WP4: Trace gases networking: Volatile organic carbon and nitrogen oxides
Deliverable D4.14: Recommendation on sustainability of QA and SOPs for NOxy in Europe

Authors: S. Gilge and C. Plass-Duelmer

Deutscher Wetterdienst, Hohenpeissenberg, Germany

Summary:

During ACTRIS, a round robin intercomparison of NO (D 4.4) and a side-by-side intercomparison of NO and NO_2 (D 4.6) were performed to assess and evaluate the quality of calibration gases in use in the European RI ACTRIS and the ability of laboratories to correctly determine ambient mixing ratios of NO and NO_2 using standard instrumentation and QA/QC. The latter was combined with state-of-the-art commercial NO_x and research instruments for direct NO_2 determination by optical methods. The participants were given feedback on their performance in the comparison experiments and suggestions were provided of how to improve (D 4.4 and 4.6). Results and evaluation will be published in a peer reviewed journal like AMT.

Results, improvements and standardised procedures were further developed and discussed during several workshops (Hohenpeissenberg, 2012, Dübendorf and Jülich, 2014) leading to the formulation of the first available, standardised NO_x measurement guidelines (D4.2 and 4.10). These summarize the state-of-the-art recommendations for long-term NO_x measurements and contain standard instrumentation and maintenance, sampling, artefact description and correction, QA and QC including standard and zero gas measurement, uncertainty determination and data reporting procedures to EBAS which includes the necessary metadata, uncertainty, precision and flag information. Only data submissions complying with these rules have been decided to be labelled as ACTRIS data in EBAS. The WCC-NO_x (FZ-Juelich) developed an audit procedure (D4.8) and procedures for standardized annual station data evaluation. Data and station performance were discussed during meetings and action items were given back to the stations in order to improve their data. It is planned to hold such data workshop every year to ensure, further develop, and sustain the high QA/QC standards by ACTRIS.

The ACTRIS measurement guidelines are the basis for GAW guidelines, which are currently developed in GAW SAG. Overall, ACTRIS achieved a learning situation for stations leading to sustainable standardizations in measurements, QA/QC, uncertainty evaluation and data submission. Furthermore, integrated views were brought to the participants and vice versa by exchange with other components of ACTRIS, including ground based remote sensing techniques for NO_2 (D. 4.12). ACTRIS achieved a strong link between the stations and established joint workshops. These activities will be - and are strongly recommended to be - continued on initiative of the participating laboratories, in the framework of ACTRIS-2 and on the long term in an ACTRIS ERIC. ACTRIS NA4-NOx activities provide the basis for sustainable future NO_x observations in Europe (ACTRIS-2, ACTRIS ERIC and EMEP) and the world (GAW).

Content:

1. NOx Round Robin experiment in Europe

A total number of 18 European laboratories involved in long-term monitoring participated in the ACTRIS NO-round robin intercomparison activity organised and overseen by DWD Hohenpeissenberg in Feb-Aug 2012. 16 laboratories reported results until Dec 2012, one withdrew due to instrumental problems and one did not submit yet. Participants were asked to analyse the sent ACTRIS mixture following a well described procedure. Two laboratories with larger deviations from the reference values were rapidly informed and help was offered to improve the measurements.

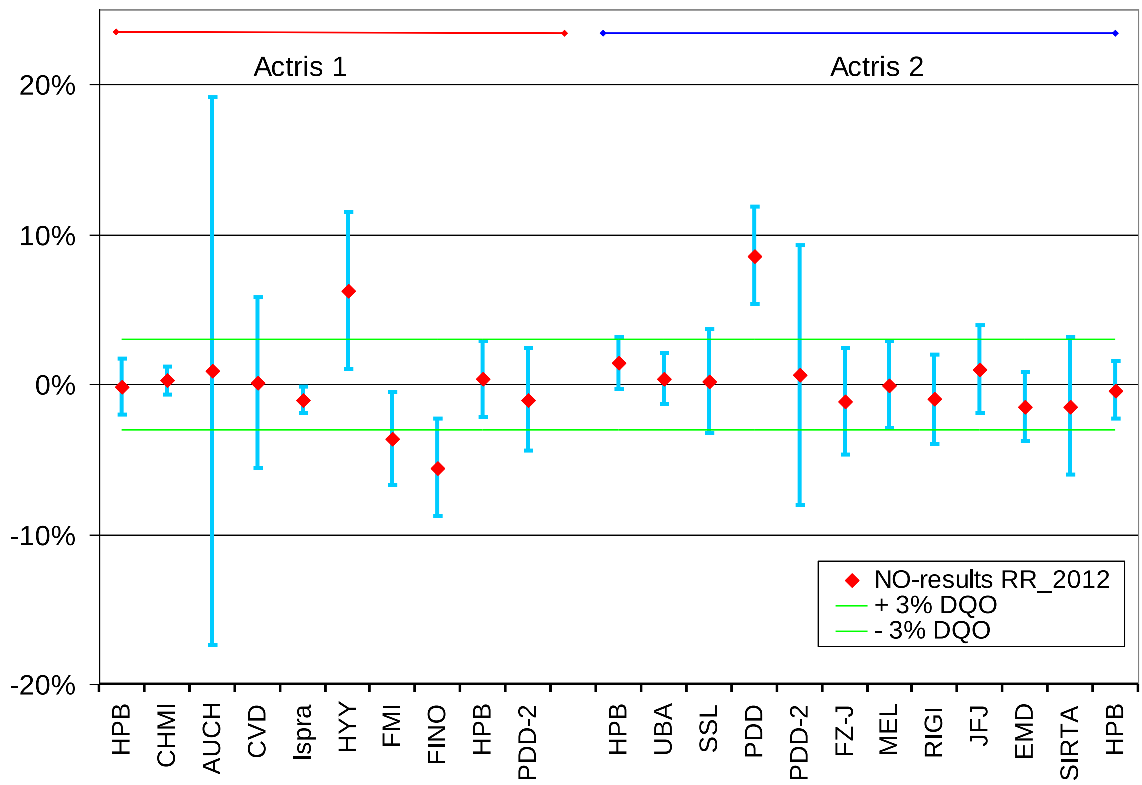

Fig. 1: ACTRIS Nitirc Oxide Round Robin results obtained by January 2013. Shown are the relative deviations from the reference mixing ratios in respective cylinders and the corresponding uncertainty estimates (blue bars). Green lines: ± 3% of reference value according to GAW data quality objectives.

The results of this NO round robin intercomparison mostly showed results in line with the data quality objective (DQO) by ACTRIS and GAW for NO measurements of 3%. In particular, 13 of the 16 participating laboratories achieved results within the DQO with uncertainties of less than 3%, 8 labs were even within 1% of the reference. However, only 6 laboratories achieved expanded combined uncertainties (k=2) of less than 3%. Reasons for deviations and /or larger uncertainty were generally ascribed to one or several of the following reasons:

- the laboratory standard at the station is not of sufficiently high quality
- the analyser or the dilution system drift such that uncertainties of 3% or more exist
- not enough replicate measurements were made to reduce the uncertainty

Consequently, the following recommendations were given to achieve results well within the DQO's:

- use a laboratory standard with certified expanded uncertainty of about 1% (at least 2%)
- a second working standard should be used to identify changes in the lab standard
- drifts in the dilution and analyser should regularly be checked and should be less than 2% in equilibrated systems. It is recommended to follow the instruction of the measurement guideline and use appropriate dilution systems, line material, zero gas, and general maintenance of the analyser. If drift remains too high, send analyser to manufacturer for fixing.
- It is recommended to do three replicate measurements.

Overall, this round robin demonstrated that inter-laboratory comparability of standard measurements can be achieved well in line with the DQO. However, it should be pointed out that the obtained deviations and uncertainties are smaller than in ambient air measurements. For ambient measurements, there are following additional sources of uncertainty:

i) the systematic uncertainty of the dilution system and calibration (this cancelled out in the round robin as laboratory standard and ACTRIS gas were diluted the same way in most labs)

ii) mixing ratios are much smaller and zero drift and repeatability of measurements become increasing contributions in the overall uncertainties

iii) interactions in the NO-NO_2-O_3 system and varying absolute humidity will require corrections with associated uncertainties (see Measurement Guideline)

A detailed explanation of the performance during this intercomparison exercise will be published. Simultaneous with the intercomparison, the procedures for how to determine the uncertainty of a NO_x 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 NOx measurements: their used laboratory standards are checked versus the NO reference scale, they are notified about potential problems of their analytical systems and possible solutions are suggested, they are trained in data evaluation following standardized principles and they established close relations within the network and with the World Calibration Centre for NO_x (WCC-NO_x).

2. NO_x – side-by-side intercomparison

A total number of 13 European laboratories participated in the ACTRIS NO_x-side-by-side (s-b-s) intercomparison activity comprising laboratories involved in long-term monitoring, institutes involved in instrument development, and a company with a commercial instrument. The comparison was organized and overseen by DWD Hohenpeissenberg in November 2012. A ring-manifold was used with all instruments connected to the manifold and synthetic mixtures as well as ambient air and spiked ambient air supplied to the manifold. DWD and FZ-Juelich (WCC-NO_x) acted as reference laboratories at the beginning and end of the manifold, respectively. Various synthetic mixtures with mixing ratios in the range between zero and about 40 ppb for NO and NO_2 were run, test mixtures with NH_3 and HNO_3 as well as ambient air encountering a wide range from very clean (<0.5 ppb NO_x) to polluted (several 10 ppb NO_x) conditions. Most of the participating instruments used chemiluminescence detection (CLD) for NO coupled with photolytic conversion with xenon lamp (PLC), blue-light converter (BLC) for NO_2, or molybdenum converter for NO_{2+}. Additionally, four instruments for NO_2 took part using new optical techniques with cavity enhanced absorption (CEAS), cavity ring down spectroscopy (CRDS), cavity attenuated phase shift (CAPS) and laser induced fluorescence (LIF).

Site	Institution	Shortcut	Participants	Device	Method	Position Manifold
Ispra (I)	Joint Research Centre of European Union (JRC)	**IPR**	Friedrich Lagler	**Thermo 42C & 42i**	**CLD / Mo converter**	**3**
Univeristy of York (GB), Cape Verde Observatory (CVO)	National Centre for Atmospheric Science (NCAS)	**CVO**	James Lee, Will Manning	**Air Quality Desisn Inc.**	**CLD / PLC**	**6**
Košetice / Prague (CZ)	Czech Hydrometeorolo-gical Institute (CHMI)	**CHMI**	Jan Silhavy	**TEI-42S**	**CLD / Mo converter**	**4**
Cabauw (NL)	Koninklijk Nederlands Meteorologisch Instituut (KNMI)	**KNMI**	Mirjam den Hoed	**2-3 NO_2-sondes**	**NO_2 sonde, Luminol-CLD**	**2**
French EMEP sites: Revin, Tardière, Peyrusse (F)	Ecole des Mines de Douai	**MD-DCE**	Stéphane Sauvage, Emmanuel Tison	**Thermo 42iTL**	**CLD / BLC**	**5**
SIRTA (F)	Laboratoire des Sciences du Climat et de l'Environne-ment (LSCE)	**Sirta**	Nicolas Bonnaire	**Teledyne T200UP**	**CLD / BLC**	**8**
Puy de Dôme (F)	Observatoire de Physique du Globe de Clermont-Ferrand (OPGC)	**PUY**	Jean-Marc Pichon, Laetitia Bouvier	**TEI 42 CTL**	**CLD / Mo converter**	**3**
Mainz (D)	Max-Planck-Institute for Environmental research (MPI)	**LIF**	Umar Javed, Markus Rudolf	**Gandalf LIF instrument for NO_2**	**Laser-induced fluorescence**	**11**
Heidelberg (D)	University of Heidelberg, Institute for Environmental Physics (IUP)	**DOAS**	Christoph Kleinschmitt, Martin Horbanski, Udo Frieß	**NO_2 CE-DOAS**	**Cavity Enhanced DOAS**	**9**
WCC/FZJ (D)	Research Center Juelich, World Calibration Center	**FZJ**	Franz Rohrer	**modified Eco-physics 780 TR**	**CLD / BLC**	**10**
Cyprus (CY)	Energy, Environment and Water Research Center (EEWRC)	**CYI**	Mihalis Vrekoussis	**TEI 42C**	**CLD / BLC and Mo-converter**	**8**
Pallas-Sodankylä (FIN)	Finnish Meteorological Institute (FMI)	**FMI**	Jari Walden, Timo Antilla	**TEI 42 iTLE**	**CLD / Mo converter**	**7**
Hohenpeissenberg (D)	German Meteorological Service (DWD) Hohenpeissebenrg Meteorological Observatory (HPB)	**HPB**	Stefan Gilge, Dietmar Weyrauch, Christian Plass-Duelmer	**TEI 42 CTL**	**CLD / BLC**	**1**
				Ecophys. 770 AL ppt	**CLD / PLC**	
				Aerodyne CAPS	**Cavity attenu-ated phase shift**	
-	Los Gatos Research, Hekatech	**LGR**	Christian Plass-Duelmer-	**LGR NO_2 Analyzer**	**cavity enhanced laser absorption spectroscopy**	**8**

Table 1: Participants in ACTRIS-NO_x s-b-s intercomparison with information provided to the position on manifold, institution, used method and device.

Following conclusions were achieved:

- All instruments showed good linearity over the entire concentration range of the s-b-s intercomparison

- In synthetic mixtures, deviations from reference values (integrated results, fit lines) were generally < 3% for NO and < 5% for NO_2 but exceptions existed and point towards inappropriate calibration and converter efficiency determination.
- NO_x calculations during different steps of gas phase titration showed inappropriate converter efficiency determination for some of the instruments
- Ambient air measurements show partly substantial deviations and the participants were encouraged to review their data carefully. However, not all groups gave feedback; so some issues remained unclear. Probably these issues are due to non-adequate calibration intervals, not precise enough determination of converter efficiency, or malfunction of one or more system components. All operators were encouraged to frequently calibrate their system and check their calculated converter efficiency as well as metadata.
- All instruments equipped with Mo converters showed too high NO_2 mixing ratios (presupposed they are calibrated correctly). This outcome emphasized the GAW-SAG-RG's recommendation NOT to use Mo converter for NO_2 measurements.
- The lower detection limits were mostly <50 ppt for NO and <100 ppt for NO_2 indicating that GAW-DQOs (level 1) are accessible with commercial instruments as long as CLD instruments with pre-chambers (i.e. "TL" instruments from TE) are used. CLD instruments without pre-chamber are not recommended.
- Only the best performing CLDs with photolytic converter (NO_2) achieve similar high quality as direct methods (CRDS, LIF, CAPS, and CEAS), however, best performing instruments for NO_2 were CE-DOAS, LIF and CAPS.

The link between ground-based in-situ NO_2 surface concentration observations and vertical profiles and columns densities measured by the MAX-DOAS (Multi-AXis Differential Optical Absorption Spectroscopy) remote sensing technique was investigated with focus on two stations Jungfraujoch and Hohenpeißenberg. Results of this study have been reported in deliverable 4.12 (Link between surface and column information of NO_2).

The results will be published and discussed with respect to reference concentrations, characteristics of the respective techniques, blank and calibration issues, and uncertainties. Overall, this will aid confidence in the quality of long-term NOx measurements, however, also identifies problems. These issues will be further taken up in the forthcoming ACTRIS-2 and corresponding research and cooperation in the European network.

3. Annual data QA workshops

Three workshops on data quality assurance and quality control (QA/QC) have been performed at Hohenpeissenberg in June 2012, 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 NO_x RR results, draft guidelines to measurements, QA/QC, uncertainty determination, and the annual data reporting.

In the second and third workshops at Dübendorf and Jülich, NO_x measurement guidelines and monitoring data were discussed. The participants of long term monitoring programs submit annually their NO_x data to EBAS. For the first time in Jülich, the data were compiled, a standardized QC procedure involving NO at night, NO/NO_2 ratios, and daily/annual cycles developed by WCC-NO_x (FZ-Juelich) was applied, and data were directly compared to each other.

These data workshops were decided to form an integral step in the data submission process (agreement of ACTRIS-NO_x-participants, WCC-NO_x, and EBAS data center):

- Preliminary data submission in spring for the data of the preceding year
- Data workshop in early summer with action items for stations to check and improve
- Re-submission of final data in early autumn

These steps are essential to improve the NO_x data quality, but it also needs man power and resources. All participants expressed their willingness to further carry out such yearly workshops, as all recognized 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 NO_x has been set up in September 2014 (Deliverable 4.10). This is the basic concept for further GAW MGs, which are currently developed in GAW SAG. They contain rationale, data quality objectives, NO_x measurement setup, sampling, measurement techniques, quality assurance, and data management. The SOPs or MGs provide a guideline for good measurement practice for the analysis of NO_x and is considered a major component of sustainable ACTRIS NO_x observation work.

5. References and Dissemination Activities

QA/QC of European NOx measurements by round robin and side by side experiment at Hohenpeissenberg Meteorological Observatory in the framework of ACTRIS. S. Gilge, C. Plass-Duelmer, D. Weyrauch, F. Rohrer, and the ACTRIS-NOx Team, Vienna, Austria, EGU 2013, 09/04/2013

Tropospheric nitrogen dioxide column retrieval based on ground-based zenith-sky DOAS observations; Tack, F., F. Hendrick, F. Goutail, C. Fayt, A. Merlaud, G. Pinardi, J.-P. Pommereau, and M. Van Roozendael; General Assembly of the European Geosciences Union, Vienna, Austria; 30/04/2014, BIRA-IASB

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-Dülmer, 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, DWD