

WP4- NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides
Deliverable D4.5: Results of VOC side-by-side inter-comparison exercise of ambient air and test gases

Table of contents

1. Abstract	1
2. Introduction.....	2
3. Results of side-by-side inter-comparisons.....	3
3.1 Hyytiälä.....	3
3.2 Hohenpeissenberg 1	4
3.3 Hohenpeissenberg 2	5
4. Results of VOC air-sampled canisters	7
4.1 Alkanes	7
4.2 Alkenes	9
4.3 Alkyne.....	10
4.4 Aromatics	10
5. Outlook.....	10

1. Abstract

Side-by-side inter-comparisons were performed at Hyytiälä and Hohenpeissenberg (two inter-comparisons) in 2012. At both sites several VOC and OVOC were investigated in ambient air. At Hyytiälä the measurements were performed with a PTR-MS (from University of Helsinki), a Markes-GC-MS (from Finnish Meteorological Institute) and a MADS-GC-MS (from Empa), at Hohenpeissenberg with a GC-FID and GC-FID/MS (both from DWD Hohenpeissenberg), a MADS-GC-FID (from Empa), and a GC-2FID (from Mines Douai), respectively. At Hyytiälä, the different instruments reported similar mole fractions of toluene, benzene, and acetone. Similar results for the before mentioned compounds and some other VOC were reported from both campaigns at Hohenpeissenberg. The results of the OVOC are still under investigation. In addition, canister measurements of VOC in ambient air were performed by Hohenpeissenberg and Kosetice. In general, these results were comparable to those of the round robin (Deliverable D4.3). For autumn 2013 a side-by-side inter-comparison for OVOC is planned at Hohenpeissenberg.

2. Introduction

Volatile organic compounds (VOC) are important atmospheric trace gases, which are emitted by anthropogenic as well as biogenic sources. Measurement capacities for these air pollutants in Europe are widespread but coordination is generally absent or is only part of short-term research projects. The main gaps within existing measurement networks include the application of standardized operation procedures and the limited use of common calibration standards and scales. Additionally to the ACTRIS round robin exercise for VOC mixtures (Deliverable D4.3), VOC side-by-side inter-comparison exercises of ambient air were performed at the following sites:

- Hyytiälä (Finland): measurement of several VOC and OVOC (oxygenated volatile organic compound) during April 2012, involved institutions: University of Helsinki (PTR-MS), Finnish Meteorological Institute (Markes-GC-MS) and Empa (MADS-GC-MS).
- DWD Hohenpeissenberg (Germany): measurement of several VOC and OVOC during summer 2012 and spring 2013, involved institutions: Hohenpeissenberg (GC-FID and GC-FID/MS) and Empa (ADS-GC-MS).
- DWD Hohenpeissenberg (Germany): measurement of VOC, OVOC, Terpenes during November 2012, involved institutions: Hohenpeissenberg (GC-FID, on-line) and Mines Douai (GC-2FID, off-line).
- Canister comparisons: measurements of VOC during winter 2012/2013, involved institutions: DWD Hohenpeissenberg (GC-FID), Kosetice (GC-FID), Empa (GC-FID), Monte Cimone (GC-MS), and Ispra (GC-FID)

During autumn 2013 a further side-by-side inter-comparison at DWD-Hohenpeissenberg is foreseen for the measurement of OVOC. In this inter-comparison the focus will be on concurrent GC and PTR-MS systems.

Other side-by-side inter-comparisons at one location were not feasible, because (i) all participants of the VOC round robin needed their instruments at the station sites for (on-line) measurements, and (ii) not all instruments are easy transportable. Therefore, we agreed at the workshop at DWD Hohenpeissenberg in June 2012 (see ACTRIS-web) that Empa Dübendorf sends canisters with ambient air to the participants (for VOC analysis) and that the participants do a parallel canister sampling with their stations routine sampling procedure and send the canisters back to Empa for VOC analysis.

3. Results of side-by-side inter-comparisons

3.1 Hyytiälä

During April 2012 a side-by-side inter-comparison at Hyytiälä was performed for the measurement of selected VOC and OVOC. The University of Helsinki (UHEL) provided a PTR-MS instrument, the Finnish Meteorological Institute (FMI) a Markes-GC-MS and Empa a MADS-GC-MS. In Figure 1a the results of toluene is depicted. The trends of the measurements are similar for the three instruments, but there were slight differences in the mole fractions. It seems that FMI measured slightly lower mole fractions in comparison to UHEL and Empa, whereas UHEL reported somewhat higher values. In general, larger differences in the OVOC mole fractions (e.g. ethanol, methanol, benzene) were reported from the three institutes than for the VOC. In contrast, the acetone mole fraction reported from UHEL and Empa were consistent to each other (Figure 1b). FMI did not report this compound.

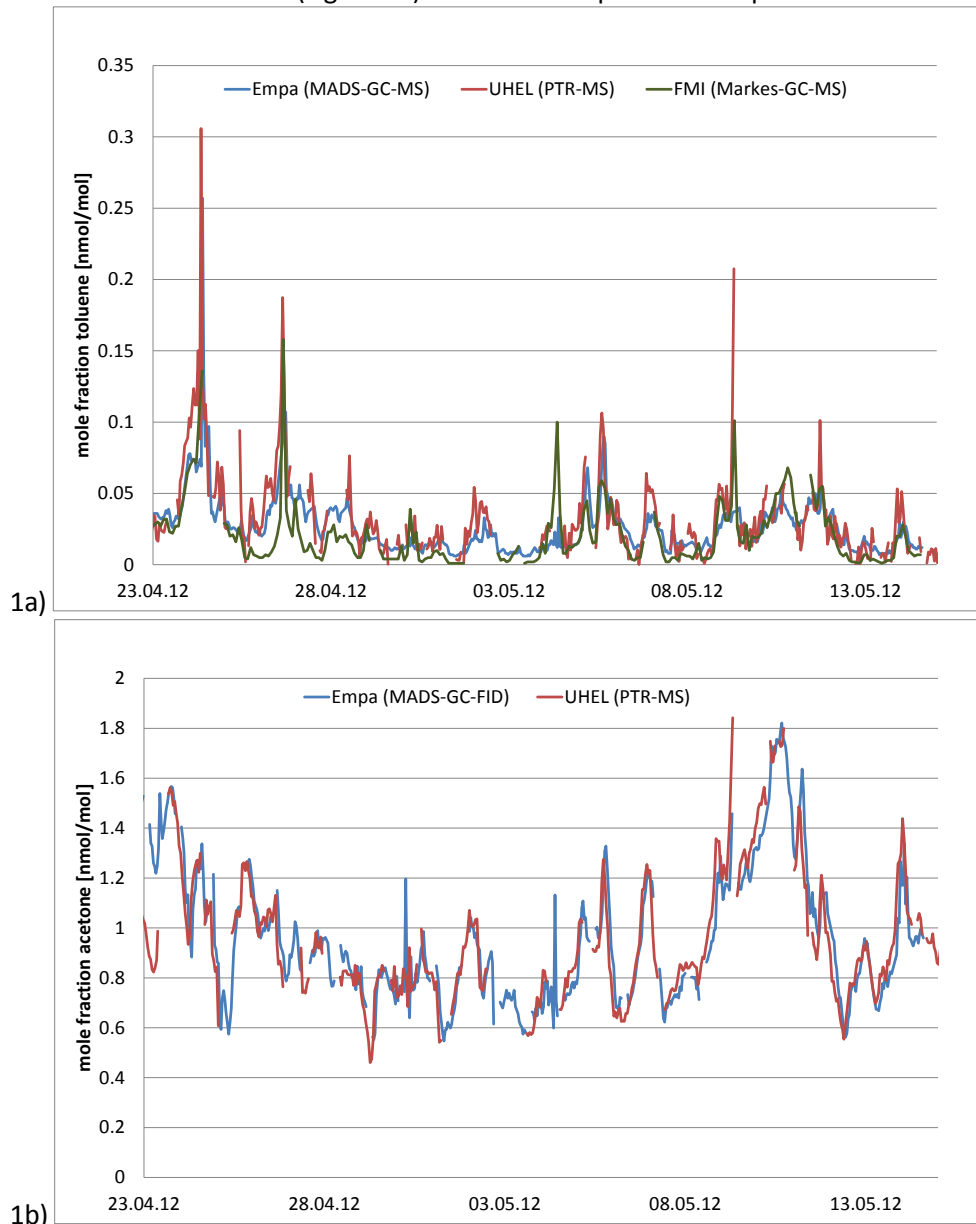
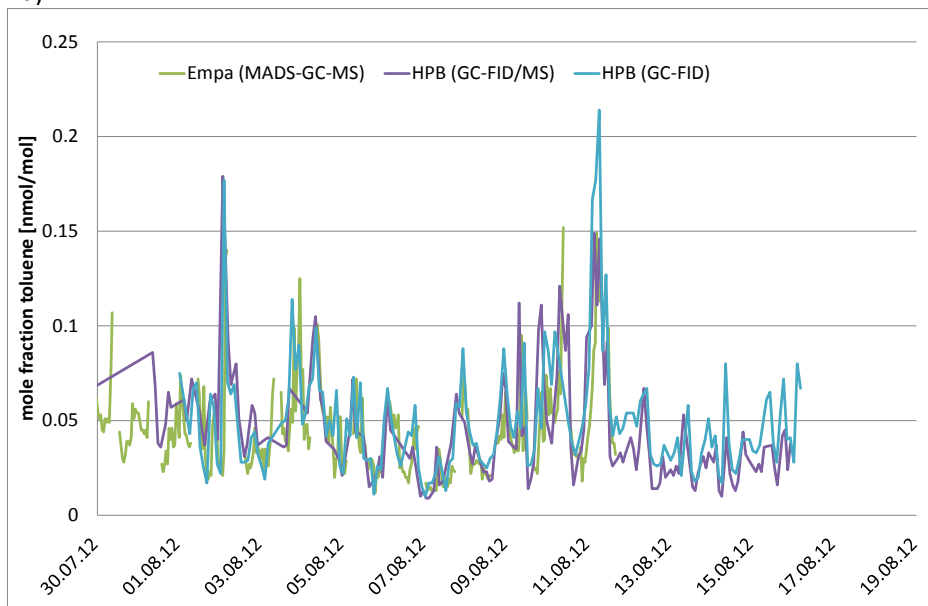


Figure 1: Mole fractions of a) toluene and b) acetone measured at Hyytiälä using a PTR-MS(UHEL; red line), a Markes-GC-MS (FMI; green line), and a MADS-GC-MS (Empa; red line).

3.2 Hohenpeissenberg 1

During summer 2012 an inter-comparison at Hohenpeissenberg was performed for the analysis of selected VOC and OVOC. The involved institutions were DWD Hohenpeissenberg (HPB) and Empa. HPB measured with a GC-FID and with a new instrument a GC-FID/MS; Empa performed the measurements with an MADS-GC-MS. For toluene the results of the measurements were consistent for all three instruments (Figure 2a). For benzene, two instruments (HPB GC-FID and Empa MADS-GC-MS) gave the same results, but the new instrument of HPB (GC-FID/MS) reported higher values for this compound (Figure 2b). The results of OVOC (e.g. methanol, acetone) were less promising: the instruments reported different mole fractions, usually the instruments from HPB reported higher mole fractions compared to the Empa instrument. To understand better this discrepancies different tests (e.g. measurement of different used standards, standard additions) were and will be performed. In addition, the instrument of Empa is placed at the moment at HPB to compare the measurements again.

2a)



2b)

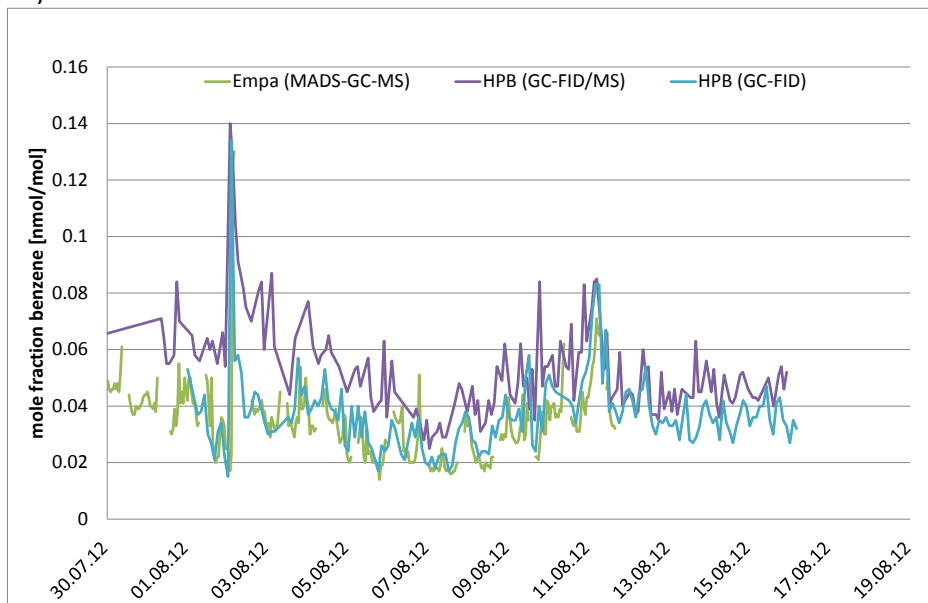


Figure 2: Mole fractions of a) toluene and b) benzene at Hohenpeissenberg using a GC-FID/MS (HPB; magenta line), a GC-FID (HPB; light blue line), and a MADS-GC-MS (Empa; light green line).

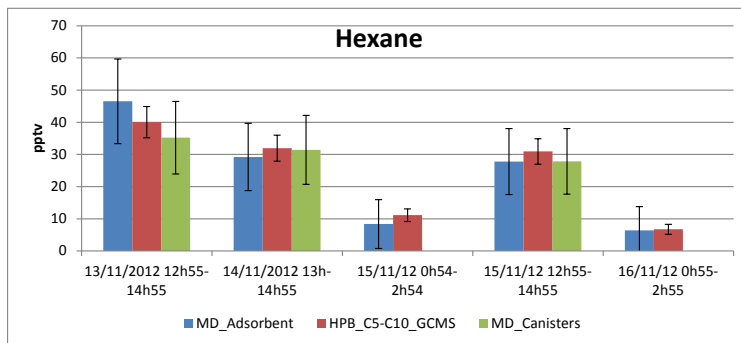
3.3 Hohenpeissenberg 2

During November 2012 an inter-comparison at Hohenpeissenberg was performed for the analysis of VOC, OVOC, and terpenes. The involved institutions were DWD HPB and Ecole de Mines Douai (MD; France). For this inter-comparison the instrument of Mines Douai (GC-2FID) was not transported to HPB. Instead canisters were filled or air was sucked through tubes filled with adsorbent material parallel to on-line measurements at HPB. Air samples were taken at different times (noon or midnight) during one week in November. Canisters and tubes were analysed at Mines Douai at a later date.

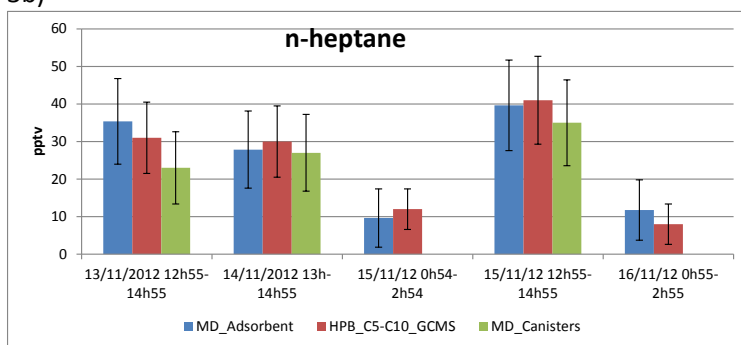
In the following plots the mole fractions of different VOC measured by HPB and MD are depicted. HPB reported the values of the on-line measurements, MD of the canisters and from the adsorbent materials. For the alkanes hexane and n-heptane (Figure 3a-b) as well as for the aromatics toluene, benzene, ethylbenzene, o-xylene, and m,p-xylene (Figure 3c-g) the reported mole fractions were consistent to each other.

For the OVOC and the terpenes the evaluation of the measurements is still on-going. Therefore, these results will be reported at a later time.

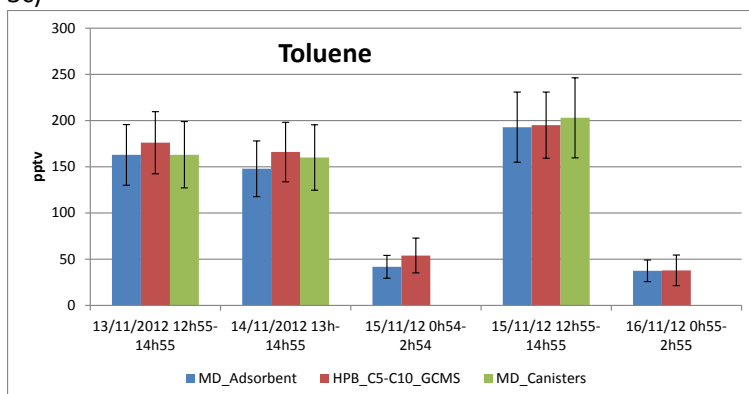
3a)



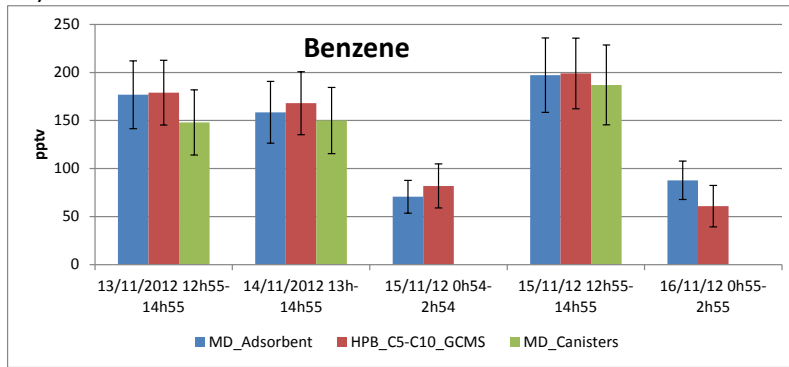
3b)



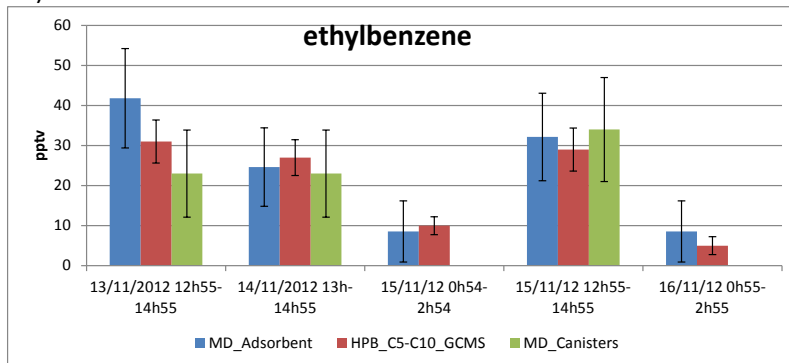
3c)



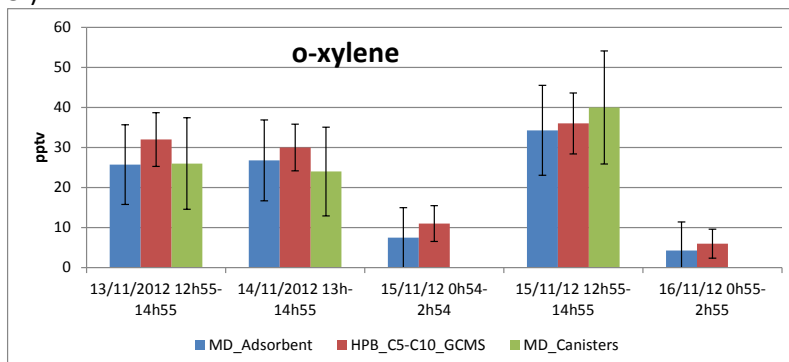
3d)



3e)



3f)



3g)

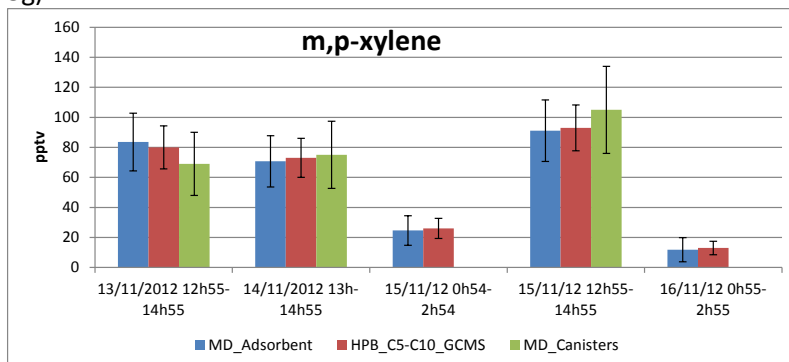


Figure 3: Reported mole fractions [nmol/mol] of Mines des Douai and Hohenpeissenberg for a) hexane, b) n-heptane, c) toluene, d) benzene, e) ethylbenzene, f) o-xylene, and g) m,p-xylene. The blue bars indicate the results of the adsorbents (MD, off-line), the red ones those of HPB (GC-MS online), and the green ones those of the canisters (MD, off-line).

4. Results of VOC air-sampled canisters

Empa filled SUMMA treated stainless steel-canisters with ambient air from Dübendorf (suburban area of Zurich/Switzerland). Before sending the canisters with a pressure of 2.5 bars to the participants, Empa analysed them for VOC. The participants performed the analysis in the same way as during the VOC round robin. Following this, the participants did a parallel canister sampling with their stations routine sampling procedure and sent them to Empa for VOC analysis. All results were submitted to Empa for comparison.

4.1 Alkanes

For Ethane, HPB reported a mole fraction which was around 15% lower than KOS (Figure 4a). This is consistent with the round robin exercise, where the values were also different by around 15%. The difference between the reported values for propane was less than 10% between KOS and HPB (Figure 4b), similar to the round robin results. KOS reported a lower mole fraction of n-butane and 2-methylpropane compared to HPB (around 10% lower) (Figure 4c and 4d). Also here similar differences were reported during the round robin from both stations. For n-pentane and 2-methylbutane, KOS and HPB reported similar values, which is also consistent with the round robin results (Figure 4e and 4f). The mole fraction of n-hexane was lower than 0.1 nmol/mol. The first value reported from HPB is comparable to that one of KOS, the second value is lower (Figure 4g), but this is might due to the low mole fraction. In contrast, during the round robin HPB reported a higher value compared to KOS. KOS value was in the range of the reference value. For n-heptane, HPB reported around 10% lower values than KOS (Figure 4h). This difference was not observed during the round robin, where both stations measured this compound in the same range.

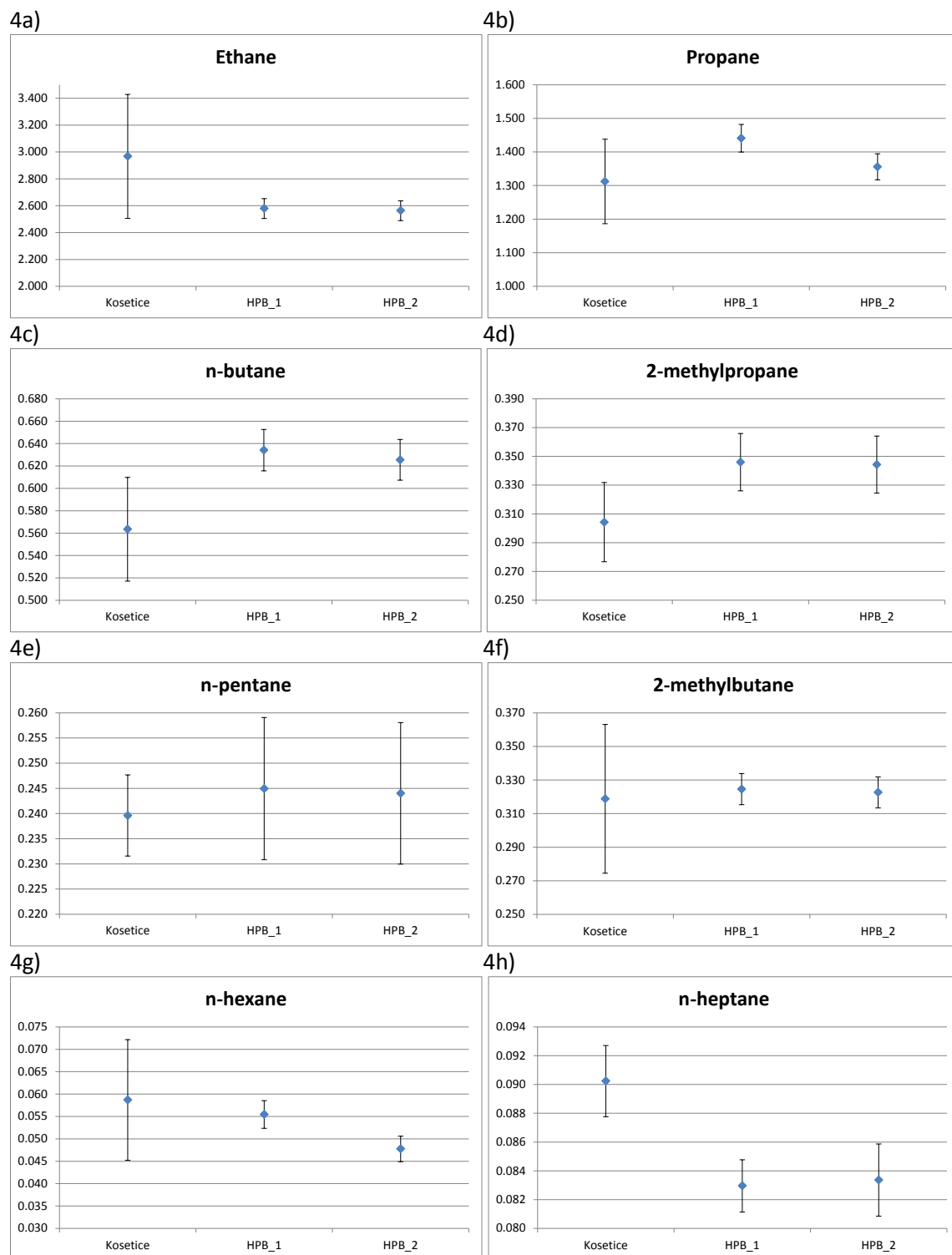


Figure 4: Reported mole fractions [nmol/mol] of Kosetice and Hohenpeissenberg for a) ethane, b) propane, c) n-butane, d) 2-methylpropane, e) n-pentane, f) 2-methylbutane, g) n-hexane, and h) n-heptane.

4.2 Alkenes

KOS measured a more than 20% lower mole fraction of ethene compared to HPB (Figure 5a). A similar observation was made during the round robin. Probably KOS had a breakthrough during the trapping phase which would indicate the lower reported mole fractions. For propene KOS and the first value of HPB were in the same range. In contrast, the second value of HPB was nearly twice as high as the first one (Figure 5b). During the round robin a lower value of KOS compared to HPB was observed, too, but the value of HPB was in the 5% ACTRIS DQO-range of the reference value and KOS was in the 10% GAW DQO range. As for propene a similar observation was made for 1,3-butadiene. KOS and the first measurement of HPB were in the same range, the second one of HPB was around 70% lower (Figure 5c). We observed a similar “loss” of 1,3-butadiene in the ACTRIS round robin canisters, where a drift between the first and second measurement occurred. But here, the two canisters were measured at the same time, and we suspect that in one canister 1,3-butadiene degraded much faster than in the other one. During the round robin, KOS and HPB reported similar 1,3-butadiene values. As for 1,3-butadiene the mole fraction of isoprene was also very low (>0.1 nmol/mol) and a similar pattern was observed (with a lower value of isoprene in the second canister of HPB) (Figure 5d). Again, during round robin both stations reported similar values of this compound.

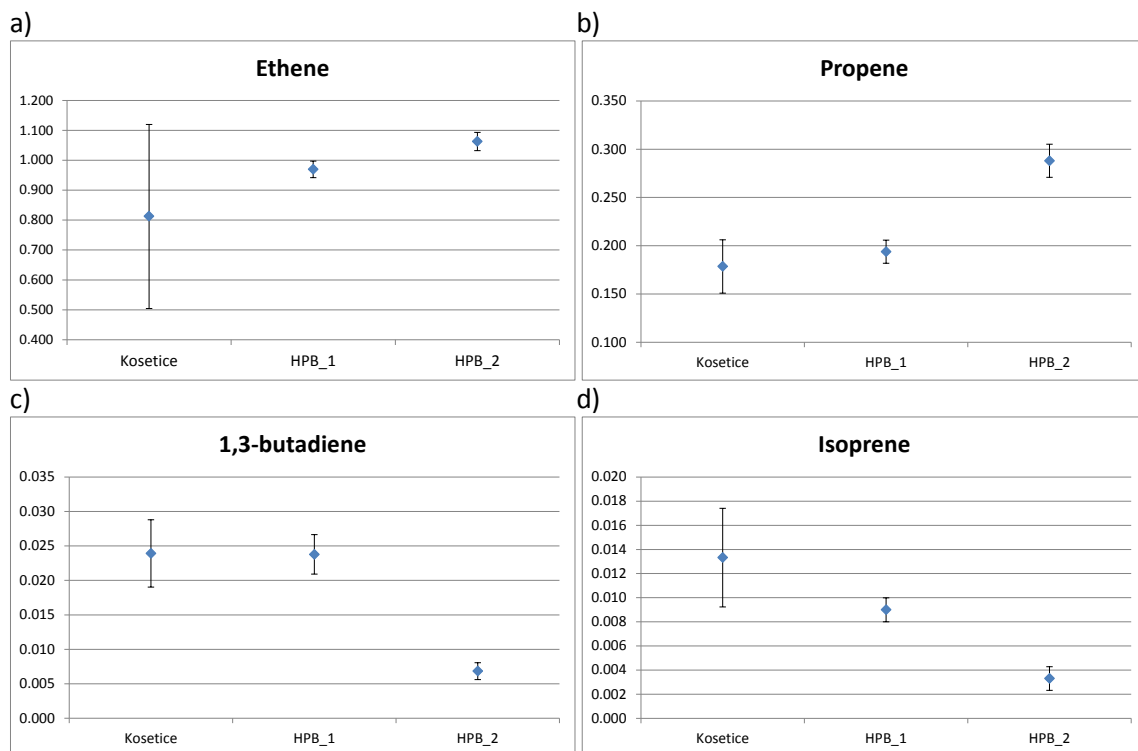


Figure 5: Reported mole fraction [nmol/mol] of KOSetice and Hohenpeissenberg for a) ethene, b) propene, c) 1,3-butadiene, and d) isoprene.

4.3 Alkyne

KOS reported a mole fraction of ethyne which was around 20% lower as those of HPB (Figure 6). This observation was also made during the round robin, but there the difference was even larger (around 60%).

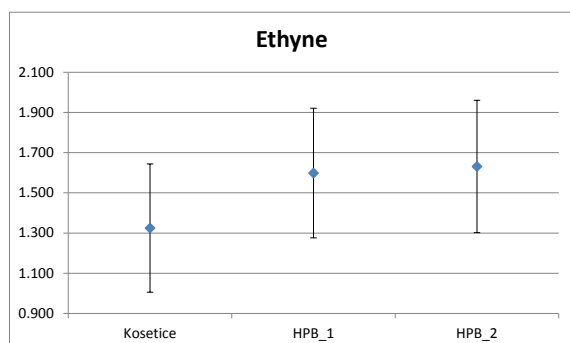


Figure 6: Reported mole fraction [nmol/mol] of Kosetice and Hohenpeissenberg for ethyne.

4.4 Aromatics

The aromatics were not stable in the different canisters; therefore no results of these compounds were reported.

5. Outlook

In autumn 2013 a side-by-side inter-comparison for OVOC is foreseen at DWD Hohenpeissenberg. The inter-comparison will focus on concurrent GC- and PTR-MS systems and is scheduled for one week. The exact date will be determined upon availability of participants. This activity supports the integration of European ground-based stations equipped with advanced atmospheric probing instrumentation for short-lived gas-phase species covered by the Network Activity 4 (NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides) and JRA-2 (Comprehensive gas phase and aerosol chemistry) of ACTRIS.