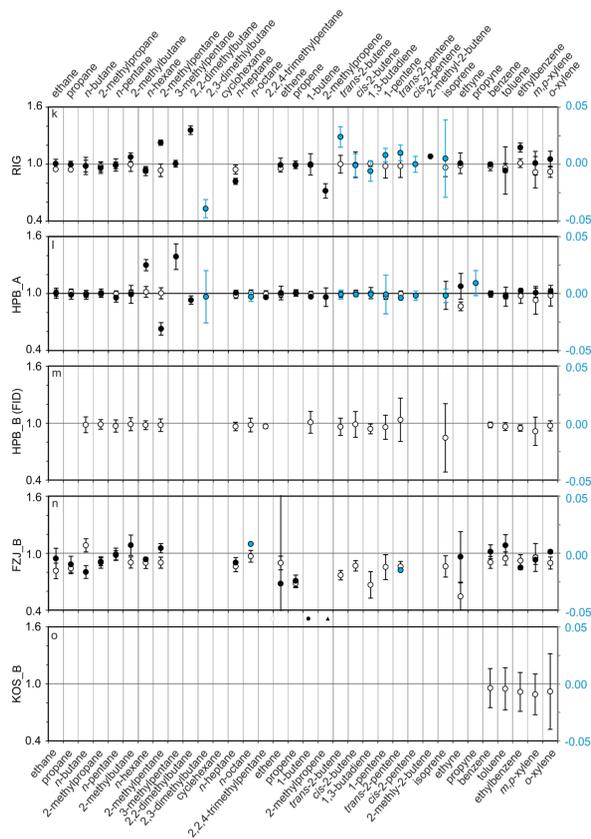


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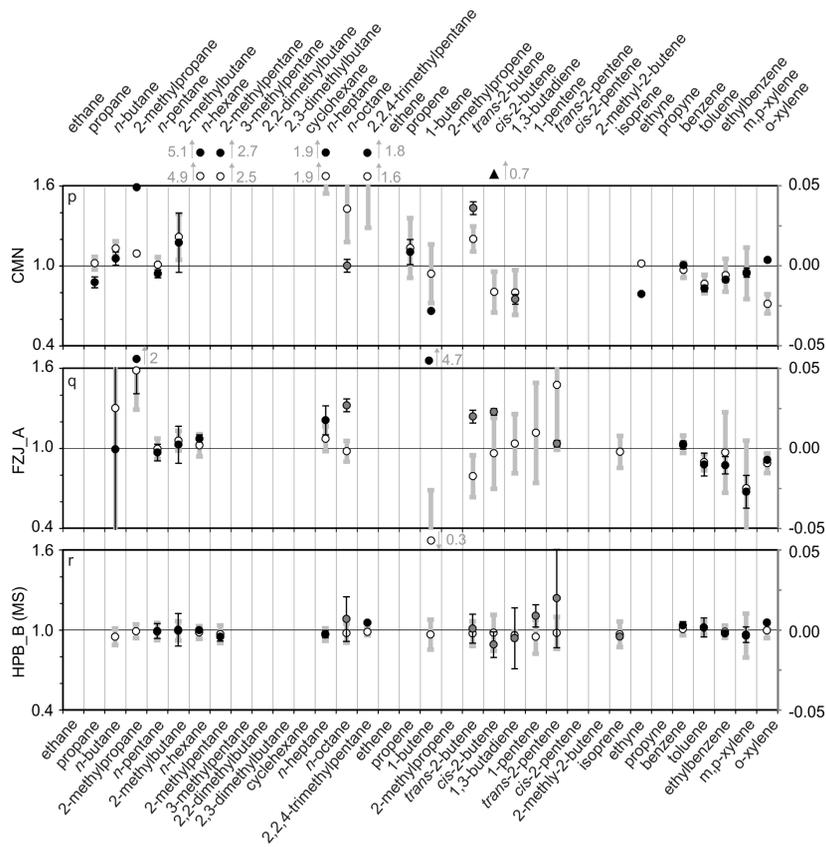


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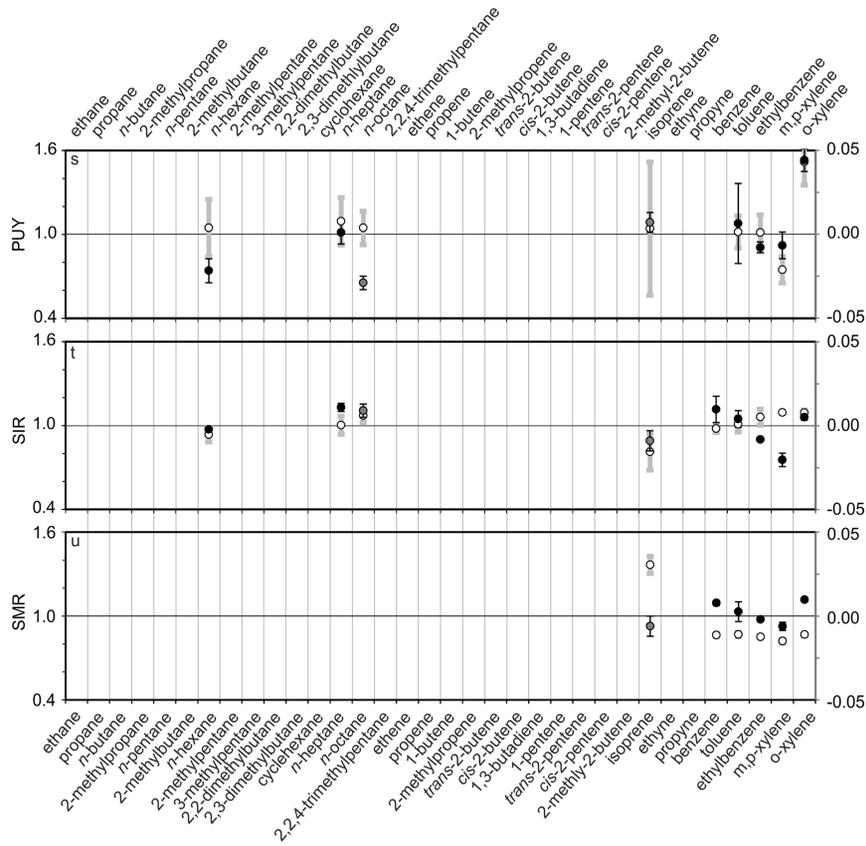


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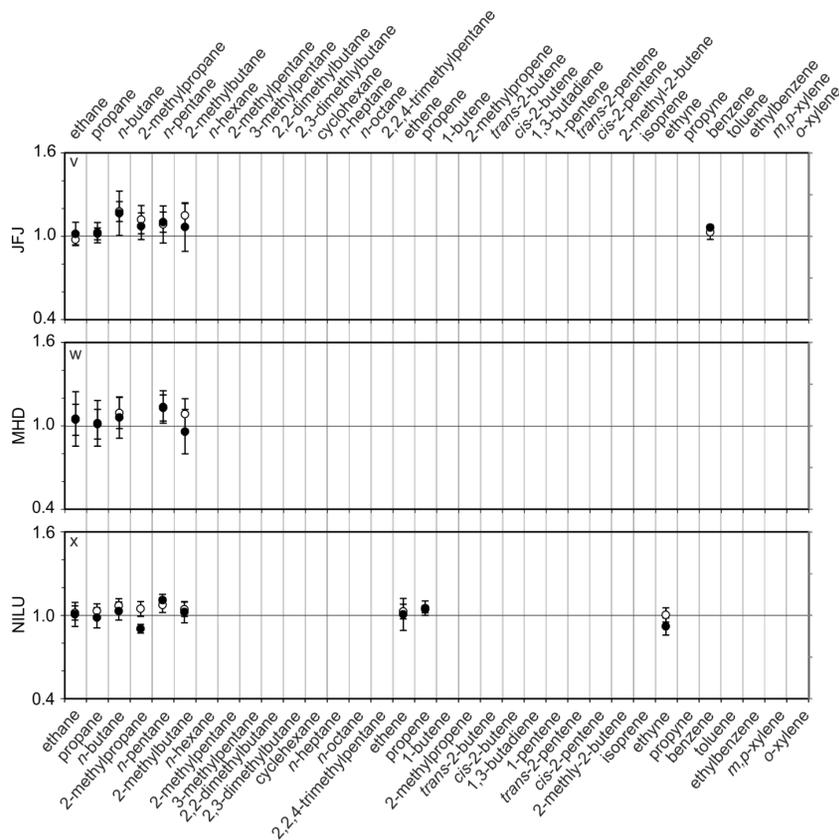


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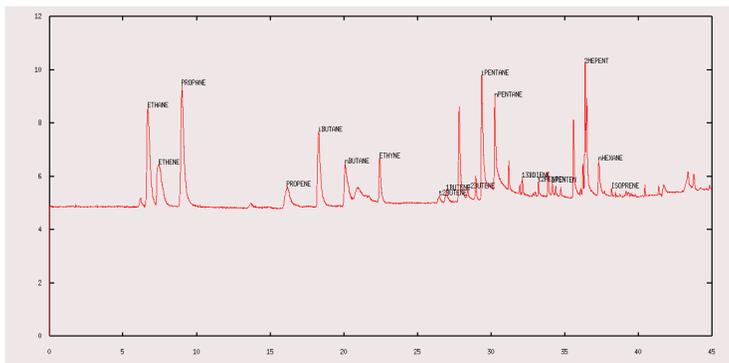
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a) Chromatogram in NMHC_air for AUC (PLOT-column).



b) Chromatogram in NMHC_air for HAR (PLOT-column).

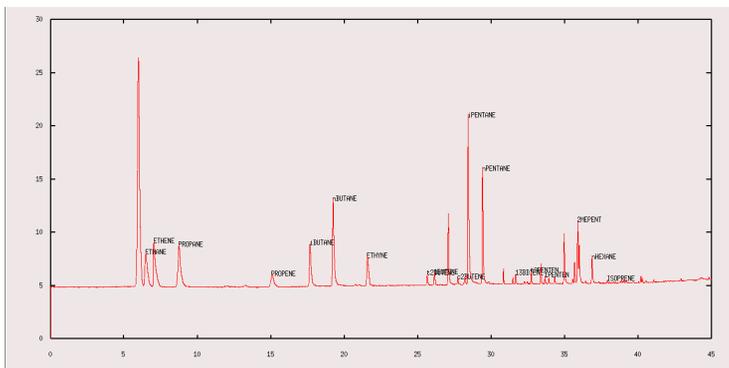
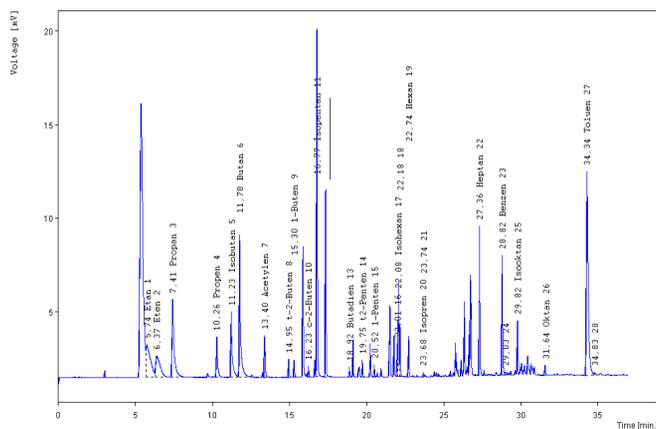


Figure 6. Examples of chromatograms. **(a)** Chromatogram in NMHC_air for AUC (PLOT-column). **(b)** Chromatogram in NMHC_air for HAR (PLOT-column). **(c)** Chromatogram in NMHC_air for KOS_A (PLOT-column). **(d)** Chromatogram in NMHC_air for PAL (PLOT-column).

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c) Chromatogram in NMHC_air for KOS_A (PLOT-column).



d) Chromatogram in NMHC_air for PAL (PLOT-column).

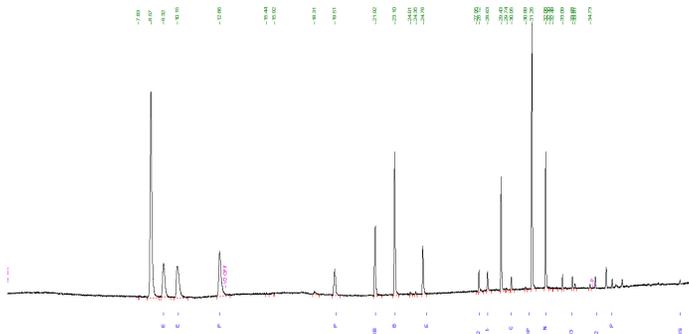


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