WP4- NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides
Deliverable D4.10: Standardized operating procedures (SOPs) for NOxy measurements

1 Introduction

ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) is a European Project aiming at integrating European ground-based stations equipped with advanced atmospheric probing instrumentation for aerosols, clouds, and short-lived gas-phase species. ACTRIS has the essential role to support building of new knowledge as well as policy issues on climate change, air quality, and long-range transport of pollutants.

2 Rationale and Objectives

Several governmental institutions, mainly meteorological services and environmental protection agencies in Europe aim at providing reliable long-term observations of the chemical composition and physical properties of the atmosphere relevant for understanding atmospheric chemistry and climate change. Reactive gases are one of the foci; this group includes besides surface ozone (O_3), carbon monoxide (CO) and volatile organic compounds (VOC) also nitrogen oxides (NOx := nitric oxide (NO) and nitrogen dioxide (NO_2)), which are present only in trace quantities in the atmosphere but play an important role in atmospheric chemistry.
Measurements of nitrogen oxides have been made for decades using a number of different techniques and calibration scales. However, in Europe there are only a couple of sites performing continuous, in situ measurements of nitrogen oxides. This document was created by the ACTRIS community with the objective to document the measurement techniques in use and to contribute to a convergence of these techniques in Europe to establish a harmonized European data set of atmospheric nitrogen oxides observations.
Compatibility of data from different observational platforms and sites is of crucial importance for the early detection of trends or slight variations in chemical composition of the atmosphere. In many cases, decades of time series are required to assess these changes with a certain degree of confidence. Support of the long-term stability of the reference scales and its propagation to in-situ measurements are particular prerequisites to meet these demands.
In this document we focus on continuous in situ measurements of NO and NO_2 performed at surface stations. Thus, these Measurement Guidelines for NO and NO_2 are intended for use at ACTRIS sites and any other measurement platform with already existing NOx measurement capabilities and in particular at facilities where such measurements have recently been added to the programme or will be added in the foreseeable future.

3 Data Quality Objectives for NO and NO_2 Measurements

Data quality objectives (DQOs) define the type, quality and quantity required of primary data and derived parameters to yield information that can be used to support decisions. In particular, DQOs specify tolerable levels of uncertainty in the data, required completeness, comparability and representativeness based on the decisions to be made [WMO, 2007].
In case of NO and NO_2 the DQOs presented in Table 1 constitute a compromise between the scientific need, the physical and chemical properties of the studied compounds and the current feasibility of available instrumentation. The scientific needs refer to (i) long-term monitoring to derive changes and trends in the atmospheric composition, (ii) monitoring to enable analyses of source-receptor relationships and transport processes, (iii) the investigation of photochemical processes, or the combination of these issues. More specifically, these needs relate to the following requirements:

- For long term measurements, trends exceeding 1% per year should be discernable, hourly measurements with a minimum 66% coverage and appropriate accuracy (see Table 1) are required.
- Examination of source-receptor relationships and transport processes need a time resolution of at least one hour since air mass change occurs in this time frame.

- For chemical process studies a time resolution comparable to the lifetime of nitrogen oxides is required, which is in the range of a few minutes to days.

It is recommended that measurements are performed on a continuous basis.
Taking into account the typical lifetime of nitrogen oxides and the remoteness of the station with respect to distance from source areas, it is useful to set 3 different levels of DQOs according to the site characteristics, e.g. the typically encountered mole fractions of NO_x.

Table 1 - Data Quality Objectives (DQOs) for NO and NO2 under differing conditions

Level	**1 (basic)**	**2 (enhanced)**	**3 (high)**
Site characteristics	Continental basic	Continental background	Pristine, marine background, free troposphere
Mean mole fraction NOx	> 1 ppb	0.1 – 1 ppb	< 0.1 ppb
Scope (corresponding time resolution)	long term monitoring, trends (1 hour), source-receptor-relationship, transport processes (hour-minute), photochemical process studies (minute)		
Detection Limit (1 hour, 3σ)	NO: 50 ppt NO_2:100 ppt	NO: 10 ppt NO_2:20 ppt	NO: 1 ppt NO_2:5 ppt
uncertainty (1 hour, 2σ)[1]	NO: 40 ppt or 3% NO_2:80 ppt or 5%	NO: 8 ppt or 3% NO_2:15 ppt or 5%	NO: 1 ppt or 3% NO_2:3 ppt or 5%
uncertainty (1 month, 2σ)[2]	NO: 2.5% NO_2: 3%	NO: 2.5% NO_2: 3%	NO: 1 ppt or 2.5% NO_2:3 ppt or 3%
data coverage	66%		
suggested method[3]	CLD / PLC	CLD / PLC	CLD / PLC
Alternative / upcoming methods[4] (backup or QC reasons)	CRDS ; LIF ; DOAS ; TDLAS	CRDS ; LIF ; TDLAS	LIF

[1] *whichever is the larger, e.g. for level 2 "enhanced" at NO_2 of 1 ppb an uncertainty of 50 ppt is required (5% of 1 ppb), at 0.2 ppb an uncertainty of 15 ppt would be required.*
[2] *assuming that the random uncertainties are negligible compared to the calibration uncertainty*
[3] *see list of acronyms (Annex 1) for full method names*
[4] *methods that are either new and not yet fully tested for their long-term applicability or research type instrumentation that is demanding to operate, thus, prone to incorrect handling and therefore not fully suitable for long-term monitoring*

Table 1 summarises the scientific goals, instrumental techniques, and sensitivity requirements for ACTRIS NO_x sites with different characteristics, including continental, continental background, and pristine marine locations. It should be recognized that Table 1 presents initial DQO requirements to be achieved in the NO_x network. These are expected to evolve in time for each site depending on the available technologies and the experience gained particularly in the early phase of ACTRIS NO and NO_2 monitoring.
Commercial instruments are available with specifications meeting the requirements for both continental basic (Level 1, "basic") and continental background environments (Level 2, enhanced) but only research instruments developed by skilled investigators are capable of providing high-precision measurements in pristine conditions (Level 3).
In spite of a clear scientific need to establish the data quality objectives, the above formulated requirements will indeed present a difficult measurement challenge given the low levels of NO and NO_2 expected at many of the ACTRIS NO_x sites. Further, the need to quantify trends accurately over time at low ambient levels of NO and NO_2 places an additional burden on even the best measurement techniques, so that careful operation by well-trained staff and thorough attention to details is required to achieve the DQOs necessary to make valuable measurements of NO and NO_2.

4 Measurement Setup

4.1. Location and site requirements

Location and site requirements are closely related to the typical requirements for ACTRIS stations. As a primary requirement the station location should be chosen such that, for the variables measured, it is regionally representative (which means it should be typical in population, plantation, weather conditions and so on for the respective area) and is normally free of influence of significant local pollution sources.
Since it is important to avoid local contamination sources the sample collection location on site should be set upwind of any buildings, garages, parking lots, generators, other emission sources – any nearby areas where fossil fuels or biomass may be combusted. Station personnel should also remain downwind of sample collection and refrain from smoking as necessary.
Measurements sites should provide facilities which allow the operation of the instrumentation needed. This usually requires sufficient electrical power, a suitable data acquisition system and depending on the instrumentation other supplies. Additionally calibration gases, traceable back to the primary standard and a calibration unit with the possibility of gas phase titration (for calibration of NO_2) is needed. Furthermore, a constant temperature (air-conditioning) is required for most measurements and instrumentation should not be exposed to sunlight. Internet connection for (automated) data transfer to the data processing and analysis centre as well as for remote access of the data acquisition system is highly recommend in particular for station with infrequent operators on-site. This ensures a timely backup of the measurement data allows basic maintenance and potentially provides the opportunity for problem identification and trouble-shooting from remote in case of instrumental issues. Finally, well trained personnel are essential.

4.2. Air inlet design

Typically nitrogen oxides are measured along with ground based ozone. Since the latter one is much more sensitive to inlet line material, the material used for collecting ozone (e.g. PFA Teflon™) is also suitable for nitrogen oxides. For measuring only nitrogen oxides also stainless steel can be used. However, due to possible interferences of NO_x measurements caused by O_3 (see section 7) simultaneously monitoring of O_3 mole fractions is strongly recommended. The NO, NO_2 and O_3 analyzers should be equipped with an inlet line filters (Teflon) that should be changed on a regular time basis (see 7.1).
Principally there are some inlet line issues to be considered:

- Changes in traces gas concentrations in the inlet line may be caused by heterogeneous processes, namely by interactions between gas phase and wall of the inlet line: adsorption, absorption, diffusion and chemical reactions at the wall.
  ⇒The material of the inlet line must have a smooth (otherwise it is prone to adsorption), non-porous (otherwise absorption & diffusion) and inert (otherwise reaction) surface. An approved material is PFA-Teflon™, a perfluoralkoxy-Teflon™ with totally fluoridated propylene side chains:
  $$-\left[CF_2 - CF_2\right]_m - \left[CF\left(-O - C_3F_7\right) - CF_2\right]_n$$
  For measuring ozone never use stainless steel tubes or fittings anywhere in the system since they remove ozone very effectively. Be aware that PFA lines without cover are 100% transparent for j_{NO2} (important for calculation of ozone artefacts, see below).
- Due to condensation of vapours (organic / inorganic) and aerosol deposition in the inlet during operation, the properties of the wetted surfaces might change with time.
  ⇒ The solution for this problem is constant heating and regular cleaning of the inlet line. The cleaning interval has to be chosen such that no trace substance loss occurs but measurement interruption is short. This strongly depends on site conditions. A suggestion is: once per year at remote, twice per year at clean rural and up to monthly at urban sites, respectively. The temperature of the inlet line has to be chosen high enough that no condensation occurs but not

too high that thermal decomposition of other trace gases (e.g. PAN) will become an artefact. Controlled heating a few degrees (3-4°) above ambient temperature is best. Slight heating does not efficiently prevent aerosol deposition in the inlet.

- Gas phase processes also may lead to changes in trace gas concentration, because of different conditions in the inlet line compared to ambient. For example the reaction: $NO_2 + h\nu \rightarrow NO + O$ is stopped due to the lack of sunlight in the inlet line, while the back reaction: $NO + O_3 \rightarrow NO_2 + O_2$ continues, leading to an enhanced NO_2/NO ratio.
  $\Rightarrow$ The residence time (tube length x diameter / flow velocity) in the inlet line must be kept as short as possible. Recommended is a residence time of less than 5 seconds, better below 2s. However, length is mostly defined by laboratory and inlet design. With a small diameter the surface/volume ratio gets worse and surface artefacts are enhanced. Along with an enhancement of flow velocity, a pressure decrease could occur and this in turn could shift the gas-particle partitioning towards the gas phase e.g. HNO_3 (aq) $\rightarrow$ HNO_3 (g); PAN depletion or depletion of $N_2O_5 \rightarrow NO_2 + NO_3$ could occur. When designing a new inlet line, the above mentioned problems must be taken into account. A very good way to test the inlet line is by feeding a small tube (e.g. 1/16" or 1/8" tube into the existing ¼" or larger inlet line) with constant calibration gas flow into the inlet line such that the mole fractions of NO and NO_2 are measured at various positions of this "standard addition tube" along the inlet line between inlet and instrument and changes in the concentrations of NO or NO_2 can be detected.
  Additionally the signals for NO and NO_2 should be corrected for ozone and H_2O artifacts as described in chapter 7.3.

5 Measurement Techniques

5.1. Techniques for NO

5.1.1. Chemiluminescence

GAW recommends the gas-phase reaction of nitric oxide (NO) in a low-pressure ozone-induced chemiluminescence detector (CLD) for measurement of ambient NO. This technique (Fontijn et al., 1970) follows the reactions:

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (1)$$

$$NO_2^* + M \rightarrow NO_2 \quad (2)$$

$$NO_2^* \rightarrow NO_2 + h\cdot\nu \quad (590 \leq \lambda \leq 3000\ nm) \quad (3)$$

Ozone, produced by an internal O_3 source, is added in excess quantity for reaction (1). The emitted light $h\cdot\nu$ is measured with a photomultiplier tube (PMT). This provides a sensitive and selective measurement of NO once the detector response is determined according to equation 4:

Ambient NO = (ambient signal – background signal – artefact signal) / sensitivity (4)

The signals are given as counts as measured by the PMT, the sensitivity of the detector is given as counts·ppb^{-1}.

The following sketches give a schematic overview of operating mode:

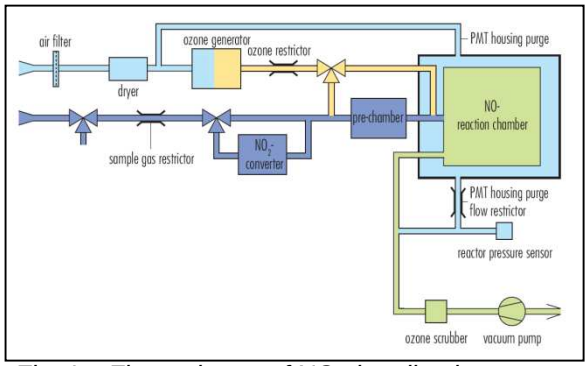

Fig. 1a: Flow scheme of NO chemiluminescence detector (courtesy of ECO Physics)

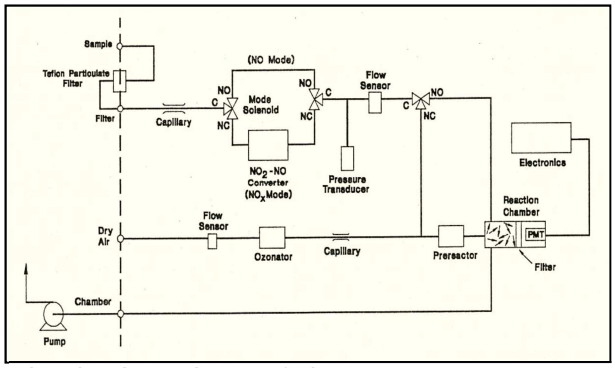

Fig. 1b: Flow scheme of Thermo Instruments 42 TL NO chemiluminescence detector

In the reaction chamber ambient air is mixed with O_3 and reactions (1)-(3) take place. The light released from reaction (3) passes a window, equipped with a red/infrared filter (according to the wavelengths of emission) and enters the photomultiplier tube (PMT) connected to the reaction chamber. Since the reactions are very fast the geometry of the reaction chamber has an influence on the sensitivity: The reactions should take place directly in front of the PMT window. For a better signal/noise ratio the PMT is cooled, e.g. by a Peltier cooling device. Due to potentially sub-ambient temperature, the PMT window is purged by dry air to avoid condensation.

In most instruments, the ozone generator provides high ozone levels (in ppm range) by silent electrical discharges which are necessary for a fast reaction sequence. To speed up the reaction velocity it is recommended to use pure oxygen instead of dry air for generating ozone. Using pure oxygen enhances the sensitivity roughly by a factor of 2. The supply with pure oxygen can be implemented with pressurized oxygen (Quality ≥ 4.8) in cylinders. Commercially available oxygen generators are also capable of producing oxygen of sufficient quality. Experience showed that the long term stability of the ozone generator could be enhanced by the use of a short length (some 2 centimeter) of silicone tubing in the line supplying oxygen to the generator to provide a very small but significant amount of humidity which diffuses through the silicon from lab air. A reduction in background signal could be achieved by humidifying the oxygen/ozone flow before its entrance into the low pressure region of the instrument with help of a water bubbler or an inverse Nafion™ dryer. This precaution reduces an unspecific chemiluminescence of ozone generated inside the reaction cell or on its walls. However the latter described improvement could also cause some problems if set up isn't done properly. For that this procedure is recommended only for experienced users.
According to reaction (2), a huge part of excited NO_2* molecules is deactivated radiationless by collision with N_2, O_2 or water molecules. To minimize this, low pressure and therefore a strong pump is recommended. However a too small pressure and therefore a short residence time impedes quantitative reaction of NO with O_3, leading to lower signal. (Hint: Experiments with an ECO Physics CLD 770 AL ppt showed lowering pressure down to 20 mbar still led to an increasing signal.)
Besides NO, some other hydrocarbons (alkenes) and other trace substances react with O_3 followed by chemiluminescence of OH in the red/infrared region. Since most of the other reactions are slow compared to NO+O_3 the use of a prechamber can solve this problem: During "prechamber mode" the NO+O_3 reaction takes place inside the prechamber so that only the slower reactions of O_3 with interfering agents are counted. This interference signal together with the dark current of the PMT and unspecific chemiluminescence of ozone generated in the reaction cell or on the walls is called the "detector background signal (bkgrd)". The prechamber volume must effectively mix the reagent and sample streams and allow sufficient reaction time to destroy ambient NO before the sample enters the reaction chamber. In case the ozone concentration is too low or the residence time in the prechamber is too small the background signal of the instrument is enhanced and the detection limit is worsened. In case the residence time in the prechamber is too large, the interference signal is already reduced in the reaction chamber giving rise to too small interference correction with the consequence that part of the interference signal might be counted as NO signal. A good compromise is a residence time in the prechamber on the order of 2 reaction time scales of NO+O_3. However, design and dimensions are chosen by the manufacturer. A high-conductance Teflon three-way solenoid valve is typically used to switch reagent O_3 between sample mode (O_3 added directly to CLD chamber) and background mode (O_3 added upstream to the prechamber). Detector background levels must be determined routinely, approximately at least once per hour, or best, at every measurement cycle to account for potential instrumental drifts over time.
A detector "artefact", or unwanted differences (positive or negative) in signal relative to the measured detector background, can often be observed in CLDs even when sampling NO-free air. Artefact levels can be determined by overflowing the sample inlet with an excess of ultrapure cylinder air (synthetic air), and alternating between sample and background (prechamber) modes. Artefact signals can arise from spurious CLD pressure differences between these two modes, or from real, non-zero amounts of NO in even ultrapure cylinder air. Detector artefact levels must be determined routinely, approximately once every two days to make an accurate determination of ambient NO in the low picomole/mole (pptv) range. For measurement sites far from NO sources – including potential biogenic/soil sources of NO

within a few meters of the inlet – ambient night time NO concentrations are expected to be identical to zero due to reaction with ambient O_3. If ozone is > 10 to 20 ppb , a comparison of the detector background signal to the ambient signal measured during dark periods of the night should give a very good measure of the detector artefact signal. Having a detector signal close to zero during night in the presence of significant amounts of ambient O_3 (NO mole fractions at rural and remote sites tend to be very low during night due to reaction for NO with O_3 forming NO_2 and the missing back-reaction (photolysis) of NO_2 forming NO during night) but significantly different from zero during zero air measurement one should inspect the zero gas for possible leaks or exhausted cleaning cartridges. Having substantial and similar counts during zero air and night-time ambient air measurement is a strong hint for a detector artefact signal (It is very unlikely to have similar counts originating from NO residuals in zero air AND from sources in ambient air during night-time.).
By calculating the difference between "measurement mode", "prechamber mode" and "artefact signal" according to equation (4), a highly selective signal for the ambient NO mole fraction is achieved.
Principally this technique is only able to measure NO, all other nitrogen oxides must be converted.

5.1.2. Other techniques for NO

Other known techniques like the chemiluminescence reaction of NO_2 with Luminol™ after conversion of NO to NO_2 by Cr_2O_7 are not recommended by GAW. Since NO mole fractions are typically lower than NO_2 mole fractions, conversion of NO to NO_2 and subsequent measurement leads to small differences at large signals and therefore to higher uncertainty. Additionally, at "Luminol technique", due to sensitivity chances caused by maturing of Luminol solution and instability in flows, unattended operation over longer time period seems to be very difficult.
Recently, other techniques like Quantum Cascade Laser Absorption Spectroscopy (QCLAS) and Long Path Absorption Photometry (LOPAP) (measuring NO_2 directly and NO after conversion with dichromate) have proven their capabilities and have also been tested at Jungfraujoch GAW Global site, supported by ACTRIS TNA. First results look very promising. However, these instruments are currently not commercially available and/or very expensive and require well trained personnel. Furthermore, extended tests proving the applicability for long-term monitoring purposes are still outstanding. See also Chapter 5.2.3 for an extended list of new NO_2 measurement technologies that might be partly suitable for NO measurements, at least when combining with a NO to NO_2 converter prior to analysis.

5.2. Techniques for NO_2

5.2.1. NO_2 Photolysis and detection as NO

GAW recommends the photolytic conversion (PLC) of ambient nitrogen dioxide (NO_2) using an adequate broad band light source like Xenon high pressure or metal halide lamps or small band ultraviolet light-emitting diodes (UV-LEDs) (then called "blue light converter" (BLC)) followed by CLD for measurement of the converted NO_2 as NO. Following photolysis, the CLD signal is due to ambient NO, plus the fraction of NO_2 converted to NO. Ambient NO_2 can be calculated by difference (Kley and McFarland, 1980) providing a sensitive and selective measurement of NO_2 once the photolysis efficiency "S_C" of the converter is determined.
Ambient air is irradiated with appropriate wavelengths and NO_2 is photolysed to NO and ozone. Subsequently ambient air enters the CLD and the sum of the converted fraction of NO_2 and ambient NO is measured and described as NO.c.. The residence time in the photolysis chamber should be about one second, but is often longer. Enlarement of the residence time inside the photolytic converter increases the conversion efficiency but at the same time enhances the back reaction of NO with O_3. There are two different approaches for tubing: PLCs are typically equipped with a 3-way-solenoid and a bypass pump, at BLCs the LED can be switched on and off. This causes different approaches by calculating the ozone interferences (see below).

Since the measurement of NO /NO_2 is sequential, the NO_2 mole fraction in ambient air has to be calculated in the following way:

background measurement $\Rightarrow$ prechamber measurement $\Rightarrow$ bkgrd
NO measurement $\Rightarrow$ reaction chamber measurement $\Rightarrow$ NO

NO.c measurement $\Rightarrow$ converter + reaction chamber measurement $\Rightarrow$ NO.c

calculation NO_2: $$NO_2 = \frac{[NO.c - bkgrd] - [NO - bkgrd]}{S_C}$$

calculation NO_x: $$NO_x = \frac{[NO.c - bkgrd] - [NO - bkgrd]}{S_C} + [NO - bkgrd]$$

Taking into account loss of NO and enhancement of NO_2 due to ozone reaction in inlet line and photolytic converter and due to quenching effects caused by water vapor, a formulae as given in section 7.3 must be used for calculating most accurate NO and NO_2 ambient air mole fractions. Thus, please take note that the accurate determination of NO and NO_2 implies the availability of quality-controlled H_2O and O_3 observations. The measurement of NO_2 by using photolytic conversion to NO is highly specific, but not without interference. Please note that, depending on the wavelength spectrum of the photolysis source, between 5% to 15% of HONO might by photolysed to NO. The reason for this is the similar absorption spectrum of NO_2 and HONO in the wavelength range below 400nm. For a broad band photolysis spectrum similar to sunlight (for example from a Xe high pressure lamp), the photolysis frequency of HONO is 1/6 of that of NO_2. For the line spectrum of a BLC this interference migh be as small as 5% depending on the LED used.

5.2.2. Chemical NO_2 reduction & detection as NO

Chemical reduction of NO_2 at a hot metal surface (mostly molybdenum) is widely used. The efficiency is larger than 98% with a strong decay at the end of lifetime. The big disadvantage of this set up is that not only NO_2, but also other nitrogen oxides are reduced (e.g. PAN, HNO_3). This could lead to an analytical error of 100% or more in rural/remote areas (see e.g. Steinbacher et al., 2007). For this reason it is clearly recommended NOT to use chemical converters but instead PLC / BLC converters in networks like ACTRIS or GAW.

5.2.3. Other techniques for NO_2 detection

In the recent past, other techniques such as laser induced fluorescence (LIF) (Thornton et al., 2000), Tunable Diode Laser Spectroscopy (TDLS) (Li et al., 2004), Quantum Cascade Laser Absorption Spectroscopy (QCLAS) (Tuzson et al., 2013), Cavity Ring Down Spectroscopy (CRDS) (Fuchs et al., 2009), Cavity Attenuated Phase Shift (CAPS) technology (Kebabian et al., 2008) and Long Path Absorption Photometry (LOPAP) (Villena et al., 2011) were also applied to NO2 detection at trace levels in the atmosphere. Most of them are still research type instrumentation while also first commercial instruments become available. Results of a comprehensive laboratory study comparing some of the above mentioned techniques can be found in Fuchs et al. (2010). However, these instruments first have to prove their suitability for long-term monitoring within the DQO specified in this Guideline. ACTRIS took part in such studies and contribute to the evaluation of new instruments. Progress in measurement technology also nowadays allows to continuously monitor the atmospheric NO2 burden in the lowermost few hundred meters above ground with Ground-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) (Hendrik et al., 2014). Such measurements can complement the traditional ground-based in-situ observations, can provide a more integrated view on the NO2 levels and could be used for an independent quality control of the in-situ observations.

6 Primary standards and calibration centre for NO and NO_2

6.1. Central calibration laboratory (CCL) and primary standard (PS)

The role of the Central Calibration Laboratory (CCL) is to maintain and disseminate primary standards to which measurement results within the GAW- and ACTRIS-network can be made traceable [WMO, 2008] thus underpinning the long-term accuracy of data.

Probably National Physical Laboratory (NPL, United Kingdom) is going to take over the role as CCL in collaboration with Bureau International des Poids et Mesures (BIPM, France). The calibration gas for round robins will originate from NPL.
At present only NO in nitrogen is foreseen as primary standard, usable also for NO_2 by gas phase titration (GPT). NO in N_2 (≥ 5.0) is stable in the range of 450 ppb ≤ m.r. ≤ 10 ‰ in specifically passivated cylinders. Drift at 50 ppm standard is about -0.2% - -0.02% $year^{-1}$. Maybe in the future there will be an additional NO_2 standard. First tests showed a robust standard of 10 ppm NO_2 in the presence of 1000 ppm O_2. Depending on the material of the cylinder HNO_3 is formed in the range of 10 - 200 ppb. Intercomparison of NMI's yielded deviations are < 0.5%.

6.2. World Calibration Centre (WCC)

The main task of WCC is to assist the GAW and ACTRIS sites to archieve the data quality objectives described in chapter 3 and to document the respective status of data quality. Additionally the WCC links the in-situ observations to the primary standard. This should be done through regular calibrations, round robins, side-by-side measurements and audits. The role of WCC is described in detail at WMO/GAW Report No. 172 (WMO TD No. 1384, 2007).

The Research Centre Juelich (Germany) has been assigned by WMO to operate the WCC for NO_x in GAW. In ACTRIS this institution works as calibration centre, too.

7 Quality Assurance and Quality Control

7.1. Measurement and measurement protocol

Typically the chemiluminescence analyzers measure NO and NO_2 mole fractions sequentially, but quasi continuously (see chapter 5). In order to archive the best data possible, quality checks on a regular basis are required. The following actions are suggestions which have to be adapted for the special requirements at the individual sites.
All actions taken on the instrument or related to the instrument (inlet, pump, data aquisition, ...) must be documented in a station logbook with the respective time. The time zone of the logbook entries should also be clearly documented. Special care has to be taken for the documentation of the material, dimension, flow, temperature, and pressure of all components of the inlet system from the inlet point to the NO instrument. Log books should be regularly copied for backup reasons. Data should be regularly backuped on an external memory device.
On regulary time intervals the following items should be checked (check lists help):

1.) Routinely checks (e.g. every time the operator is on site):
Connections to the instrument:

- Electrical power: Is the cord really fixed?
- Data aquisition: Are all cables fixed
- Inlet line: is the inlet line leak-proof? Is no room air pulled in? (Unusual spikes in data corresponding to presence of personal in lab are hints towards a leaky inlet line.) Are there any signs of condensaion in the inlet line? Are the flow and temperature(s) of the inlet line in the allowed range (control unit of inlet line)? (Hint: Measure the inlet flow at the beginning of the line and compare to the sum of individual instrument flows.)
- Dry air supply for flushing the PMT window: Is the dry air correctly connected? Is the drying unit working well, or has the silica gel cartridge to be regenerated? It is very important to feed dry air into the CLD which is used for rinsing the PMT window. Humidity leads to condensation at the PMT window follwod by significant loss of sensitivity. Too much humidity also can lead to a demolition of the PMT or connected electronics.
- In case the CLD is operated with pure oxygen for supplying the ozonator **(Hint: To improve the sensitivity of CLD the ozone generator should be operated with pure oxygen.)** : Is the oxygen supply correctly connected and is the pressure of the oxygen cylinder sufficient? Check for time

to order a new oxygen cylinder (consider delivery time). Commercially available oxygen generators are also capable of producing oxygen of sufficient quality.

- Is the clock of the data acquisition system ok?

Check of (meta)data:

All metadata should be stored, the use of data aquisition systems is recommended.

- Is the inlet flow and the chamber pressure in the expected range? Is there a drift in chamber pressure? Since chamber pressure directly affects the sensitivity of the instrument (quenching) it has to be constant. Otherwise recalibration is needed. Drift in chamber pressure or inlet flow might be a hint for a blockage of the inlet line or a weakening of the pump.
- Are the temperatures (PMT, reaction chamber, photolysis cell, CLD) in the allowed ranges? Especially the PMT temperature is important since it directly affects the noise of measurement.
- Are the NO and NO_2 data in a typical range? NO_2 data are typically some 2-10 times higher than NO during day time. If they are more or less equal, this is a strong hint of defective conversion.
- Is the background signal in the prechamber mode in the expected range? Problems might be a hint for a weakening of the ozone generator.
- Are there "artifact signals" during night (in the presence of ambient O_3 > 20 ppb) and during measurement with zero air (see 5.1. and 7.3.)?
- Do the data displayed at the instrument match with the respective data in the data file of the aquisition system? This is a simple and effective test whether the data flow from instument to data storage is o.k..

2.) Routinely maintenance

- every 2nd day (depending on aspired precision of measurement): calibration (span check) and determination of conversion efficiency
- every 2nd week (depending on pollution level): change of inlet line filter
- every 3rd month (depending on pollution level and - in case of use of drying cartridges for dry air generation - capacity of drying cartridge): change of filters at dry air and oxygen inlet; regeneration of drying cartridge. First the CLD is shifted to stand by mode. Then the filters and cartridges are exchanged. (Hint: It is convenient to use a silica gel and a drierite ($CaSO_4$) cartridge in serial connection. The silica gel absorbs most of humidity, subsequently the dew point is further lowered by the drierite. The silica gel can be easily regenerated by means of a microwave during some minutes. During that time the system can continue operation with the drierite cartrige alone Iin this case the CLD needn't put to stand-by mode. With this setup the drierite cartridge has to be regenerated only every third month in a cabinet dryer.)
- every 6th month (depending on pollution level): cleaning of reaction chamber, cleaning of photolysis chamber; (durable loss in counting rate is a hint toward a dirty cell, loss in conversion efficiency even when using a new lamp is a hint towarts a dirty photolysis chamber). Refer to instrument manual for dissassembling reaction and photolysis chamber. Warning: The PMT, as long as under electrical power, will be destroyed by incident light. Once dissambled the cleansing is like the following: First rinse with deionised water. For more persistent deposits use a lint-free cloth. Don't scratch the walls or any glass part. Don't use organic solvents or acids!
- every 6th month: multi-point calibration with primary station standard.
- on demand: At NO_2 conversion efficiency below 40% or unsteadiness of lamp: Change of Xe-photolysis lamp, (other conditions and limits for other types of converters e.g. Blue Light Converter).
- How fast are the sensitivity values and conversion efficiencies drifting with time?
- How big is the enhancement of the zero mode by NO? This gives a hint on O_3 generator lifetime.
- Some instruments require periodic replacement of consumables, e.g. valves, or maintenance of the pump (e.g. regular membrane replacements). Refer to instrument manuals for details.

7.2. Calibration procedure

Since the chemiluminescence technique is not an absolute measuring method and sensitivity depends on parameters like cell temperature or pressure, which can change with time, frequent zero and span checks are mandatory.

Depending on data quality objectives, recalibrations have to be performed on regular basis and in such intervals that the expected deviation between consecutive calibrations is lower than the uncertainty of the measurement. Zero checks are not as important as span checks for the more sensitive instruments which are equipped with a prechamber. However, to ensure that zero air contains only traces of nitrogen oxides causing a signal well below the detection limit, zero checks should always be performed together with span checks. According to the DQOs, recalibration should be performed at least once per week, every second day, twice a day for level 1, 2, and 3 sites, respectively. It is recommended to calibrate the CLD at typical ambient air concentration. The instrument linearity should be checked up to the maximum of expected range at the respective site at least once a year.

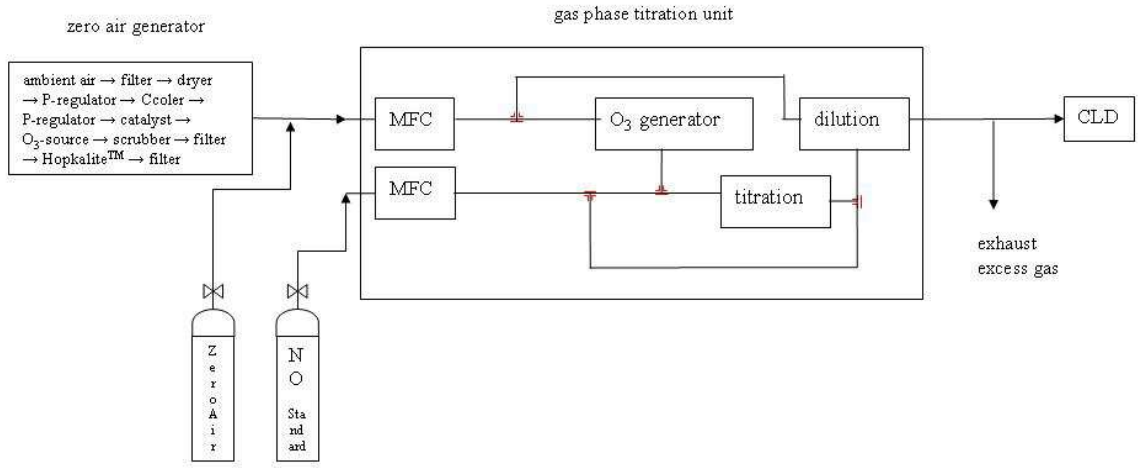

Fig. 2: sketch of calibration configuration

For calibration, special equipment is needed and special care has to be taken to achieve reliable results: A zero air supply is needed (as the sketch indicates zero air in cylinders or alternatively a zero air generator should be used), which exceeds the gas consumption of the analyzer by about a factor of 2 and has a sufficiently high purity such that the remaining nitrogen oxides concentrations are less than the detection limit of the respective analyser (Hint: Eco Physics offers a zero air generator which provides nitrogen oxides free air (< 5 ppt). An alternative is the use of adsorbent traps (activated charcoal and Sofnofill™ or Hopkalit™). The lifetime of these catalysts/absorbers strongly depends on the quality of air which has to be cleaned, of course. If zero air has been o.k. for some time and then tends get measurable amounts of nitrogen oxides, change the cleaning cartridges.). Each station should have at least a laboratory standard by the CCL or traceable to the CCL and a second certified standard ("working-standard") as a check at each station. The NO working standard is used at the station for regular calibrations. It has to be diluted with zero-air to achieve a suitable concentration range. For this, a dilution unit with flow controllers or passive elements like critical orifices or restrictors has to be used which need to be carefully characterized to achieve the required dilution factors and accuracy. From comparisons between working standard and station-standard it has to be checked that no drift occurs.

During constant NO mole fractions in ambient air (e.g. during night) the detector sensitivity to NO can also be determined by spiking with standard additions, using a known mole fraction of NO in the low micromole/mole (ppmv) range, added at the inlet tip to the ambient air sample stream to produce a calibration in the low nmole/mole (ppbv) range. The advantage is calibrating in a real air matrix, so the data will not need to be corrected (at the given humidity) to account for ambient water vapor quenching effects according to Ridley et al. (1992) before being applied to the ambient data. The disadvantage is that this technique relies on constant ambient NO mole fractions during calibration which means that it needs to be repeated several times (switching between ambient NO and spiked NO) and only if constant span factors are achieved it can be used.

When first attached to the NO standard cylinder pressure regulators must be flushed 4-5 times with cylinder contents. After that the regulators remain under pressure for at least 24 hours in order to

achieve equilibrium. After again flushing 4-5 times they are ready for use. This procedure is required to prevent residual atmospheric O_2 from reacting with NO and altering the cylinder mole fraction. The duration of the calibration procedure should be sufficient long to ensure a zero drift in the calibration signal.
If NO_2 is measured at the site, the PLC-CLD system must be calibrated also for NO_2. Since NO_2 is generally not stable in cylinders, it is recommended to produce NO_2 out of NO standard gas by gas phase titration with ozone (it is not recommended to buy gas mixtures, which contain both NO and NO_2 since the O_2 added to stabilize NO_2 would react with NO to form NO_2). Thus, a gas phase titration (GPT) unit is needed, which consists of a dilution unit (which is also needed for the NO calibration, see above) and an ozone generator. The GPT ozone source must be very stable over time. Irradiation of zero air with the 185 nm UV output from a temperature-controlled Hg pen-ray lamp has proved to be suitable. Silent electrical discharge is not appropriate for ozone production because it is not stable enough for GPT and generates small amounts of NO_2.
Other methods for calibration of NO_2 include permeation sources or high pressure cylinders with NO_2 concentrations in the high ppm range. As the permeation device includes further error sources than dilution, e.g. the uncertainty of a constant permeation rate and the dilutions from NO_2-mixtures requires a second dilution step due to the high concentration involved, these methods generally have higher uncertainties than the methods recommended above. Accordingly, these should only be used as an extra quality check.
Calibrations should be performed under the same conditions as the ambient air measurements. Generally the NO_2 calibration should always immediately follow the NO calibration as it includes the NO chemiluminescence sensitivity.

Practical procedure:

1. Check that all instruments and tools needed for calibration are connected and work.
2. Warm-up time of GPT with ozone generator should be at least 1 hour. Rinse the calibration unit with a high mole fraction of ozone (e.g. 100 ppb) during that time (warm up of ozone source and cleaning of tubing).
3. Flow of zero air for at least 20 min, connect CLD with calibration source and acquire zero air counts for at least 10 minutes (depending on type of CLD). (Hint: Compare the readouts (counts) of prechamber mode and measurement mode: Significant higher levels during measurement mode are an indication of NO impurities in zero air, higher levels only during NO.c measurement mode (sample flowing through PLC/BLC) is an indication of NO_2 impurities in zero air. If it is not possible to look at the count rates (e.g. TE 42) change span to a high level and have a look on the "mole fractions" at the respective modes.) These NO or NO_2 impurities in zero gas will become critical if their amount exceeds the LDL of the respective system. In this case inspect your zero air supply.
4. Adjust the desired span point and allow the system to run for at least 20 minutes, then acquire the span air counts for at least 10 minutes.
5. After determination of the new calibration factors for NO, one can continue with NO_2 calibration.
6. Let the desired NO concentration (without ozone) flow into the system and acquire the data for NO- ($NO_{(1)}$) and NO_2 channel ($NO.c_{(1)}$) for at least 10 minutes each (Hint: Higher $NO.c_{(1)}$ signal compared to $NO_{(1)}$ is an indication of NO_2 impurities in the standard gas and/or zero air).
7. Choose an ozone concentration so that 80% of the primary NO amount is titrated. Give the system at least 20 minutes to stabilize.
8. After stabilisation acquire the data for the NO- ($NO_{(2)}$) and NO_2- ($NO.c_{(2)}$) channel for at least 10 minutes (each).
9. Subsequently the NO_x analyzer is reattached to the inlet line, GPT unit and zero air supply are switched off and pressure reducer of standard gas cylinder is shut off.

The converter efficiency is calculated as follows:

The effective produced NO_2 amount results from: $[NO_2] = [NO_{(1)} - NO_{(2)}]$

The converted NO_2 amount by PLC is calculated by: $[(NO.c_{(2)} - NO_{(2)}) - (NO.c_{(1)} - NO_{(1)})]$
Accordingly the efficiency factor is calculated by:

$$S_C = \frac{[(NO.c_{(2)} - NO_{(2)}) - (NO.c_{(1)} - NO_{(1)})]}{[NO_{(1)} - NO_{(2)}]} = 1 - \frac{NO.c_{(1)} - NO.c_{(2)}}{NO_{(1)} - NO_{(2)}}$$

7.3. Corrective actions facing possible interferences

7.3.1. Interferences caused by water vapor

Since water vapor is an effective quenching substance in the CLD reaction chamber parts of the excited NO_2 molecules are quenched by H_2O molecules. For example this accounts for about 4% signal loss due to an absolute humidity of 9 g/m³ (corresponds to 50% RH at 20°C). Accordingly, a correction factor has to be applied:

$$[NO]_{H_2Ocorr} = [NO] \cdot (1 + \alpha \cdot [H_2O]) \quad \text{with} \quad \alpha = (4.3 \pm 0.3) \cdot 10^{-3} \cdot \frac{flow_{sampleair}}{flow_{ozone} + flow_{sampleair}}$$

$[H_2O]$ has the unit parts per thousand or ppth or ‰ in this equation.
Formula by Parrish et al, 1991, adopted and modified by Franz Rohrer (WCC NOx).

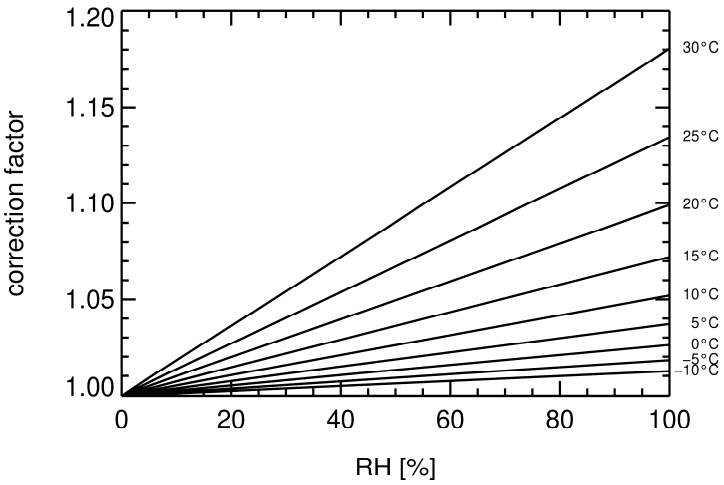

Fig. 3: correction factor $(1+\alpha \cdot [H_2O])$ of the NO chemiluminescence signal for quenching by H_2O (at 1013 hPa).

7.3.1. Artefacts caused by ozone

As mentioned in chapter 4.2. after entering the inlet line, the NO_2 photolysis is stopped whereas the reaction of NO and O_3 continues, leading to overestimation of NO_2 and underestimation of NO.

To allow for this, the following formulae should be used for correction of the measured raw signal to achieve ambient air concentrations:

S_C : conversion efficiency of PLC or BLC
J_C : photolysis rate of NO_2 in converter
$[NO]_M$: analyzers readout for NO
$[NO_2]_M$: analyzers readout for NO_2
$[NO]_{E1}$: measured NO signal [ppb] without photolytic converter (LED off or bypass)
$[NO]_{E2}$: measured NO signal [ppb] with photolytic converter
$[NO]_0$: NO mole fraction at the entry of inlet line
$[NO_2]_0$: NO_2 mole fraction at the entry of inlet line
$[NO]_L$: NO mole fraction at the entry of converter at time t_L
$[O_3]_0$: O_3 mole fraction [ppb] at the entry of inlet line

t_L : time [sec] from entry inlet line to entry of converter
t_{C1} : duration of stay [sec] in converter or bypass line (in case of LED off or bypass)
t_{C2} : duration of stay [sec] in converter
t_{E1} : t_L+t_{C1}
t_{E2} : t_L+t_{C2}
$k(O_3+NO)$: reaction rate constant for $NO+O_3$
k_{O3} : $k(O_3+NO)*[O_3]*10^{-9}*M$

In first step the analyzers readout for NO and NO_2, $[NO]_M$ and $[NO_2]_M$, respectively, have to be reconverted to the related NO signals $[NO]_{E1}$ and $[NO]_{E2}$.

$$[NO]_M = [NO]_{E1} \qquad \text{and} \qquad [NO_2]_M = \frac{[NO]_{E2} - [NO]_{E1}}{S_C}$$

These are the typical formulae for calculating the NOx mole fractions without ozone correction.

With the intermediate parameters J_c; which is the photolysis rate inside the PLC and $[NO]_{PSS}$ and $[NO_2]_{PSS}$, which are the equilibrium mole fractions of NO and NO_2 inside the PLC, respectively,

$$J_c = \frac{-\ln(1-S_C)}{t_{C2}}$$

$$[NO]_{PSS} = \frac{J_C}{J_C + k_{O3}} \cdot ([NO]_0 + [NO_2]_0)$$ in photolytic converter

$$[NO_2]_{PSS} = \frac{k_{O3}}{J_C + k_{O3}} \cdot ([NO]_0 + [NO_2]_0)$$ in photolytic converter

one can calculate the NO and NO_2 mole fraction at the entrance of the inlet line, $[NO]_0$ and $[NO_2]_0$:

⇨ Calculation of NO:

$$[NO]_0 = [NO]_{E1} \cdot \exp\{k_{O3} \cdot t_{E1}\}$$

⇨ Calculation of NO_2:

$$[NO_2]_0 = \left(\frac{J_C + k_{O_3}}{J_C}\right) \cdot \left(\frac{[NO]_{E2} - [NO]_{E1} \cdot \exp\{-(k_{O3} \cdot (t_{C2} - t_{C1}) + J_C \cdot t_{C2})\}}{1 - \exp\{-(k_{O3} + J_C) \cdot t_{C2}\}}\right) - [NO]_0$$

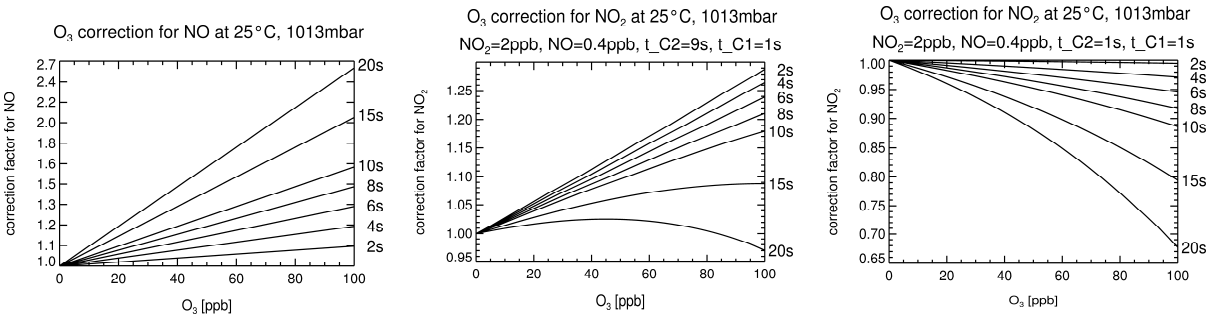

Fig 4: Correction factors for NO and NO_2 due to reactions of O_3 in the inlet line and in the photolytic converter. The values at the right side of each panel denote the residence time in the inlet line. S_c is set to 50%.

7.4. Quality control procedures (Audit , round robin, side-by side measurement)

Besides routine calibration and quality checks, intercomparisons are essential for intercomparable, quality proofed data. Main intercomparison procedures are: round robin, side-by-side experiments and audits, as well as exchange of experiences at common workshops etc..

7.4.1. Round Robin

In 2012 the ACTRIS-NO round robin took place with 18 participants of European laboratories involved in long-term monitoring nitrogen oxides. The activities were organized and overseen by DWD Hohen-peissenberg . Two NO in N_2 mixtures in the µmol/mol range were purchased from NPL and used as ACTRIS test gases. Participants were asked to analyse the sent ACTRIS mixture following a well described procedure. Results were submitted by the participants using form sheets to achieve comparable methods of data and uncertainty evaluation.
This intercomparison ensures the tracebility of the used laboratory standards at ACTRIS sites to a common ACTRIS standard. This is the basic requirement for comparable measurements in Europe.
Details concerning the results and their analyses can be found in the respective ACTRIS document WP4_D4.4_M24.

7.4.2. Side-by-side-experiment

Side-by-side intercomparisons should guarantee that identical samples are analysed by collocated instruments. This is either achieved by instruments sampling in ambient air side-by-side assuming homogenous trace gas distribution at the sample gas intakes, or by instruments sampling from a common manifold or atmospheric simulation chamber. One of the advantages of side-by-side intercomparisons is that much more complex sample gas matrixes can be analyzed and also the mole fractions can be varied in a controlled manner such that a range from the detection limits of the instruments to polluted conditions is encountered. This enables a full characterization of the detection limit, the linear range, the span, and of potential artifacts of interfering gases which are present in the complex test gas mixtures used.
A total number of 13 European laboratories involved in long-term monitoring, institutes involved in instrument development, and a company with a commercial instrument participated in the ACTRIS NO_x-side-by-side (s-b-s) intercomparison activity organised and overseen by DWD Hohenpeissenberg in November 2012. A ring-manifold was used with all instrument 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).
Details concerning the results and their analyses can be found in the respective ACTRIS document WP4_D4.6_M24.

7.4.3. Audit

Audits are most powerful QC tool. The NO and NO_2 measurements itself as well as all parameter which influence the measurements or the quality of measurments are under examination “in situ”.
Station audits are performed by the designated WCC for NOx, the FZ-Juelich. The first Audit has taken place in July 2014 at the Hohenpeissenberg Meteorological Observatory.

7.5. Measurement uncertainties

Measurement uncertainty is defined as the parameter associated with the result of a measurement that characterized the dispersion of the values that could be reasonably attributed to the measurand. The uncertainty is estimated following the "Guide for expressing uncertainty in measurements" (GUM).
The uncertainty contributions in NO calibration measurements are the flow rates of mass-flow regulating devices, the uncertainty of certified reference material, the zero gas purity, the repeatability of the analyzer, and drifts of the analyzer. Additionally, for NO_2 the photolytic converter efficiency has to be included.
In ambient measurements the uncertainty contributions due to zero, span, and repeatability of the measurements have to be considered, additionally that of corrections applied to the data as described in section 7.3, especially for O_3 in the inlet line and PLC and water vapor in the CLD measurement chamber.

8 Data Management

8.1. Data evaluation, flagging and control

A detailed procedure should be developed for evaluating the measurement data. It contains statistical analysis of the span-factors, zero gas readings and converter efficiency analyses supported by visual inspection of the temporal development over longer time periods, e.g. typically a year. The time series are checked versus the instrument-log and discontinuities in the time series should be associated to documented instrument changes. In case a discontinuity cannot be attributed to documented instrumental changes, other explanations for the behavior of the instrument have to be analyzed by careful inspection of the meta-data like chamber pressure or flow rate. In case no explanation for a discontinuity can be identified, an uncertainty contribution in the same magnitude as the discontinuity has to be considered. Generally, the zero gas readings should be in the range of the expected detection limit and the standard deviation of span factors and converter efficiencies in the range of estimated uncertainties, e.g. typically a few percent.
The calibration data are then used to determine a best fit to the span function of the instrument in time: usually, the scatter in the calibration data in frequent span and zero measurements is larger than the drift in floating averages of these values and accordingly floating averages of the span factors should be used in data evaluation.
The instrument readings in ambient measurements are transformed to mole fraction values using the above described averaged span factor functions in time. It is recommended to evaluate the mole fractions, repeatability of measurements and the uncertainty together with the flags in one step, e.g. by use of spread sheet calculations, and using the information from the Log. Thus, discontinuities in the time series are apparent and can directly be attributed to the log and be associated with higher uncertainties and corresponding flags.
The reproducibility of measurements could either be determined by multiple measurements of a highly diluted calibration gas and assessing additional impacts due to fluctuations in the zero and due to interfering species in ambient air, or, what is recommended here, by extracting appropriate periods from routine, continuous ambient air measurements. The latter has a number of advantages as (1) it characterizes the scatter for real ambient air, (2) it is available in the data sets and does not need extra measurements, and (3) it can be automatically withdrawn from the measurement series by statistical criteria. The procedure shall evaluate all series of 10 consecutive measurements (both NO and NO_2) and determine their absolute scatter by means of the standard deviations in nmol/mol. Then, an average of those 10 periods with the lowest standard deviation is built and used as the reproducibility of ambient NO or NO_2 measurements, respectively.
Data of NO and NO_2 are plotted together with ozone (and an anthropogenic tracer as black carbon or CO, if available) in quality-check-charts covering periods of typically 2 weeks. These data are checked for NO periods at night which are obtained with ambient ozone present (> 10 ppb) and under conditions of fairly low scatter. In such situations the NO should go down to zero, if not there is a zero off-set in the data and a correction has to be applied covering the deviation from zero and a corresponding uncertainty has to be considered in these measurements. Pollution episodes are characterized by elevated NO_2 and lower levels of ozone, in case of local pollutions the NO and NO_2 signals are highly

variable and anti-correlated with ozone, NO_2 may occasionally be negative. Such episodes should be flagged as polluted data but should be left in the data set.
Furthermore, annual cycles should be plotted and compared to corresponding cycles from recent years, wind roses shall demonstrate no local or strongly inhomogenous source patterns in the surrounding of the station, and percentile distributions of monthly values help to identify periods of unusual instrument operation.

8.2. Metadata and ancillary data

Data sets have to be sent to the EBAS (see 8.3 below) data centre, for which the traceability of the "final" level-2 data is achieved by a clear procedure based on the "raw" (level-0) or "original" data and ancillary and metadata. Essential ancillary data are: PMT temperature, reaction cell pressure, ambient ozone concentration, ambient temperature and humidity and other meteorological data. Very useful metadata are other, integration time, high voltage of PMT, chamber/instrument temperatures, (all) calibration factors, and length and diameter of inlet line.

8.3. Data archiving and data submission

The global data archive for in situ nitrogen oxides data is the World Data Centre for Greenhouse Gases (WDCGG) maintained by the Japan Meteorological Agency (JMA, http://gaw.kishou.go.jp/wdcgg). All NO and NO_2 data obtained as part of the GAW programme should be submitted without undue delay (attempts should be made to update the archives every one year or more often) to the responsible World Data Centre. WDCGG accepts irregularly spaced data (such as events, flask samples) and continuous data. Of the latter, hourly data as well as higher aggregates are archived. In addition to the NO/NO_2 data, WDCGG also encourages submission of meteorological data.
The format used by WDCGG for the data is plain ASCII encoded text in tabular form, preceded by a section containing metadata. Quality checks performed by WDCGG currently include consistency checks as well as checks on data integrity. WDCGG uses "-9(99…)" with different numbers of digits depending on the field to indicate missing values. Data submitters are advised to consult the WDCGG data submission guidelines (WMO/GAW Report no. 188) or to contact WDCGG prior to data submission.
All data (raw and final data including all metadata at highest time resolution) must be stored on different data storage media stored at different locations (not only at respective site).
For European data, there was an agreement between EBAS (NILU) and the WDCGG (Tokyo) that EBAS shall act as a sub/node data center for WDCGG, and thus all the European infrastructure project ACTRIS nitrogen oxides data submitted to EBAS according to their rules developed during the ACTRIS project will be mirrored by EBAS to WDCGG. EBAS foresees data submission with three data levels: Level-0, -1 and -2. Basic hereby is a regular, annual data submission of final, fully quality assured 1-hour averaged data (NO, NO_2, NO_{2+}, NO_y in ppb), including uncertainty, reproducibility, variability and data flagging (Level-2 data). The deadline for submission depends on the framework reported to, currently (2014) for EMEP and ACTRIS data it is 31 July of the following year.
In Advanced Data Reporting, the traceability of data back to the time of measurement shall be achieved by submitting raw data (instrument reading) in high time resolution (1 min) accompanied by a list of metadata to characterize the instrumental status. Time for reporting is UTC and no corrections are applied for data below the detection limit (take data as they are) (Level-0). With the same time resolution, level-1 are supplied that have the same time resolution as the raw data (level-2) but with evaluated mol fractions.
Near-Real-Time data reporting should be available to the user within max. 3 hours of measurement. Data are processed and screened automatically by the data supplier; they have lower quality and higher uncertainty as with regularly reported data.

The following list of flags shall be used in NOx data reporting:

Flag	Data Valid / Invalid	Description
000	**V**	**Valid measurement**
120	V	Sample reanalyzed with similar result
185	V	Possible local contamination indicated by wind direction or velocity
380	V	More than 50% of measurements below detection limit
382	V	More than 75% of measurements below detection limit
390	V	Data completeness less than 50%
392	V	Data completeness less than 75%
394	V	Data completeness less than 90%
420	V	Preliminary data
457	V	Extremely low value, outside four times standard deviation in a lognormal distribution
458	V	Extremely high value, outside four times standard deviation in a lognormal distribution
459	I	Extreme value, unspecified error
460	I	Contamination suspected
651	V	Agricultural activity nearby
652	V	Construction activity nearby
659	I	Unspecified instrument / sampling anormaly
660	V	Unspecified instrument / sampling anormaly
780	V	Value below detection or quantification limit, data element contains estimated or measured value
797	V	Data element taken from co—located instrument
899	I	Measurement undefined, unspecified reason
980	I	Missing due to calibration or zero/span check
999	I	Missing measurement, unspecific reason

Table 2: data quality flags as recommended by EBAS

All ACTRIS nitrogen oxides data are reported to, and stored in the EBAS atmospheric database http://ebas.nilu.no The EBAS database, originally designed for the European Monitoring and Evaluation Programme (EMEP), today archives data on atmospheric composition from ground stations around the globe, as well as aircraft and ship platforms. All datasets in EBAS are associated to one or more projects/frameworks, having individual rules for data disclosure. Most data stored in EBAS are originating from programs encouraging an unlimited and open data policy for non-commercial use. Offer of co-authorship is made through personal contact with the data providers or owners whenever considerate use is made of their data. In all cases, an acknowledgment must be made to the data providers or owners and to the project name when these data are used within a publication.

The ACTRIS data portal links EBAS data, together with data from the two other ACTRIS databases, EARLINET and CloudNet, into one common data portal. The portal facilitates the combined analysis of all ACTRIS data, offering advanced tools for plotting and combining ACTRIS data from the three

fundamental databases, and mapping tools for user defined visualization of distribution atmospheric sites and variables across networks and projects.

The following section provides a summary of the data submission procedures for nitrogen oxide data to EBAS. The text below only address the main points as defined by August 2014, for a complete and, at any time, updated document please reference http://ebas-submit.nilu.no/

Nitrogen oxide in situ data are qualified as ACTRIS data only if the measurement data are reported to EBAS by using the templates recommended by the ACTRIS trace gas community, and following the procedures described in the current document. ACTRIS partners shall label their contribution to EBAS with project/framework "ACTRIS". The data can also be associated to other programs and frameworks like GAW-WDCGG-node, EMEP, etc. Data submitted to EBAS need to be formatted in the EBAS NASA-Ames format by the data provider. The EBAS NASA-Ames format is based on the ASCII text NASA-Ames 1001 format, but contains additional metadata specifications ensuring proper documentation of the setup and procedures for each measurement principle. Specific templates for each of measurement principle are available from http://ebas-submit.nilu.no/ under the tab Submit Data -> Regular Annual Data Reporting -> NOx (regular).

An EBAS NASA Ames file consist of two parts; a metadata header and a column formatted data part. The header section contains a number of important metadata items describing the measurement site, data variable, instrument, measurement principle and operating procedure. If nothing change in the measurement set up, the header will remain the same from year to year, and the measurement data will be visible as one continuous dataset in the database. The data section of an EBAS NASA Ames file consists of a fixed column number format ASCII table, including time stamp, data value and flag for each single measurement point or data average point. The data formatting templates give the user a detailed line-by-line explanation of what metadata that should be included on which line of the header, in terms of correct procedure and wording. Further information are available by clicking on the respective line number from the template. Flagging of data should be done according to the ACTRIS nitrogen oxides and EMEP guidelines. For time being only flags from the tables at the format template pages are recommended, but a complete list of flags available in EBAS is located at http://www.nilu.no/projects/ccc/flags/flags.html

The data centre recommends to first create the data table and then add the header. Name the file over using the filename stated in the header.

The data submission deadline for the ACTRIS project is following the EMEP submission deadline, for time being (August 2014) this is 31.July for data from the year before. Example: 31.July 2014 is reporting deadline for 2013 data. The files containing the data submissions must be uploaded to the EBAS anonymous FTP site, accessible at:
ftp://ebas-submissions.nilu.no/incoming using the submitters email as password.
This site is for security reasons a blind drop page, so the submitter will not be able to see the data after submission, but an auto-mail from the system will be sent to the data submitter if the submission was successful.

All ACTRIS partners and associated partners operating one or more instrument measuring trace gases are expected to report their data within the reporting deadline, following the guidelines.
After the data submission all datasets will be handles by the data format checker in EBAS, and contact between the data submitter and the EBAS team will be established. Feedback is given to the data submitter if critical errors in the file format or in the data part are detected. Data submitted to EBAS can be expected available in the EBAS and ACTRIS data portals around to months after the submission.

The EBAS database team provides support on data formatting, data submission and use of EBAS, and can be contacted by e-mail at ebas@nilu.no

8.4. Data revision

Data providers can revise their data that have been submitted to EBAS by changing the data, adjusting the revision data, and increasing the version number in the EBAS data submission templates.

References

GAW Report 195, WMO/GAW Expert Workshop on Global Long-term Measurements of Nitrogen Oxides and Recommendations for GAW Nitrogen Oxides Network (Hohenpeissenberg, Germany, 8-9 October 2009), (WMO/TD-No. 1570), February 2011.

WORLD METEOROLOGICAL ORGANIZATION, GLOBAL ATMOSPHERE WATCH , No. 172: WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015, A Contribution to the Implementation of the WMO Strategic Plan: 2008-2011, WMO TD NO. 1384, pp16, 2007.

ACTRIS-Report: WP4 – NA 4: Trace gases networking: Volatile organic carbon and nitrogen oxides; Deliverable D4.4: Results of Round Robin exercise of NO, April 2013

ACTRIS-Report: WP4 – NA 4: Trace gases networking: Volatile organic carbon and nitrogen oxides; Deliverable D4.6: Results of NOx side-by-side inter-comparison exercise of ambient air and test gases, April 2013

Thornton, J. A., P. J. Woolridge, R. C. Cohen, 2000. Atmospheric NO2: In situ laser-induced fluorescence detection at parts per trillion mixing ratios. Analytical Chemistry, 72, 528–539.

Tuzson B., K. Zeyer, M. Steinbacher, J. B. McManus, D. D. Nelson, M. S. Zahniser, L. Emmenegger, 2013. Selective measurements of NO, NO2 and NOy in the free troposphere using quantum cascade laser spectroscopy, Atmospheric Measurement Techniques, 6, 927-936.

Fuchs H., W. P. Dube, B. M. Lerner, N. L. Wagner, E. J. Williams, S. S. Brown, 2009. A Sensitive and Versatile Detector for Atmospheric NO2 and NOx Based on Blue Diode Laser Cavity Ring-Down Spectroscopy, Environmental Science and Technology, 43, 7831-7836.

Kebabian, P. L., E.C. Wood, S.C. Herndon, A. Freedman, 2008. Practical Alternative to Chemiluminescence Detection of Nitrogen Dioxide: Cavity Attenuated Phase Shift Spectroscopy, Environmental Science and Technology, 42, 6040-6045

Villena, G., I. Bejan, R. Kurtenbach, J. Kleffmann, 2011. Development of a new Long Path Absorption Photometer (LOPAP) instrument for the sensitive detection of NO2 in the atmosphere, Atmospheric Measurement Techniques, 4, 1663-1676.

Fuchs, H., et al., 2010, Intercomparison of measurements of NO2 concentrations in the atmosphere simulation chamber SAPHIR during the NO3Comp campaign, Atmospheric Measurement Techniques, 3, 21-37.

Hendrick, F., J.-F. Müller, K. Clémer, P. Wang, M. De Mazière, C. Fayt, C. Gielen, C. Hermans, J. Z. Ma, G. Pinardi, T. Stavrakou, T. Vlemmix, M. Van Roozendael, 2014. Four years of ground-based MAX-DOAS observations of HONO and NO2 in the Beijing area, Atmospheric Measurement Techniques, 14, 765-781.

Annex I Abbreviations and acronyms

CLD	chemiluminescence detector
PLC	photolysis detector
BLC	blue light detector
CRDS	cavity ring down spectroscopy
LIF	laser induced fluorescence
DOAS	differential optical absorption spectroscopy
TDLAS	tunable differential laser absorption spectroscopy
CAPS	cavity attenuated phase shift (spectroscopy)
DQO(s)	data quality objective(s)

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