WP4- JRA4: Trace gases networking: Volatile organic carbon and nitrogen oxides
Deliverable D4.13: Recommendation on sustainability of QA and SOPs for VOC in Europe

Summary:

Within the ACTRIS work package 4 (trace gases networking: Volatile organic carbon and nitrogen oxides) a Round Robin intercomparison was performed, assessing the performance of 18 European laboratories for the analysis of atmospheric VOCs. The participants analysed two dry gas mixtures (in nitrogen and whole air) in pressurised cylinders, following a standardised operation procedure including zero- and calibration gas measurements. The measurements were either performed by gas chromatography-flame ionisation detection (GC-FID) or by gas chromatography-mass spectrometry (GC-MS). Factors affecting the performance of the participating laboratories were identified and discussed in the peer reviewed Journal AMT (Hoerger et al. 2014).

In addition, side-by-side intercomparisons took place at Hyytiälä (Finland) and DWD-Hohenpeissenberg (Germany). In Hyytiälä, the performance of proton transfer reaction mass spectrometry (PTR-MS) and GC-MS was compared during a campaign in April-May 2012. Correlations and possible biases between the measurements of methanol, acetaldehyde, acetone, benzene and toluene were assessed (Kajos et al. 2015). During the side-by-side intercomparison, which took place at DWD-Hohenpeissenberg, oxygenated VOCs (OVOCs) were measured with ten different instruments during October 2013. Overall, promising results were obtained with generally good agreements for non-oxygenated VOCs and ketones and deviations for methanol and acetaldehyde. Observed deviations are in discussion with respect to reference concentrations, characteristics of the respective techniques, blank and calibration issues and uncertainties. A corresponding publication is in process (Englert et al. in preparation). Measurement issues as well as quality assessment and quality control will be further taken up in ACTRIS-2 and the corresponding research and cooperation within the European network (e.g. link to link to the EURAMET project key-VOC (2014-2017)).

Workshops on data quality assurance (QA) and quality control (QC) took place at Hohenpeissenberg in 2012, and Dübendorf and Jülich both in 2014. Guidelines for VOC measurements, QA and QC including standard and zero gas measurement, and uncertainty determination were discussed at those workshops and developed in accordance with GAW/WMO. Data reporting procedures to EBAS were further developed within ACTRIS and now include the necessary metadata information, uncertainty and precision information. Only data submissions complying with these rules are labelled as ACTRIS data. The participants of long-term VOC monitoring programs submit annually their VOC data to EBAS. From compiled data a direct comparison of the stations by using monthly means and correlation plots were generated for each compounds and station. Data and station performance were discussed during the meetings and action items were set up and distributed afterwards with the aim to improve the data quality and to eliminate erroneous data. Tools were provided by Empa to each station for QC. It is planned to hold such a data workshop every year to ensure and sustain the high QA/QC standards by ACTRIS.

An ACTRIS standard operation procedure (SOP) for the analysis of VOCs has been set up in September 2014. This is used to develop a NMHC GAW measurement guideline together with the GAW VOC-Expert
Team and the SAG, which will be published in the second half of 2015. The SOPs/MGs will provide the basis for sustainable, standardized future VOC observations in Europe (ACTRIS-2 and EMEP) and GAW. However, the process needs to be carried on to further develop MGs for OVOC and monoterpenes, and include PTR-MS measurements.

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1. Summary of VOC intercomparison experiment in Europe

Eighteen institutions participated in a European intercomparison experiment for the analysis of volatile organic compounds (VOCs) in nitrogen and ambient air in 2012. The performance of these institutions involved in long-term non-methane hydrocarbon (NMHC) measurements in ambient air within the framework of Global Atmosphere Watch (GAW) and the European Monitoring and Evaluation Programme (EMEP) was assessed with respect to the ACTRIS and GAW data quality objectives (DQOs). Compared to previous intercomparisons the DQOs of ACTRIS were much more demanding with deviations to a reference value of less than 5% and repeatability of better than 2% for NMHC mole fractions above 0.1 nmol/mol.

The participants were asked to analyse two dry gas mixtures in pressurised cylinders, a 30-component NMHC mixture in nitrogen (NMHC_N₂) at approximately 1 nmol/mol and a whole air sample (NMHC_air), following a standardised operation procedure including zero- and calibration gas measurements. Furthermore, participants had to report details on their instruments and assess their measurement uncertainties. The performance of the different instruments is summarized in Figure 1.

The NMHCs were analysed either by gas chromatography-flame ionisation detection (GC-FID) or by gas chromatography-mass spectrometry (GC-MS). A significant number of instruments were capable of measuring NMHC in nitrogen (NMHC_N₂) 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. Note that NMHC_N₂ was almost identical to the NPL calibration standards used at the stations and a substantial number of deviations was not expected. Participants generally achieved very good repeatability in their measurements in line with the objectives.

In compressed whole air (NMHC_air) generally more frequent and larger deviations to the assigned values compared to NMHC_N₂ were observed (77% of the reported values were within the GAW DQOs, but only 48% were 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). It shows the frequency distribution plots in NMHC_N₂ and NMHC_air for the different compound groups (alkanes, alkenes and alkynes, and aromatics) and different instrument systems (GC-FID or GC-MS).
Figure 1: Frequency distributions of the results of the NMHC Round Robin intercomaprison exercise in NMHC_N2 (a-d) and NMHC_air (e-h). On the x-axis the classes of deviations (in %) to the assigned values are indicated, the class ± 5% corresponds to results within ACTRIS DQOs. On the y-axis the frequency in % of the different compound groups (as indicated in the legends) are shown. For mole fractions < 100 nmol/mol the classes are in nmol/mol, but for simplicity reasons % are shown (e.g. ±5% corresponds to ±5 nmol/mol). PE= Perkin Elmer.
Beside the more complex matrix and the larger NMHC mole fraction span in NMHC_air compared to NMHC_N2 blanks observed in zero-gas measurements in some of the systems, especially those using a Nafion® Dryer, was an important issue to poor results. The study highlights the importance of good zero-gas measurements to determine realistic blank values to be subtracted from measurement results. Another factor contributing to the poorer NMHC_air results is the reduced chromatographic resolution, particularly in the range of C4-C6-compounds. Generally, those systems using direct calibrations in the nmol/mol-range achieved better results than those using whole air calibration standards (two-step calibration). 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) as the two-step calibration and more complex matrix in whole air calibration standards introduce additional potential errors. For ethyne, losses may occur due to breakthrough in the adsorption trap. Additionally, ethyne has a specific normalized C-response of 1 or higher and 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 proved to be a powerful tool helping identifying problems in a number of analytical systems. However, as long as a system behaves similarly in different sample gas matrices, deviations in the C-response may cancel, resulting in correct mole fractions. 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. Almost all 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 generally 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. Another important result of this intercomparison was that in more than 25% of the reported results uncertainties were substantially underestimated and major uncertainty contributions were not correctly assessed. Last but not least, erroneous results were also caused by the occasionally inattentive data submission (mistakes and incomplete information). While these problems were detected and resolved in the relatively small dataset of this intercomparison, it is an issue with submission of insufficiently controlled datasets to public data centres and end-users. The “Perkin Elmer Online Ozone Precursor Analyser” was 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. This intercomparison showed that the ACTRIS DQOs, whilst demanding, are achievable with state-of-the art measurement systems. However, essential for achieving high-quality results are experienced operators, a comprehensive quality assurance and quality control system (including well-established and cross-referenced calibration gas scales), well characterised systems, and sufficient man-power to operate the systems and evaluate the data. The detailed explanation of the performance during this intercomparison exercise was published by Hoerger et al. (2014). Simultaneous with the intercomparison, the procedures for how to determine the uncertainty of a VOC measurement system were developed and participants were trained in applying this procedure. Overall, the intercomparison gave the stations a lot of feed-back they need for successful long-term operation of VOC measurements: their used laboratory standards are checked versus the reference scale, their ability to measure simple and close to ambient air VOC mixtures is verified, they
are notified about potential problems of their analytical systems and possible solutions are suggested,
young-trained in data evaluation following standardized principles and they established close relations
within the network and with the World Calibration Centre for VOC (WCC-VOC).

2. VOC and OVOC – Side-by-Side intercomparison

VOC and OVOC side-by-side intercomparison exercises of ambient air were performed at the following
sites:
- Hyytiala (Finland): measurement of several VOCs and OVOCs during April 2012, involved institutions:
  University of Helsinki (PTR-MS), Finnish Meteorological Institute (Markes-GC-MS) and Empa (MADS-GC-
  MS).
Proton transfer reaction mass spectrometry (PTR-MS) and gas chromatography mass spectrometry (GC-
MS) allow real time measurements of various atmospheric volatile organic compounds (VOC). Performance of four different mass spectrometers for atmospheric VOC concentration measurements
was studied by parallel measurements in ambient conditions. The instruments were two proton transfer
reaction mass spectrometers and two gas chromatograph mass spectrometers. The compounds
measured by all instruments were methanol, acetaldehyde, acetone, benzene and toluene. The
measurements were conducted at a rural boreal forest site in southern Finland between April 13th and
May 14\textsuperscript{th} in 2012. Correlations and possible biases between concentrations measured with the four
different instruments were studied and are presented in this paper. Very good correlation was found for
benzene and acetone measurements between all instruments (mean R was 0.88 for both compounds),
while for acetaldehyde and toluene the correlation was weaker (mean R 0.50 and 0.62, respectively). For
some compounds, notably for methane, there was considerable systematic difference between mixing
ratios measured by the different instruments, despite the very good correlation between them (mean R
0.90). The systematic difference occurs as difference in the linear regression slope between
measurements conducted between instruments, rather than as off-set. Thus it indicates that the
systematic uncertainty in the sensitivity of a given instrument can lead to an uncertainty of 50-100% in
the methanol emission as measured by the commonly used methods. For more details see Kajos et al.

- 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-FID/FID, 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)

The results of these intercomparisons have been discussed in Deliverable D4.5: Results of VOC side-by-
side intercomparison exercise of ambient air and test gases.
The link between ground-based in-situ ethane surface concentration observations and vertical profiles and columns densities measured by FTIR (Fourier Transform Infrared) remote sensing technique was investigated with focus at Jungfraujoch/Switzerland. Results of this study have been reported in deliverable 4.11 (Link between surface and column information of VOC).

During autumn 2013 a further side-by-side intercomparison with focus on OVOCs was conducted at DWD-Hohenpeissenberg:
A side-by-side intercomparison campaign took place in October 2013 at DWD Hohenpeissenberg Meteorological Observatory, a Global Atmosphere Watch (GAW) station. Seven groups with ten different state-of-the-art OVOC measurement techniques participated in this intercomparison (see Table 1).

Table 1: Institutions with the respective instruments participating at the side-by-side intercomparison at DWD Hohenpeissenberg.

<table>
<thead>
<tr>
<th>Institution</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWD-Hohenpeissenberg Observatory, Germany</td>
<td>GC-FID/MS</td>
</tr>
<tr>
<td>Empa Materials Science and Technology, Switzerland</td>
<td>GC-MS; GC-FID/FID</td>
</tr>
<tr>
<td>University of York (NCAS), United Kingdom</td>
<td>GC-FID/FID</td>
</tr>
<tr>
<td>Mines de Douai; France</td>
<td>GC-FID/MS; PTR-ToF-MS; DNPH cartridges-HPLC/UV</td>
</tr>
<tr>
<td>NILU, Norway/ Innsbruck University, Austria</td>
<td>PTR-ToF-MS</td>
</tr>
<tr>
<td>MPI-Chemie Mainz, Germany</td>
<td>PTR-ToF-MS</td>
</tr>
<tr>
<td>University of Colorado (INSTAAR), USA</td>
<td>Adsorbent tubes-GC-FID/MS</td>
</tr>
</tbody>
</table>

All instruments were connected to a common manifold, which was fed with synthetic air mixtures, zero air, pure ambient air and spiked ambient air at controlled ozone and humidity levels. Compared to a previous OVOC intercomparison at the SAPHIR chamber in Juelich (Apel et al., 2008), the Hohenpeissenberg intercomparison expanded the range of tested mole fractions in synthetic and ambient air conditions down to pmol/mol, typical amounts at the stations of the monitoring networks GAW and EMEP. In March 2014, the participants of this OVOC campaign met again for an intercomparison data workshop at the University of York. Measurements of the non-oxygenated VOC benzene, toluene and isoprene showed a good agreement between all instruments. Also, good results were observed for the ketones methylethylketone (MEK) and acetone. For methanol, three GC systems showed high losses in ambient air measurements. For acetaldehyde clear deviations among the instruments were observed in both synthetic and ambient air. The GC systems often reported higher measurements than the PTR-MS systems possibly resulting from acetaldehyde artefacts or interferences from other compounds.

Overall, promising results were obtained with generally good agreements for non-oxygenated VOC and ketones and deviations for methanol and acetaldehyde. PTR-MS seem to better determine these critical compounds; however, the results are not always consistent between these instruments. In contrast, GC based systems have the ability to resolve compounds with the same masses e.g. acetone and propanal or methacrolein and MVK. The deviations observed will be published and discussed with respect to reference concentrations, characteristics of the respective techniques, blank and calibration issues and uncertainties. Overall, this will add confidence in a number of NMHC and OVOC compounds obtained from long-term measurements, however, also identifies problematic compounds for which reliable
measurements within the uncertainty objectives appear possible only for selected instruments. These issues will be further taken up in the forthcoming ACTRIS-2 and corresponding research and cooperation in the European network. Examples for this are ongoing developments at a number of ACTRIS participating laboratories to better understand and solve the observed problems, and the close link to the EURAMET project key-VOC (2014-2017) which links to the results of this ACTRIS study and further addresses improvements and standardization of main components of OVOC measuring systems.

3. Annual data QA workshops

Four workshops on data quality assurance and quality control (QA/QC) have been performed at Hohenpeissenberg in June 2012, York in March 2014, at Dübendorf in June 2014, and at Jülich in November 2014 (see http://www.actris.net/Members/Meetings/WPMeetings.aspx).

The first workshop held at Hohenpeissenberg was about the VOC Round Robin results, guidelines to measurements, QA/QC, uncertainty determination, and the annual data reporting. In York first results of the OVOC side-by-side intercomparison performed at DWD-Hohenpeissenberg were discussed (Englert et al. in preparation).

In the third and fourth workshops at Dübendorf and Jülich VOC monitoring data were discussed. The participants of long term VOC monitoring programs submit annually their VOC data to EBAS. Empa either received this data from EBAS or directly from the data submitter. The data were compiled so that they can be directly compared to each other. Monthly means and correlation plots were generated for each compound and station. Data and station performance were discussed during the meetings and action items were set up and distributed afterwards with the aim to improve the data quality and to eliminate erroneous data.

Further an excel file was provided by Empa to each station for self-dependent QA/QC. For instance VOC time series, correlation plots, and ratios can be plotted (Figure 2-4).

![Figure 2: propane time series for 2011 at Monte Cimone.](image-url)
Figure 3: Correlation of propane and n-butane for 2011 at Monte Cimone.

Figure 4: Propane/n-butane-ratios during 2011 at Monte Cimone.

These data workshops are a step in the data submission process, which was carried out in agreement and with contribution of the EBAS data center. It is roughly outlined in the following:

- Preliminary data submission in spring e.g. 2014 for the data of the 2013
- Data workshop in early summer 2014
- Re-submission of data 2014 in early autumn

(Remark: that in 2015 we will not keep this time frame due to the change from ACTRIS to ACTRIS-2).
This is an essential step to improve the VOC data quality, but it also needs man power and resources. All participants expressed their willingness to further carry out such yearly workshops, as all realized them as very important. However, apart from this commitment there will be a need for establishing sustainable structures for such workshops and an institution should be given the lead. This will be part of the ACTRIS European Roadmap and RI initiative and it is proposed to give the GAW WCC’s the role and the needed resources.

4. ACTRIS standard operation procedure (SOP) to GAW measurement guidelines (MG)

An ACTRIS SOP for the analysis of VOCs has been set up in September 2014 (see Deliverable 4.9: Final SOPs for VOCs measurements). This is the basic concept for further GAW MGs, which is currently developed in GAW SAG and which will be published in the second half of 2015. It contains topics like introduction, data quality objectives, VOCs measurement setup, sampling, measurement techniques, quality assurance, and data management. The SOP or MG provides a guideline for good measurement practice for the analysis of VOC and is considered a major component of sustainable ACTRIS VOC work.

5. References


Englert et al., Side-by-side intercomparison for OVOC in the framework of ACTRIS NA4, in preparation


6. Dissemination activity

OVOC Measurements within ACTRIS-JRA2; 04/09/2012; Granada, Spain; DWD

ACTRIS-GAW: OVOC GC concepts and intercomparison; 11/09/2012; York, UK; DWD

ACTRIS-GAW: Recommendations and Requirements in VOC Analysis Proposed in the Draft ACTRIS Measurement Guideline; 11/09/2012; York, UK; DWD

ACTRIS-GAW: Uncertainty Evaluation in VOC Analysis - Draft VOC Measurement Guidelines; 11/09/2012; York, UK; DWD

Long-term monitoring of volatile organic compounds at the background and suburban sites in the Czech Republic. Milan Vana, Jaroslav Pekarek, Beijing, China, 16-21.9.2012, The 12th IGAC conference; 17/09/2012; CHMI


ACTRIS-inter-laboratory comparison of VOCs in Europe: Measurements of synthetic mixture and ambient air from pressurized cylinders; C. Hoerger, C. Plass-Duelmer, R. Steinbrecher, E. Weiss, A. Werner, S. Reimann, et al., (EGU 2013) Vienna, Austria, 09/04/2013, Empa

ACTRIS: VOCs intercomparison experiment in Europe; EMEP TFMM Bologna, 10/04/2014, Empa

C$_2$H$_6$ measurements in the Alps: linking ground-based to total-column measurements, an analysis of in-situ, FTIR and model data. TFMM meeting, Bologna, 09/04/2014, 13/01/2014, BIRA-IASB

Retrieval of HCHO from MAX-DOAS measurements at the high-altitude alpine station of Jungfraujoch (46.5°N, 8.0°E); Hendrick, F., C. Fayt, B. Franco, C. Gielen, C. Hermans, E. Mahieu, J.-F. Müller, G. Pinardi, T. Stavrakou, and M. Van Roozendael; General Assembly of the European Geosciences Union, Vienna, Austria; 30/04/2014, BIRA-IASB;

VOCs at Hohenpeißenberg during HOPE 2012. A. Werner, C. Plass-Duelmer, J. Englert, K. Michl, and Erasmus Tensing, Vienna, Austria, EGU 12/04/2013, DWD

Access to measurements of reactive trace gases in Europe; developments and improvements within the frame of ACTRIS, A. M. Fjaeraa, Third Urbino Symposium "Air Quality and Climate Change: Interactions and Feedbacks", Urbino, Italy, 13-16 September 2011 (NILU)

Activities to improve harmonization and quality of European VOC and NOx long-term monitoring within ACTRIS. C. Plass-Duelmer, S. Reimann, and the ACTRIS NA4 participants, Vienna, Austria, EGU 2013, 09/04/2013

Total OH Reactivity at Hohenpeissenberg during HOPE-2012. C. Plass-Duelmer, T. Elste, J. Englert, S. Gilge, and Anja Werner, Vienna, EGU 12/04/2013, DWD
Towards an improved European Infrastructure for reactive trace gas monitoring within ACTRIS. C. Plass-Duelmer, S. Reimann, S. Gilge, A. Werner, C. Hoerger, and the ACTRIS Team, ACCENT plus in Urbino, Italy, 19/03/2013

Trace gases networking: Volatile organic carbon and nitrogen oxides (ACTRIS-NA4); C. Plass-Duelmer, German QA/SAC Meeting Garmisch Partenkirchen, 11/09/2013, DWD

Time Series and Trends of Reactive Trace Gases at GAW Global Site Hohenpeissenberg; Bologna; EMEP; Convention on long-range transboundary air pollution; Task Force on Measurement and Modelling Meeting, 09/04/2014, NILU