
(York, United Kingdom, 12 - 14 April 2016)
GAW Report No. 232


(York, United Kingdom, 12-14 April 2016)
EDITORIAL NOTE

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# TABLE OF CONTENTS

## PART A: REPORT OF THE INTERNATIONAL WORKSHOP ON THE NITROGEN CYCLE

1. Recommendations ........................................................................................................... 1  

Annex I - List of workshop participants .............................................................................. 3  

Annex II - Workshop agenda ................................................................................................ 4

## PART B: REPORT OF THE EXPERT MEETING ON NITROGEN OXIDES

Group picture ......................................................................................................................... 7  

Introduction .......................................................................................................................... 8  

1. Background to the Measurement of Nitrogen Oxides within GAW ................................. 9  

2. Overview of the Observational Network and Requirements ........................................... 11  
   2.1 Data Quality Objectives for NOx measurements ......................................................... 11  
   2.2 Network coverage ...................................................................................................... 12  
   2.3 Aircraft measurements ............................................................................................. 13  
   2.4 Other global networks measuring NOx ..................................................................... 13  
   2.5 Perspectives towards NOy measurements ................................................................. 14  

3. Measurement Techniques ............................................................................................... 14  
   3.1 NO measurements ..................................................................................................... 14  
   3.2 NO2 measurements ................................................................................................. 15  
   3.3 NOy and NH3 measurements .................................................................................. 16  
   3.4 Recent advances ...................................................................................................... 16  
      3.4.1. Direct optical NO2 measurements techniques ................................................... 16  
      3.4.2. MAX-DOAS .................................................................................................... 16  
      3.4.3. Use of low-cost sensors .................................................................................. 17  

4. Quality Assurance .......................................................................................................... 18  
   4.1 Calibration technique ............................................................................................... 18  
   4.2 Gas standards .......................................................................................................... 19  
   4.3 Zero air generation .................................................................................................. 20  

5. Data Archiving ................................................................................................................ 21  

6. Measurement Guidelines ............................................................................................... 22  
   6.1 Current state ............................................................................................................ 22  
   6.2 Discussions and recommendations .......................................................................... 22  
   6.3 List of actions .......................................................................................................... 23  

7. Summary of presentations at the meeting ......................................................................... 25  

References ............................................................................................................................ 28  

Annex I - List of expert meeting participants........................................................................ 30  

Annex II - Meeting agenda ................................................................................................. 31
Measuring NOx with multiple instruments – the more information, the bigger the uncertainty?  
*Robert Holla, Dagmar Kubistin, Christian Plass-Dülmer and Stefan Gilge*

NOx and NOy measurements at Hohenpeissenberg, Germany  
*Dagmar Kubistin, Robert Holla, Christian Plass-Dülmer and Stefan Gilge*

MAX-DOAS observations of NO2 in NDACC: Status and perspectives  
*F. Hendrick, C. Gielen, G. Pinardi, B. Langerock, M. De Mazière, M. Van Roozendael and the NDACC UV-vis Working Group*

First Experiences with Electrochemical Gas Sensors  
*Stefan Gilge*

Underpinning measurements of NOx: status of the CCL for NO  
*Paul Brewer, Dave Worton and Kate Resner*

Twenty years of ambient observations of nitrogen oxides and specified hydrocarbons in air masses dominated by traffic emissions in Germany  
*Christian Ehlers, Dieter Klemp, Franz Rohrer, Djuro Mihelcic, Robert Wegener, Astrid Kiendler-Scharr and Andreas Wahner*
1. RECOMMENDATIONS

The World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) International workshop on the Nitrogen Cycle, was held at the University of York, York, United Kingdom, from 13 to 14 April 2016. There were 25 participants. The list of participants and workshop agenda are available in Annexes I and II respectively.

The presentations included discussion of the GAW focus on “Research Enabling Services”, with the theme that “Atmospheric Composition Matters” to human health, weather forecasting, climate, terrestrial and aquatic ecosystems, agricultural productivity, aeronautical operations, renewable energy production, and more. Nitrogen cycle research is one of the new cross-cutting activities in GAW that enables ecosystem services in particular. There were presentations on GAW focal areas including aerosols, greenhouse gases, reactive gases and total atmospheric deposition.

See http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html

The broader nitrogen cycle research and observational community were also present at the meeting. These included participants from the Task Force on Reactive Nitrogen (TFRN) of the Convention on Long-Range Transport of Air Pollution (LRTAP), the International Nitrogen Management System (INMS), UN/GESAMP Working Group on the Atmospheric Input of Chemicals to the Ocean, agricultural, metrological and effects communities. Discussion was about the facts that globally and regionally nitrogen is a key environmental constituent that can have deleterious effects on air and water quality, climate change, ecosystems and soil quality while simultaneously being the key to global food production. This tension between food production and environmental degradation is a key scientific and policy issue of today. The key issue is how to globally increase the “nitrogen use efficiency”.

See http://www.inms.international/

A focus of this workshop was on how WMO/GAW can ensure that GAW products contribute to the broader nitrogen cycle agenda and in particular how the mutual beneficial links can be established with the International Nitrogen Management System (INMS) initiative. The two pathways are through observations and modelling.

**GAW can assist by providing INMS with information on the concentrations and flows of fixed nitrogen through the atmosphere.** GAW currently coordinates observations of N$_2$O and NOx in the gas phase and NH$_4^+$ and NO$_3^-$ in the aerosol phase and in total deposition.

The workshop identified that NH$_3$ is not measured in the gas phase as part of the core GAW programme and is a substantial contributor to atmospheric fixed nitrogen concentrations and flows. Given the recent developments in measurement techniques and metrology of NH$_3$ including presentations at the workshop, **the workshop recommended that gaseous NH$_3$ be identified as low hanging fruit for GAW to focus on research efforts, measurement guideline development and measurements activities where possible.**
The workshop noted that there is a gap in regulation of ammonia emissions at the international level. There is also a critical gap identified between NH$_3$ observations and emission inventories communities. On the measurement side, it was noted that widely used measurement protocols for ammonia measurements (using passive sampling techniques) have not been updated for 20 years and in a view of recent developments of observational methods the recommendations (e.g. European Monitoring and Evaluation Programme (EMEP) measurement guidelines) should be updated. It would be useful for the GAW community that is involved in NH$_3$ measurements to get involved in the revision of these measurement guidelines to ensure the uptake of this recommendation in the GAW Programme.

The workshop identified that both reduced and oxidized organic nitrogen compounds are not measured in the gas phase, aerosol and total deposition as part of the core GAW Programme and that these organic nitrogen compounds most likely make a substantial contributor to atmospheric fixed nitrogen concentrations and flows. Given the recent developments in measurement techniques and presentations at the workshop, the workshop recommended that organic nitrogen compounds in the gas phase, aerosol phase and total deposition be identified as an important area for GAW to focus research efforts and measurements activities where possible. It was also recommended that a workshop be conducted to assess the state of knowledge related to organic nitrogen.

The workshop identified that integration of GAW nitrogen measurement activities (both reactive nitrogen compounds and nitrous oxide) within nitrogen cycle studies is an essential and currently incomplete contribution to the GAW goal of “Research Enabling Services”. This work is more advanced in GAW with respect to the carbon containing gases and the carbon cycle. The workshop recommended that closer ties be developed between the GAW nitrogen community and both the users of global and regional emissions inventories (e.g. Global Emissions Inventory Activity (GEIA) and United Nations Framework Convention on Climate Change (UNFCCC)) and the users of global and regional chemical transport mode that include reactive gases, aerosol and deposition. This has the potential, through model-measurement-fusion (MMF), to contribute to the improvement of knowledge of the regional and global atmospheric cycles of fixed nitrogen. It was also recommended that inverse modelling techniques to infer fluxes are much broader utilized in GAW. The results of such modelling can provide useful insights on the nitrogen fluxes as a top-down approach to emission estimates and it can be useful in support of policy making. The workshop also recommended improving the density of N related observations in rural/agricultural areas which is critical for high quality flux inversion.

WMO/GAW should improve its ties with the agricultural community. It may be beneficial to establish joint projects in the areas where pilot projects in support of the Global Framework for Climate Services (GFCSs) are taking place due to the high sensitivity of the nitrogen cycle to climate change and its importance for fertilizer management. Finally, the workshop identified that there is a lack of “intelligent” or “sensitivity” analyses of the contributions of individual or regional conglomerations of GAW stations rating their usefulness for policy questions. The workshop recommended that GAW encourage such research including methods of network design so that the GAW network is both highly productive in terms of contributions and simultaneously efficient in use of resources. In this respect the recommendation was made to work closer with the satellite community that has extensive expertise in observational network design experiments. The final network design should be appropriate to demonstrate the effects of emission regulations on the levels of fixed nitrogen components in the environment.
LIST OF WORKSHOP PARTICIPANTS
International Workshop on the Nitrogen Cycle
University of York, York, UK, 13-14 April 2016

Alex Baker, University of East Anglia, UK
Christine Braban, Center for Ecology and Hydrology, NERC, UK
Paul Brewer, NPL, UK
Simona Castaldi, Second University of Naples, Italy
Howard, Clare, Center for Ecology and Hydrology, NERC, UK
Cláudia Marques dos Santos Cordovil, Instituto Superior de Agronomia, Lisbon, Portugal
Robert Duce, Departments of Oceanography and Atmospheric Sciences, Texas A&M University, USA
Ian Galbally, CSIRO Oceans and Atmosphere, Australia
Corinne Galy-Lacaux, Laboratoire d’Aérologie CNRS HDR, France
Brad Hall, NOAA, USA
Detlev Helmig, INSTAAR, University of Colorado, USA
Francois Hendrick, Royal Belgian Institute for Space Aeronomy, Belgium
Kevin Hicks, University of York, UK
Robert Holla, DWD, Germany
Tim Jickells, University of East Anglia, UK
Dagmar Kubistin, DWD, Germany
James Lee, University of York, UK
Ally Lewis, University of York, UK
Paul Monks, University of Leicester, UK
Thanos Nenes, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, USA
Elizabeth Pattey, Agriculture and Agri-Food, Canada
Christian Plass-Dülmer, DWD, Germany
Chris Reed, University of York, UK
Mark Sutton, Center for Ecology and Hydrology, NERC, UK
Oksana Tarasova, World Meteorological Organization, Switzerland
WORKSHOP AGENDA
International Workshop on the Nitrogen Cycle
University of York, York, UK, 13-14 April 2016

Wednesday, 13 April
13:30-13:40 Welcome and meeting objectives
James Lee, University of York
Oksana Tarasova, WMO

Session 1 - Introductions and setting up the scene
Chair: Oksana Tarasova
13:40-13:55 Perspective of SSC on cross-cutting activities and N cycle research
Paul Monks, Uni of Leicester, GAW SSC

13:55-14:10 Reactive Nitrogen in LRTAP Convention
CLÁUDIA Marques dos Santos CORDOVIL, Instituto Superior de Agronomia, Universidade de Lisboa

14:10-14:25 Added value of complementary observations of Nitrogen species – example of Cape Grim
Ian Galbally, CSIRO

Session 2 - Nitrogen in the group of Reactive Gases
Chair: Oksana Tarasova
14:25-14:40 Overview of N components addressed in the GAW Reactive Gases programme
Christian Plass-Dülmer, DWD

14:40-14:55 NOx/NOy observations at Cape Verde
James Lee/Chris Reed, University of York

14:55-15:10 MAX-DOAS observations of NO2 in NDACC: status and perspectives
Francois Hendrick, Royal Belgian Institute for Space Aeronomy

15:10-15:40 Coffee break

Session 3 - Nitrogen in the group of Greenhouse Gases
Chair: Ian Galbally
15:40-15:55 N₂O observations and analysis - prospective of GHG SAG
Brad Hall, NOAA
Session 4 - Reactive nitrogen chemistry and exchanges over the ocean and snow
Chair: Ian Galbally

15:55-16:05  GESAMP Working Group 38 and its oceanic nitrogen deposition studies
             Robert Duce, Texas A&M University

16:05-16:20  Atmospheric Nitrogen Deposition to the Oceans: Observation- and Model-Based Estimates
             Alex Baker, University of East Anglia

16:20-16:35  Atmospheric Nitrogen Inputs to the Oceans and their Impact
             Tim Jickells, University of East Anglia

16:35-16:50  Reactive nitrogen chemistry in snow-covered environments
             Detlev Helmig, INSTAAR, University of Colorado

Session 5 - Nitrogen in aerosols  Chair: Ian Galbally

16:50-17:05  NO3/NH3 behaviour between gas and aerosol phases
             Thanos Nenes, Georgia Tech, School of Earth and Atmospheric Sciences

17:05-17:20  NO3- and NH4+ in aerosol from ACSM and filter at Hohenpeissenberg
             Robert Holla, DWD

17:40-18:00  Formulation of key discussion points  Lead by Paul Monks

Thursday, 14 April

Session 6 - Deposition of Nitrogen  Chair: Alastair Lewis

9:00-9:15  Deposition on N – prospective of the SAG TAD
            Corinne Galy-Lacaux, Laboratoire d’Aérologie, CNRS HDR

9:15-9:30  Impacts of N deposition
            Kevin Hicks, University of York

Session 7 - N cycle in agriculture and ecosystems  Chair: Alastair Lewis

9:30-9:45  N fluxes from the agricultural sector
            Elizabeth Pattey, Agriculture and Agri-Food Canada

9:45-10:00  How well do we understand and describe drivers of change of N cycle in
            natural and agro-ecosystems
            Simona Castaldi, Second University of Naples

10:15-10:30  Ammonia metrology
             Dr Christine Braban, CEH

10:30-11:00  Coffee break
## Session 8 - Integration and Discussions

**Chair: Mark Sutton**

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
<th>Lead by</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:00-11:20</td>
<td>International Nitrogen Management Initiative</td>
<td>Howard, Clare/ Mark Sutton, Center for Ecology and Hydrology, NERC, UK</td>
</tr>
<tr>
<td>11:20-12:30</td>
<td>Discussions</td>
<td>Ian Galbally and Mark Sutton</td>
</tr>
<tr>
<td></td>
<td>Gap analysis of N observations in GAW – what are the missing elements</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Products that can be delivered by GAW community</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Potential collaboration to be established (potential contribution from</td>
<td></td>
</tr>
<tr>
<td></td>
<td>agricultural community on e.g. ammonia, or metrology community with</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ammonia)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Other points identified on Wed</td>
<td></td>
</tr>
<tr>
<td>12:30-13:30</td>
<td>Lunch break</td>
<td></td>
</tr>
<tr>
<td>13:30-15:00</td>
<td>Continuation of discussions</td>
<td>Ian Galbally and Mark Sutton</td>
</tr>
<tr>
<td></td>
<td>Recommendations</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Potential pilots/activities</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Presentation of the meeting outcome at the 7th International Nitrogen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Conference (INI 2016)</td>
<td></td>
</tr>
<tr>
<td>15:00</td>
<td>Coffee break and meeting closure</td>
<td></td>
</tr>
</tbody>
</table>
PART B: REPORT OF THE EXPERT MEETING ON NITROGEN OXIDES

Participants of the Expert Meeting on Nitrogen Oxides, University of York, 12-13 April 2016
INTRODUCTION

The WMO/GAW Expert Meeting on Nitrogen Oxides was held at the University of York, York, United Kingdom from 12 to 13 April 2016. The meeting was organized to support the reactive gases component of the Global Atmosphere Watch (GAW) Programme. It is a follow up of the Expert Workshop held in Hohenpeissenberg, Germany, in 2009 (see GAW Report 195). The meeting was jointly organized by James Lee (University of York, UK), Christian Plass-Dülmer (Hohenpeissenberg Meteorological Observatory, DWD, Germany) and Oksana Tarasova (WMO/GAW Secretariat, Geneva, Switzerland).

According to the GAW Implementation Plan, global networks, agreement on standardizations, and compatibility of data from different observational platforms and sites are of crucial importance for the early detection of regional and global changes in the composition of the atmosphere, especially in connection with changing anthropogenic emissions.

Nitrogen oxides belong to the group of reactive gases which also comprise surface ozone (O$_3$), carbon monoxide (CO), volatile organic compounds (VOCs), and sulphur dioxide (SO$_2$). The reactive gases are important for various aspects of the chemistry of the troposphere and are therefore selected for a long-term observations and research in GAW. The sum of nitric oxide (NO) and nitrogen dioxide (NO$_2$) has traditionally been called NOx. The sum of oxidized nitrogen species with an oxidation number $>$1, both organic and inorganic, is referred to as NO$_y$ (see Table 1 for individual molecules) (Fahey et al., 1985). Nitrous oxide (N$_2$O) is dealt in GAW within greenhouse gas focal areas. In GAW, NO and NO$_2$ are of a central importance. They can be measured with the appropriate high quality and a quality assurance system is in the process of being fully implemented. Since the status of GAW Report 195, a World Calibration Centre (WCC) at Research Center in Juelich (Germany) and a Central Calibration Laboratory (CCL) at National Physical Laboratory (NPL, UK) have been established.

This report summarizes the presentations, discussions and recommendations made during the meeting. It also describes the status of the GAW NOx programme, new instrumental developments, several NO$_y$ components considering their maturity for inclusion in GAW, and the finalization of the NOx Measurement Guidelines as a priority goal.

The meeting was introduced by Christian Plass-Duelmer who reminded the participants of the main discussion themes:

- Instrumental developments in NOx measurement techniques, keeping in mind that the focus of the meeting should remain on Chemi-Luminescent Detector (CLD) measurements.
- The current status of converter technology (also touching on new techniques for speciated NO$_y$ measurements).
- The network coverage and gaps in global coverage.
- Quality control procedures developed by the WCC for NOx.
- Status of NOx measurement guidelines, the draft was developed in the European ACTRIS project and has been circulated and commented upon by the GAW community.
- The new GAW strategy: its implementation plan, and the need to get closer to data users and their requirements.
1. **BACKGROUND TO THE MEASUREMENT OF NITROGEN OXIDES WITHIN GAW**

The background of NOx observations was discussed at the Hohenpeissenberg workshop in October 2009 and is presented in GAW Report 195. Here, only a brief overview is provided. Oxidized nitrogen occurs in many forms in the atmosphere reflecting the reactivity of fixed nitrogen and its many oxidation states (Table 1). It differs from other groups of compounds addressed within GAW in that nearly all the individual species are interconvertible by chemical processes occurring in the atmosphere.

**Table 1 - The main forms of oxidized nitrogen present in the troposphere, with R = organic group, lifetimes are given in the order of s (seconds), min (minutes), h (hours), d (days), w (weeks). The importance of its measurement to atmospheric chemistry is also shown.**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Lifetime</th>
<th>Importance to atmospheric chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric oxide</td>
<td>NO</td>
<td>h</td>
<td>Controls OH and O₃ in the troposphere</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>NO₂</td>
<td>h-d</td>
<td>Only chemical source of O₂ in the troposphere</td>
</tr>
<tr>
<td>NOx (nitrogen oxides)</td>
<td>NO +NO₂</td>
<td>h-d</td>
<td>Dominant form of oxidized nitrogen in regional atmosphere</td>
</tr>
<tr>
<td>Nitrate radical</td>
<td>NO₃</td>
<td>s-h</td>
<td>Important oxidant in night-time chemistry. Rapidly lost by reaction with NO and photodecomposition by red light in daytime</td>
</tr>
<tr>
<td>Dinitrogen pentoxide</td>
<td>N₂O₅</td>
<td>h</td>
<td>Night-time source of nitric acid. Reservoir for nitrate radical and NOx</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>HNO₂</td>
<td>min-h</td>
<td>Alternative source of hydroxyl radicals to O₃ chemistry</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>d</td>
<td>Important acidifying agent and major sink for oxidized nitrogen</td>
</tr>
<tr>
<td>Peroxy nitric acid</td>
<td>HNO₄</td>
<td>min-d</td>
<td>Reservoir compound in upper troposphere</td>
</tr>
<tr>
<td>Nitrate aerosol</td>
<td>NO₃⁻</td>
<td>d</td>
<td>Important component of regional aerosol</td>
</tr>
<tr>
<td>Organic nitrates</td>
<td>RO-NO₂</td>
<td>W</td>
<td>Major component of oxidized nitrogen in remote marine atmosphere. Higher nitrates (4+) are tracers for tropospheric photochemistry</td>
</tr>
<tr>
<td>Peroxyacetyl nitrates (PANs)</td>
<td>R-CO₂NO₂</td>
<td>h-w</td>
<td>Reservoir compound for NOx. Tracer for tropospheric photochemistry</td>
</tr>
<tr>
<td>NOy</td>
<td>all above</td>
<td></td>
<td>NOy is the dominant form of oxidized nitrogen in the remote atmosphere</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N₂O</td>
<td>&gt;100 years</td>
<td>Important gas controlling ozone concentrations in the stratosphere. Unreactive in the troposphere. Significant greenhouse gas.</td>
</tr>
</tbody>
</table>

Figure 1 depicts an interconversion scheme (for details, see GAW Report 195).
Figure 1 - Chemical connectivity of oxidized nitrogen compounds in the troposphere. Emissions are mostly in the form of NO and NO$_2$, loss processes are dominated by rain-out/wash-out of HNO$_3$ and nitrate aerosol along with dry deposition. R is an organic group; PAN is peroxyacetyl nitrate, $\Delta T$ means thermal decomposition, $hv$ is photodissociation.

The multiple forms of oxidized nitrogen compounds that are present in the atmosphere, their coupling to numerous processes in atmospheric chemistry, and the human perturbation of the atmospheric nitrogen cycle gives rise to many science and policy related issues connected with air quality and climate change:

- Anthropogenic perturbation of global NOx and nitrogen cycles
- Changes of main anthropogenic NOx emission areas/hot spots
- Changing impact on photo-chemistry and self cleaning capacity of the atmosphere
- Impact on tropospheric ozone
- Impact on secondary aerosol
- Impact on climate via ozone, aerosols and the life-time of methane
- Impact on air quality via ozone, PM-10, and toxic photo-oxidants
- Impact on acid depositions via HNO$_3$ produced from NOx
- Global changes of nitrogen deposition with severe impacts on ecosystems

Though there is principle awareness of the global impact of nitrogen oxides, the details of the encountered processes are insufficiently understood. Higher quality GAW data with increased spatial coverage are needed to capture global distributions and trends, to study underlying processes, and to assess the influence of anthropogenic perturbations of the N-cycles and their resulting hazards.
2. OVERVIEW OF THE OBSERVATIONAL NETWORK AND REQUIREMENTS

2.1 Data Quality Objectives for NOx measurements

Data Quality Objectives define the quality of the observations which is needed for specific purpose and there are instrument independent. For NOx Data Quality objectives are formulated in terms of the low detection limit and measurement uncertainty. The Data Quality Objectives from GAW Report 195 were considered to be appropriate by the GAW-NOx Expert Group. It was decided that no further category is needed to include real pristine conditions, instead, a footnote was added to Table 2 with respect to level 3, marine background and free troposphere with < 0.1 nmol/mol NOx: "In pristine environments with NOx levels at or below 10 pmol/mol, the required detection limits and uncertainties need to be reasonably extended (e.g. to 0.1 pmol/mol for NO and 0.3 pmol/mol for NO2)."

Table 2 - Data Quality Objectives (DQOs) for NO and NO2 under differing conditions

<table>
<thead>
<tr>
<th>Level</th>
<th>1 (basic)</th>
<th>2 (enhanced)</th>
<th>3 (high) 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site characteristics</td>
<td>Continental basic</td>
<td>Continental background</td>
<td>Pristine, marine background, free troposphere</td>
</tr>
<tr>
<td>Mean mole fraction NOx</td>
<td>&gt; 1 nmol/mol</td>
<td>0.1 – 1 nmol/mol</td>
<td>&lt; 0.1 nmol/mol</td>
</tr>
<tr>
<td>Scope (corresponding time resolution)</td>
<td>Long-term monitoring, trends (1 hour), source-receptor-relationship, transport processes (hour-minute), photochemical process studies (minute)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detection Limit (1 hour, 3σ)</td>
<td>NO: 50 pmol/mol NO2:100 pmol/mol</td>
<td>NO: 10 pmol/mol NO2:20 pmol/mol</td>
<td>NO: 1 pmol/mol NO2:5 pmol/mol</td>
</tr>
<tr>
<td>Uncertainty (1 hour, 2σ) 2</td>
<td>NO: 40 pmol/mol or 3% NO2:80 pmol/mol or 5%</td>
<td>NO: 8 pmol/mol or 3% NO2:15 pmol/mol or 5%</td>
<td>NO: 1 pmol/mol or 3% NO2:3 pmol/mol or 5%</td>
</tr>
<tr>
<td>Uncertainty (1 month, 2σ) 3</td>
<td>NO: 2.5% NO2: 3%</td>
<td>NO: 2.5% NO2: 3%</td>
<td>NO: 1 pmol/mol or 2.5% NO2:3 pmol/mol or 3%</td>
</tr>
<tr>
<td>Data coverage</td>
<td>66%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suggested method 4</td>
<td>CLD/PLC</td>
<td>CLD/PLC</td>
<td>CLD/PLC</td>
</tr>
<tr>
<td>Alternative/upcoming methods 5 (backup or QC reasons)</td>
<td>CRDS; LIF; DOAS; TDLAS</td>
<td>CRDS; LIF; TDLAS</td>
<td>LIF</td>
</tr>
</tbody>
</table>

1 In pristine environments with NOx levels below 10 pmol/mol, the required detection limits and uncertainties would be 0.1 pmol/mol for NO and 0.3 pmol/mol for NO2.
2 Whichever is the larger, e.g. for level 2 “enhanced” at NO2 of 1 nmol/mol an uncertainty of 50 pmol/mol is required (5% of 1 nmol/mol), at 0.2 nmol/mol an uncertainty of 15 pmol/mol would be required.
3 Assuming that the random uncertainties are negligible compared to the calibration uncertainty
4 CLD/PLC Chemiluminescence Detection/Photolytic Conversion
5 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
2.2 Network coverage

The current GAW network of surface, in situ NO and NO$_2$ measurements as documented in the GAW Station Information System (GAWSIS) is not sufficient with respect to the number and distribution of stations involved in NOx monitoring and research: Europe is the only region with a substantial number of NO and NO$_2$ stations with photolytic conversion measurements, as recommended by GAW. With the support of ACTRIS (Aerosol, Clouds and reactive Trace gases Research InfraStructure) funded partially by the European Commission, substantial developments have been made to improve the Quality Assurance (QA) system and to increase the number of European stations that follow the quality standards according to GAW NOx recommendations. It is encouraging that several Chinese and South-East Asian stations are performing NOx observations within the Acid Deposition Monitoring Network in East Asia (EANET). Negotiations for EANET to become a GAW contributing network are on their way, and efforts shall be taken to make corresponding data soon available through GAW data centres. The European NO$_2$ stations are augmented by EMEP filter pack stations which contribute valuable data, at the cost of lower data quality and time resolution. Within GAW, EMEP is considered as an important European contribution to the programme with many stations being also GAW regional stations. The Clean Air Status and Trends Network (CASTNET) USA is a contributing network to GAW that performs measurements of reactive nitrogen species. The network managers are working currently with GAWSIS to establish metadata exchange and ensure data availability. Another potential contributing network is the Canadian Air and Precipitation Monitoring Network (CAPMoN) which should be contacted to encourage linking their observations to GAW and to achieve a global coverage of NOx observations.

![Map of NO, NO$_2$, NO$_y$](http://ds.data.jma.go.jp/gmd/wdcgg/cgi-bin/wdcgg/map_search.cgi)

Figure 2 - Data availability in GAW from 07/04/2016. The red symbols denote that the data from the station has been updated in the last 365 days (April 2016), ([http://ds.data.jma.go.jp/gmd/wdcgg/cgi-bin/wdcgg/map_search.cgi](http://ds.data.jma.go.jp/gmd/wdcgg/cgi-bin/wdcgg/map_search.cgi)).

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1 The archiving of reactive gases data was moved on 1 January 2017 from the World Data Centre for Greenhouse Gases at Japan Meteorological Agency to the newly established World Data Centre for Reactive Gases supported by Norwegian Institute of Air Research (NILU).
NOx measurements that follow GAW recommendations are still too sparse to yield global coverage, and recommendations for the network development are similar to those in GAW Report 195 (see Figure 2). The expert’s meeting recommendations to improve the spatial coverage are:

- Encourage all GAW stations to take up and report NOx measurements
- Make use of existing networks and encourage alliances (contributing networks)
- Also use existing data of poorer quality for the time being
- Encourage stations and networks to utilize new NOx techniques and NOy-species measurements and foster efforts to follow measurement guidelines and QA systems recommended by GAW
- Re-evaluate the potential of MAX-DOAS for a global NO2 network once a central processing infrastructure has been developed to be operational.

2.3 Aircraft measurements

The expert meeting discussed recommendations and issues encountered by aircraft measurements. Data from mobile platforms are appreciated as GAW data given the quality is compatible to GAW. In particular, experiences with a chemiluminescence detection instrument (CLD) equipped with Blue Light Converter (BLC) were discussed. This set up was used in the Facility for Airborne Atmospheric Measurements (FAAM) campaign (Vaughan et al., 2016).

Typically aircraft measurements use calibration cylinders with a 2% uncertainty in NO concentration. The low NOx concentrations encountered in higher altitudes are equivalent to pristine environment. Variable altitude implies pressure and humidity changes in the instrument and conversion efficiency of the sensors needs to be well characterized for various environmental conditions. Ideally inlet pressure and sample humidity should be controlled against a set value for all altitudes. Above 8 km reduced inflow pressure often compromises the measurements. The conversion efficiency increases with residence time and depends on lamp power. With changing pressure and residence time, especially the aircraft systems are prone to varying artefact of NO generation from e.g. HONO (see section on NO2 converters below).

The meeting acknowledged In-service Aircraft for a Global Observing System (IAGOS), a European research infrastructure conducting long-term observations of atmospheric composition, aerosol and cloud particles using international airlines' operating commercial aircrafts. These measurements include NOx and NOy and the methodology includes highly restrictive requirements aiming to follow GAW recommendations. IAGOS is a first network based on mobile measurements that joined GAW as a contributing network.

2.4 Other global networks measuring NOx

The Network for the Detection of Atmospheric Composition Change (NDACC) is a cross-border international research network of remote sensing stations who’s main objective is to observe and understand the physical/chemical state of the stratosphere and troposphere. Already a major contributor to WMO/GAW it works under the auspices of the United Nations Environment Programme (UNEP) and the International Ozone Commission. NDACC officially started operation in 1991. Composed of around 90 stations, 47 of which operate Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) instruments for remote sensing of NO2. With these instruments, column information and vertically resolved NO2 structures can be retrieved, however, retrieval is challenging and requires well trained personnel (See Section 4.1).
Especially, GAW DQOs are currently not achievable. The detection limit for NO$_2$ near-surface concentration is about 20 pmol/mol and the related uncertainty is about 10-30% (10-20% for vertical columns). The range of mole fraction encountered in the atmosphere in the NDACC MAX-DOAS network is from ~20 pmol/mol or less at a remote high-altitude station like Jungfraujoch in the Swiss Alps to >80 nmol/mol at a highly-polluted site like Xianghe in the Beijing suburban area. NO$_2$ retrieval from FTIR instruments only yields total column information. For several compounds other than NO$_2$, NDACC plays a key role for trend studies, ground validation of satellite data and model assessment. Satellite measurements, on the other hand, are able to provide information with global coverage on NO$_2$ such as column density from the OMI, GOME and SCIAMACHY instruments.

MAX-DOAS could complement the current GAW-NOx network, provided approval of the instrument and coordination with GAW quality assurance and checks.

### 2.5 Perspectives towards NOy measurements

Measuring speciated NOy remains a GAW objective. Special interest in HNO$_3$ (and NH$_3$) measurements in addition to NOx measurements was brought up in the cross-cutting discussions with other research- and user-groups during the N-cycle meeting on April 13 and 14, 2016. However, it was agreed to first finalize the NOx measurements guidelines and implementations for a global NO and NO$_2$ network as part of GAW before moving on to NOy. At the same time, stations are encouraged to perform further research and monitoring on NOy compound measurements and to elaborate research on cross-cutting issues (e.g. towards aerosol chemical composition, deposition, fluxes). This also includes NOy measurements with gold converter. Potential future extension to cover further NOy species in GAW should be decided. However, before adopting a reactive NOy species in the GAW Programme, the given technique must be considered as mature enough, operational capacities (with respect to stations and central facilities, CCL, WCC, and World Data Centre for Greenhouse Gases (WDCRG), and the Quality Assurances (QA) components must be set-up with the required quality and sustainability, and then a global NOy observation network can realistically be initiated.

### 3. MEASUREMENT TECHNIQUES

#### 3.1 NO measurements

The discussion on measurements of NO touched upon the current state of the technology, issues related to instrument operation (especially for low level measurements) and different recommendations for remote or continental measurements. Chemi-Luminescent Detector (CLD) remains the recommended GAW techniques for measuring NO in the widest range of conditions. Most commercial CLD instruments show no improvements after 10 years, prompting the need for more communication between manufacturers and the scientific community. Current lowest trace level that CLD systems can reach are at or below 30 pmol/mol, specially selected ones can get below 10 pmol/mol, for one minute measurements and typical uncertainties of 5-10% can be achieved. Quantum Cascade Laser (QCL) combined with cavity enhanced absorption spectrometry (CEAS) was mentioned to work well, although it remains expensive, it might be the only viable replacement, prompting the suggestion of a gradual shift from CLD to QCL in the future. CLD, however, remains the standard with proven linearity and reproducibility over a wide range.
A list of CLD artefacts on NO was set up: not understood offsets (e.g. surface effects potentially including interaction with NO₂ or water vapour), compounds reacting fast with O₃ and producing luminescence, interference due to reactions of NO with O₃ and RO₂, not considering gas-exchange times after switching between NO and NO₂ mode. A correction for the quenching of excited NO₂ by water vapour needs to be considered. This can be avoided when the sample gas is dried with Nafion®. However, it still has to be verified that there are no artefacts of NOy components in Nafion®. An alternative would be to add humidity to zero and calibration gases. This requires the same humidity as in the sample gas. However, this was considered to be not conclusive as conditions still may differ. The WCC and an upcoming NOx intercomparison in the framework of ATCRIS will further address these issues. A further alternative for remote conditions is an introduction of the standard gas to the ambient air, as exemplified at Cape Grim and Cape Verde. However, this approach requires constant humidity between consecutive additions of the standard gas. For airborne measurements, humidifying the oxygen flow to the O₃ generator was recommended as it saturates quenching and reduces the sensitivity of the sample line to humidity changes (e.g. with altitude), while not affecting anything else.

CLD-manufacturers include AQD (Air Quality Design) and Ecophysics, both trace levels, Thermo, and Teledyne. GAW does not recommend any specific manufacturers but provides a platform to discuss experiences/issues with certain set-ups.

3.2 NO₂ measurements

The current state of the photolytic converters technology, recommendations for preferred types and interference issues were discussed by the experts. There was a strong need identified to further characterise artefacts due to NOy component conversion (other than NO₂) in BLC.

Different types of photolytic converters are used, e.g. commercial and self-built BLC using appropriate diodes, and Xenon lamps. However, the conversion efficiency of xenon lamps and older type BLC converters is not so high and they degrade over time. The frequency of conversion efficiency checks was a matter of debate, some groups use about one month intervals, the others even longer or on less than weekly bases. Experience of various stations and intercomparisons should be analysed to come up with better recommendations. These will be evaluated in ACTRIS and by the WCC.

The assessment of artefacts was deemed crucial for low-level measurements of NO₂. LEDs of 385-395 nm photolyse NO₂ into NO. However, also interference from HONO (overlap in spectrum) was witnessed at 395 nm wavelength. This artefact may compromise the measurement of NO₂. The spectra of systems in use should be checked and potential artefacts quantified and considered in the uncertainty estimates. Guidelines should consider spectral information and recommend LEDs least prone to artefacts (Reed et al., 2016). New BLCs are being developed to overcome these issues. Another issue was surface artefacts due to surface adsorbed compounds and artefacts due to light from the converter LEDs. A discussion on collimation of the light beam in BLCs for minimizing wall effects and the use of quartz tubes instead of the metal chambers was not conclusive but several groups will continue work on this.
3.3 NO\textsubscript{y} and NH\textsubscript{3} measurements

For several years a few groups have used thermal dissociation at different temperatures followed by detection of the dissociated NO\textsubscript{2} by Laser-Induced Fluorescence (LIF) as a way of providing a degree of NO\textsubscript{y} speciation (e.g. Day et al., 2002. Di Carlo et al., 2013). Typically these measurements have been made on ground or aircraft based short-term campaigns. At Cape Verde, 18 months of speciated NO\textsubscript{y} (SPANs, SOrganic nitrates and nitric acid) have been taken using thermal dissociation (at 150\textdegree C, 310\textdegree C and 525\textdegree C) followed by detection of NO\textsubscript{2} (and a small amount of NO) using a second channel on the CL-BLC instrument. This relatively simple and cost effective addition to the existing NOx instrument has provided data that could be crucial in understanding the sources, reservoirs and sinks of NOx in a remote marine region.

There is ongoing development of NH\textsubscript{3} measurement techniques within the framework of the EURAMET project ENV55 MetNH3 “Metrology for ammonia in ambient air”. Lab- and field-intercomparisons are performed in 2016 and current techniques will be evaluated. Recommendations with respect to mature techniques suitable for use in the GAW Programme will come out of this project and it is recommended that the SAG RG will then discuss the findings and decide for a future strategy in NH\textsubscript{3} monitoring.

3.4 Recent advances

3.4.1 Direct optical NO\textsubscript{2} measurements techniques

New instruments are capable of direct measurements of NO\textsubscript{2} by measuring the optical properties (scattering and/or absorption), however, also being subject to interference from species with similar optical properties. The following instruments were highlighted during the expert meeting based on two measurement principles:

1. Cavity Enhanced Absorption Spectroscopy with LED or lasers
2. Cavity Attenuated Phase Shift Spectroscopy (or CAPS)

Altogether, these new NO\textsubscript{2} measurement techniques are still research type instruments for high sensitivity in the ppt range and fast response times. Short-term sensitivity and zero drifts require frequent reference gas measurements, and interferences require careful characterization. Recently developed laser spectrometers were tested for simultaneous observations of NO and NO\textsubscript{2} in pristine environments and showed promising results. Though promising, these techniques need further long-term characterization at remote GAW stations to verify their capability as GAW recommended instruments.

3.4.2 MAX-DOAS

MAX-DOAS observation of NO\textsubscript{2} is a developing technology with some 50 instruments at present (mainly distributed over Europe and mostly coordinated by NDACC). This technique is a passive, ground-based remote sensing technology integrating signal passing typically over 10 km horizontally and achieving vertical profiles but with a quality lower than required by GAW (see Section 2.4 for details on detection limit and encountered mole fractions). Data evaluation of MAX-DOAS NO\textsubscript{2} requires scientific personnel with good knowledge and experience which are challenging factors that are often not available at GAW stations. In the 2016-2018 time period a centralized data processing unit will be developed at the Royal Belgian Institute for Space Aeronomy (BIRA-IASB) under the auspices of the European Space Agency (ESA). The potential
of MAX-DOAS has already been recognized by the satellite community for ground validation of columns for several reasons: MAX-DOAS integrates over some 10 km horizontally and hence has the same spatial resolution as modern satellites; both observations rely on differential optical absorption measurements, and MAX-DOAS yields column information which is better in validation than ground based in situ observations. Thus, there is already high interest in further development of MAX-DOAS networks by the satellite community and it would be advantageous to integrate MAX-DOAS into the ground based GAW NOx measurement network. Furthermore, MAX-DOAS could potentially make the link between in situ surface concentrations and satellite column observations. MAX-DOAS is also currently used to validate NO2 profiles and vertical column densities from the EU CAMS (Copernicus Atmospheric Monitoring Service) global and regional models.

The meeting agreed on the following action points:

- MAX-DOAS should not be included in the measurement guidelines, but in this expert meeting report, the potentials of MAX-DOAS should be highlighted.
- GAW SAG-RG should decide upon opening towards MAX-DOAS and start negotiations as a potential contributing network to GAW.

### 3.4.3 Use of low-cost sensors

Currently, so called low-cost air quality sensors are increasingly promoted as a feasible alternative to classical air quality monitors. Trace gases such as NO, NO2, ozone or carbon monoxide can be measured with small electrochemical sensors that were initially developed for industrial applications where concentrations are high. Improvements in sensor technology makes it now also possible to monitor nmol/mol levels (typically tens of nmol/mol) with low-cost sensors which seems to offer an appealing alternative to the more bulky and more expensive state-of-the-art instrumentation. While it is claimed that the newest generation of low-cost air quality sensors provides adequate selectivity and sensitivity to ambient air pollutants, it is obvious that such sensors are nowadays not suitable for NO and NO2 measurements within the GAW network as precision and detection limit are far beyond the GAW data quality objectives. However, a dedicated session during the expert meeting was scheduled to share expertise concerning sensors operation, their quality control and data management, to summarize the state of knowledge in sensor technology, to assess the current performance of such sensors and to evaluate their applicability for measurements in polluted environments as proposed by UNEP.

Three presentations given by British, German and Swiss scientists and the subsequent discussion revealed the following issues:

- A plug-and-play (deploy-and-measure) application of low-cost sensors without additional efforts (quality control) prior and during operation and post-processing does not lead to meaningful results.
- Large systematic differences in the reported concentrations have been observed in the UK when several low-cost sensors of the same model and type were operated side-by-side.
- Comparison of the low-cost sensors with reference instrumentation (based on chemiluminescence principle) in Germany revealed that sometimes the atmospheric variability was also detected by the sensors while no response was found for other events.
• Long-term tests in Switzerland demonstrated that sensor sensitivity for a particular trace gas can be dependent on various environmental parameters such as sensor temperature, humidity, and other interfering trace gases; therefore:
  - when operating low-cost sensors for NO₂, other parameters that may potentially influence sensor performance (see above) should be simultaneously measured to allow an off-line correction, e.g. based on empirical regressions retrieved from long-term comparisons with reference instruments.
  - Low-cost sensors need to be individually quality-controlled / calibrated prior to implementation and during operations as each sensor (even of the same model and type, see statement above) behaves differently, its long-term sensitivity changes and sensor aging has to be monitored; preferably, all quality assurance approaches are implemented on-site due to the above mentioned sensitivity to environmental conditions and the potential influences from interfering species;
• "Black box" models that only record NO or NO₂ concentrations (after an unknown internal processing and potential correction for interferences) are not suitable as subsequent off-line correction becomes impractical.
• To maximize the benefit of low-cost sensors, a combination of a dense network of low-cost sensors and some "mature" air quality monitors might be currently the most feasible approach as it allows at least basic continuous quality control.
• Appropriate quality control strategies for sensors are under development; significant resources (additional non-low-cost instruments; manpower for operation and data analysis) have to be taken into account.
• Anticipating improvements in low-cost sensor performance, growing experience in long-term sensor operation and the development of optimized quality control strategies, low-cost sensors could become a feasible alternative to replace/complement passive sampler networks in the future as their use in sensor networks can provide information with high spatio-temporal resolution.
• Current estimated investment costs are on the order of a few hundred US$ for a sensor, but up to 1500 to 5000 US$ for a whole sensor unit that includes sensor integration, signal processing and low power wireless communication; costs are expected to decrease with increasing market penetration and demand; operational costs reach 2000 to 3000 US$ per year depending on model and setup; this includes costs for mobile data transmission and database services, as well as regular battery (if available) and sensor replacements.

Thus, the operation of low-cost sensors is demanding and operated without the necessary caution, will generally yield misleading results. The advantage of easy operation and low cost is ineffective when considering the needed reference instruments and scientific skills necessary to make meaningful corrections and measurements. GAW community is developing a statement stating these off-the-shelf sensors are not suitable for general use at the moment. Indeed, several have been tested and evaluated bringing to conclusion that technology is not developed enough yet.

4. QUALITY ASSURANCE (QA)

4.1 Calibration technique

Discussions revealed that there are currently two approaches to calibration of measurement equipment: (i) spiking onto ambient air or (ii) dilution in synthetic air, both using NO
calibration gas (NO in N₂) and, gas phase titration (NO₂). Dilution of NO in nitrogen standard mixture with synthetic air (ii) was proposed as the recommended method. However, as many in the community successfully use the standard addition to ambient air, there is no need to abandon this procedure. The advantages of the spiking method are: the same matrix is used for both calibration and atmospheric measurements and corresponding artefacts are expected to be identical; no water vapour correction is necessary because of the same humidity in measurements and calibration. However, the disadvantage is that this established method is fine, provided the ambient matrix does not change, unfortunately, it does. This requires frequent calibrations according to the parameter variability in ambient air. As an example it was pointed out that at Cape Grim, calibrations twice per day at night and afternoon are satisfactory to meet DQOs. However, a station where calibration occurs only a few times per year is considered insufficient in light of the variability of the zero and the DQOs for NOx measurements.

In order to calibrate CLD instruments, a novel approach was suggested: introducing a tracer gas into the NO standards (CO₂). Before implementation as a standard procedure, the feasibility of making a standard of 5 µmol/mol (ppm) into 40% CO₂ in N₂ needs to be determined, and it should give about 400 ppm CO₂ concentration when diluted. It was noted that Cavity-ring-down spectroscopy (CRDS) measurements are matrix dependent which requires the use of the whole air rather than N₂. Argon must also be included in artificial matrix (as matrix must match ambient air composition). This tracer approach is considered a difficult task that requires additional investigation to devise a working system and it should not be recommended as a standard procedure yet. This will be evaluated by WCC (FZ-Juelich) with corresponding standard by CCL (NPL).

4.2 Gas standards

Questions on the stability of NO and NO₂ standards for varying storage parameters like temperature (e.g. below 0°C) were discussed. The CCL (NPL) will compile available information and provide guidance on standard cylinder storage.

Standards bought from commercial gas suppliers necessarily have to have a higher uncertainty than NMI standards because the commercial gas suppliers are at the next step of the traceability chain, which include additional uncertainties arising from the validation of their mixtures to primary reference gas standards from NMIs.

The currently characterized stability of sub-µmol/mol (ppm) level NO standards was discussed. NPL reported that a loss of ~18 nmol/mol/yr (ppb/yr) has been observed for 400 nmol/mol (ppb) NO standards. In silanized/passivated cylinder types NO appears to drift linearly. The certification period of 2 years provided on NPL certificates states an uncertainty that includes this drift. For remote locations NPL suggested that dilution of high concentration standards (~50 µmol/mol), which have been observed to be stable for long periods (several years) may be the best approach for calibration of instruments.

It was suggested to include in the measurement guidelines a section on the types and use of reference standards including the choice of regulators. It was noted that different cylinder types do have significant influences on preparative losses, hence it is important to identify the reliable companies where standard cylinders are purchased. There was some discussion about whether cylinders need to be used lying on their sides or whether standing cylinders were fine to use. NPL commented that for the levels of uncertainty required by GAW there is no
difference in the position of the calibration cylinders. It was also noted that cylinders are homogenised by rolling for 2 hours after initial preparation but do not need to be re-homogenised after this.

4.3 Zero air generation

High purity nitrogen, synthetic air or cleaned ambient airs are used as zero gases. Zero gas is essential for calibration of instrumentation and also is a major contributor to the uncertainty budget of gravimetric reference standards. The influence of the zero gas increases as the amount fraction of the target component in the reference gas mixture decreases. Providing traceable and accurate quantification of impurities of the target component in zero gas is a major challenge: the detection limits of appropriate analytical techniques are often close to the amount fraction of the measure, moreover, accurate reference standards to underpin these measurements have yet to be developed.

The discussion focussed on state-of-the-art methods currently used to generate and certify zero gas standards. The methods used by the metrology community focus on accurately quantifying the zero gas, rather than trying to remove the background levels in the matrix (this is often more challenging). Capabilities have been developed for NO with a typical limit of detection of 0.5 nmol/mol, which is several orders of magnitude larger than the requirements from the monitoring community. NPL uses a standard addition method for quantification, where accurate reference standards at low nmol/mol NO in nitrogen are blended with the matrix gas under test and used to calibrate a chemiluminescence detector. The technique relies on an absolute zero and a higher concentration standard (typically 10 µmol/mol) for dilution.

The discussion focussed on the need to calibrate instruments at zero, particularly at remote stations, where NO is observed in the pmol/mol range. Zero air generators (ZAGs) or pure air generators (PAGs) are typically used. Expert community found different concentrations of impurities present in such zero air from generators even from the same manufacturers, which can cause issues. There was a proposal to use a molecular sieve at -40 °C to remove NO < 1 pmol/mol, although this needs further investigation by WCC. Catalytic removal with hydrogen and Nickel catalyst was also suggested as a possible approach to remove NOxy species. Franz Rohrer stated that he used synthetic zero air generated from liquid nitrogen and liquid oxygen, although this approach is not practical for many GAW stations due to limited availability of these components. Generally, it was noted that all systems need thorough and regular testing. Specifically, testing has to account for all potentially interfering NOxy species (i.e. HONO).

Another approach to calibrate instrumentation is to take the measurement of NO at night at stations that are not influenced by local NO sources. It was agreed that due to NO titration by O3, NO at night should be zero when ozone concentrations are above 20 nmol/mol and no nearby NO source exists. Ian Galbally noted that due to the lower concentrations of ozone in the tropics and remote southern hemisphere and due to marine/soil emissions of NO, NO might significantly differ from zero at night suggesting that this criterion may not be universally applicable to all sites and locations. James Lee stated that a comparison of zero air had not been done before and suggested it could potentially be carried out using the Juelich Saphir chamber. The use of night-time NO to check the zero of instruments should be further specified with respect to the conditions when it can be expected to be zero and the corresponding confidence. Though it is not really clear whether night-time NO under conditions specified above really is zero, the recommendation is to use this signal for off-set correction.
This recommendation is due to the fact that still artefacts causing non-zero NO readings in zero air are not fully understood and the best means to correct for biases is to subtract the night-time NO offset (for the conditions specified above). However, this has to be elaborated further in pristine conditions with very low NOx (e.g. 10 pmol/mol range).

Observations of zero-signals frequently resulted in zero drifts over many hours. An example was presented where the zero of a CAPS monitor was lower than that of a CLD-BLC instrument, and no clear dependency on NO\textsubscript{2} was seen. Other examples showed differences between 3 CLD’s at night which had been calibrated the same way and with the same zero-gas generator system.

**Recommendations and actions**

During the expert meeting, the following recommendations were agreed:

- Standard cylinder storage conditions and handling guidelines shall be provided by NPL.
- Details on the recommended dilution procedure for calibration at GAW sites shall be provided in measurement guidelines.
- The measurement guidelines should include a section on the types and use of reference standards and the choice of regulators.
- Individual procedures for calibration and zeroing by common procedures (calibration and zero gases) should be evaluated during side-by-side comparison experiments.
- Specification is required for NO night-time zero for continental areas (e.g. O\textsubscript{3} > 20 ppb), southern hemispheric air and remote pristine locations where ocean water may act as a source of NO which is not fast enough removed by reaction with O\textsubscript{3}.
- Expert group should compile a list of purification systems in use with output concentrations and uncertainties.
- Franz Rohrer will circulate details of a method to produce zero air by use of molecular sieve at -40 °C.
- Recommended approach for producing zero air to be included in the measurement guidelines.
- Further input should be sought from EMPIR MetNO2 project, which starts in 2017 and aims to further improve measurement and calibration techniques for NO\textsubscript{2} in support of GAW and with contributions of GAW stations and NOx-WCC.

5. **DATA ARCHIVING**

The global data archive for in situ nitrogen oxide data is the World Data Centre for Reactive Gases (WDCRG) at EBAS, NILU Norway (http://www.gaw-wdcrq.org/). It resumed responsibility for the reactive gases archiving from the World Data Centre for Greenhouse Gases (WDCGG) maintained by the Japan Meteorological Agency (JMA, http://ds.data.jma.go.jp/gmd/wdcgg/). All NOx data obtained as part of the GAW Programme should be submitted without undue delay (attempts should be made to update the archives at least once every year) to the Data Centre. WDCRG accepts irregularly spaced data (such as events/campaign) and continuous data. Of the latter, hourly data as well as higher aggregates are archived. A template for NOx data submission is available, meta data delivery and uncertainty information is obligatorily included. In addition, WDCRG also asks for submission of meteorological data.
The format used by WDCRG for the data is plain ASCII encoded text in tabular form (NASA AMES), preceded by a section containing metadata. Quality checks performed by WDCRG currently include consistency checks as well as checks on data integrity. WDCRG uses unique identifiers to indicate missing values. Data submitters are advised to consult the WDCRG data submission guidelines and to contact WDCRG prior to data submission.

6. MEASUREMENT GUIDELINES

6.1 Current state

A Measurement Guidelines (MG) document for NOx will be published separately from this expert meeting report. It is foreseen that this document will be a living document that will consider any substantial changes in measurement technology and with respect to experience gained in GAW-NOx measurements.

6.2 Discussions and recommendations

The Draft MG in its present form (courtesy of Stefan Gilge and co-workers) is an advanced document based on the draft produced within the European ACTRIS framework. However, a number of basic questions and conceptual issues remain in the draft that need to be clarified by the Expert Team, in order to revise the document with respect to specific aspects of structure and contents. The following questions were raised and discussion and corresponding recommendations are described here:

- The meeting agreed on measurement guidelines for NO and NO₂ by chemiluminescence detection (CLD). Other instruments and/or NOₓ species will be covered by separate guidelines.
- Currently, PFA (‘dark’) is the recommended tubing material.
- It was agreed to use corresponding schemes to those provided by manufacturers, because users want to see their systems and not be confused by other, more general schemes.
- There is one group of systematic artefacts which must be corrected. This group is comprised of NO titration by ozone and RO₂ in the inlet line and instrument, converter correction (artificial conversion of NOₓ species to NO, e.g. HONO or BrONO₂ photolysis), and water vapour correction for quenching (depending on the calibration method). The first and last effects are occurring in all instrument types whereas interferences from other photo-labile NOₓ species depend on the specific photolysis-spectrum of the respective light source. Thermal decomposition of PAN should stay well below the threshold not being a significant artefact for NOx measurements in the specific environment (which is not possible for Mo converter systems). Similarly, interference due to RO₂+NO should be commented on, and definitely short residence times in the inlet line are crucial as RO₂ is generally not measured at GAW stations.
- Other artefacts are poorly understood and most probably related to surface effects with changing matrix (calibration vs. ambient) or changing instrumental parameters (e.g. temperature). Surface equilibrium effects during calibration is also comprised of the gas cylinder, pressure regulator, transfer lines, gas phase titration, etc. These have to be better described to give a sound overview of current knowledge and experience (see also preceding sections).
• For QA following actions shall be considered: round robin exercises, side-by-side comparisons, reference instruments, target gas, internal standard in calibrated gas (see above), audits, data workshops, central data evaluation and issue tracker. These actions developed and applied in the European ACTRIS are generally appreciated by the experts and it is recommended to follow most of them as feasible by the WCC-NOx.

• It was decided to include in the Measurement Guidelines some basic information for new stations on requirements and costs and thus support their decision to start in situ NOx measurements.

• The following elements are required to establish NOx measurements:

1. Perfluoroalkoxy alkanes (PFA) inlet line. It needs to be covered against light and boast a short residence time (few seconds)
2. CLD with pre-chamber (trace-level version) and BLC or PLC and pump
3. Gas phase titration unit with O3 and zero gas supply
4. Zero gas generator
5. Laboratory standard (certified), working standard, target gas
6. (automated) plumbing system
7. Data acquisition system
8. Quality Management System
9. Skilled personnel
10. Ozone measurements
11. Water vapour measurements

• Useful metadata were agreed as: integration time, high-voltage of PMT, chamber/instrument temperatures, calibration factors, and length and inner diameter of inlet line. While essential ancillary data are: PMT temperature, reaction cell pressure, ambient ozone concentration, ambient temperature and humidity as well as other meteorological data.

• There was a discussion about writing MG in a more practical way. It was agreed that the challenging part is to convince stations to measure NOx. Once they have started it is easier to improve their quality of measurements. Accordingly, the Guidelines structure should go from basic requirements and standard operation, to artefacts and corresponding precautions, and finally cover challenging conditions like pristine marine atmosphere.

6.3 List of actions

• MG to give specific recommendations on the following aspects: calibration gas cylinder storage, high (μmol/mol) versus low (nmol/mol) NO standards, dilution procedure of high mole fraction standards, regulators and valves and tubing material.

• MG to contain specific guidelines on the appropriate methods to use for calibration (either synthetic or standard-addition/spike).

• Add a schematic of the spiking of ambient air approach.

• The automated calibration section needs to be reviewed.

• Add an outlook section on new and emerging techniques to MG.

• The characterization of artefacts to be provided in the guidelines requires further discussion and more detailed description.
• Better characterization of the HONO interference in BLC/PLC methods to be described including a more conservative estimate of uncertainty resulting from this (Chris Reed, Franz Rohrer, Ian Galbally).

• MG to include a recommended approach for zero air production (purification systems), since purification systems vary across the many GAW stations.

• Recommend NO night-time correction and provide guidelines for the conditions on how it may be used (continental background to remote marine).

• Move to an informative annex the brief overview of existing integrating techniques (passive and active).

• Add to the expert report a list of experts to consult for specific measurement approaches for NO and NO₂.

• Give the guidelines for pristine conditions later than those for continental conditions (keeping things simple first).

• Add a ‘training’ category to the QA guidelines.

• Determine and specifically outline the critical parameters that need to be reported along with data and include in MG.

• The data completeness flag is to be removed and replaced with a column specifying the number of data points used to calculate each hourly average.

• Guidelines on uncertainty and precision to be tasked to the metrology community (NPL offered their assistance).

• MG to be restructured to be simple and conceptual, with problems and challenges later in the document. The language used should be simple, avoiding scientific jargon and giving clear instructions on how to setup measurements.

The NOx expert meeting decided in which steps the MG document should be finalized:

1. Revise sections (Dagmar Kubistin, Christian Plass-Dülmer, James Lee, Martin Steinbacher and Franz Rohrer):
   - Ian Galbally, James Lee and Franz Rohrer on “uncorrected” artefact description
   - Franz Rohrer, James Lee, Ian Galbally on correction functions
   - Ian Galbally and James Lee on measurements in pristine environments
   - Paul Brewer, Dave Worton, Dagmar Kubistin and Franz Rohrer on uncertainty and precision
   - Paul Brewer, Dave Worton, Martin Steinbacher, Chris Reed and Franz Rohrer on calibration and zero gas
   - Chris Reed, Ian Galbally and Franz Rohrer on photolysis artefacts in converters
   - Robert Holla, Dagmar Kubistin, and Franz Rohrer on data reporting, quality control procedures and flagging

2. Compilation and comments by NOx Expert Group (2 months period)

3. Compilation and distribution to external reviewers (these experts need to be identified) – review (2 months period)

4. Final version

Franz Rohrer (WCC) will take over the lead for finalization of the measurement guidelines.
7. SUMMARY OF PRESENTATIONS AT THE MEETING

The following section summarizes the presentations given during the meeting along with some of the discussions. Several extended abstracts can be found in Annex III.

Dagmar Kubistin - Measurements of NOx and NOy at Hohenpeissenberg

Dagmar Kubistin presented the results of NOx and NOy measurements at the Hohenpeissenberg GAW station, where continuous observations have been performed since 1996. At 985 m height on a hilltop, 300 m above surrounding area, composed 70% of meadows and 30% of forest, the station is representative of mid-European rural areas, with average population density and a few industrial areas. The main highlights were:

- The recent diesel exhaust developments showed the importance of observing NOx.
- Measurements of NOy are available (under-represented in GAW).
- NOx is observed in higher concentrations in winter than in summer.
- NOy was mostly composed of NOx in winter, and of NO2 in summer, the summertime peak in NOy has shifted towards spring.
- The diurnal, weekly and annual cycles of NOx were observed.
- There has been a slight reduction in European NOx, and a more clear decreasing trend in NO2 if wind directions are separated.

Detlev Helmig - NOx observations in Arctic

Detlev Helmig presented NOx observations in snow environments. He gave an overview of NOx measurements in polar and alpine regions, all measurements were done with 3 instruments, and 3-4 annual cycles were measured in the Arctic. The challenges of such measurements are the low NOx concentrations, NOx- plumes produced by local generators, the high cost of transport and maintenance (about 200 000$ for one year of monitoring in polar regions), the low temperatures (-30 to -60°C) and the need for qualified personnel. These factors explain why such few data from polar regions exist, and question how much we actually know of NOx in snow environments.

Chris Reed - NOx observations at Cape Verde

The GAW station at Cape Verde (the Cape Verde Atmospheric Observatory) provides since 2006 the only long-term measurements of NOx in the tropics under background conditions (amongst many other measurements of atmospheric composition). The station uses a custom-made CLD instrument and measures NOx near-continuously since October 2006 (Lee et al., 2009). The main issues encountered with the measurements concern the conversion of NO2 to NO using a BLC. Significant interference was encountered when the converter was mounted at the sample inlet on the roof of the laboratory. These were put down to thermal decomposition of species in the ambient sample or thermal desorption of NO from the sample lines. The BLC is now mounted inside the air conditioned laboratory and such interferences are no longer observed. Great care is taken to sample NO2 free air during the calibration process in order to properly assess any interference with the BLC. Interference in the NO channel is measured by assuming NO is zero at night and taking the night-time measurements as the NO 'artefact'. NOx measurements were carried out from 2006 until 2009, and since 2015 Cape Verde provides the first speciated NOy measurements (SPANs, SOrganic nitrates and HNO3). The time-series presented demonstrated the very low mixing-ratios of NOx (10-50 pptv) in that
environment which leads to net ozone destruction. For these low levels, QA/QC and especially the treatment of artefact signals is crucial. Zero air was found to be an issue, and converter efficiency impacted NO\textsubscript{2} measurements. The sample air and zero air were dried using Nafion.

**Mhairi Coyle - NO\textsubscript{x} observations at Auchencorth Moss, near Edinburgh, UK**

Mhairi Coyle presented NO\textsubscript{x} observations at Auchencorth, near Edinburgh, UK. Established in 1995, the site became an EMEP supersite in 2006 and a GAW regional site in 2014. NO\textsubscript{x} measurements are based on ANNO\textsubscript{x} for 2011-2013, a gradient system between 1995 and September 2015 and a single height instrument from October 2015 (standard chemiluminescence NO\textsubscript{x} analysers with molybdenum convertors – a blue light instrument T200UP). It was noted that the 10Hz target was ambitious because of residence times in the instrument and a faster instrument will have to be built.

**Aurélie Colomb - NO\textsubscript{x} measurements at Puy de Dome**

Aurélie Colomb presented NO\textsubscript{x} measurements at the Puy de Dome, France. At 1465 m in altitude the station provides observations since 1876, which are mostly from the boundary layer during daytime in spring-summer, and representative of the free troposphere during night-time and for the rest of the year. It became a GAW regional station in 2012 and a global one in 2014. It has been using a BLC since 2012 to measure NO\textsubscript{x}, it was formerly done with molybdenum (still prevalent in other remote French sites). The GAW station and measurements form part of ACTRIS, and other French network of NO\textsubscript{x} measurements were mentioned (TDA, SIRTA, REV, CO-PDD, PYE). Good agreement was found between Infrared spectroscopy and NO\textsubscript{x} measurements during the CHEMCALINT field campaign (May 2014). For PDD and other stations, Optimization and standardization needs to be done in a global (harmonized) way, devised by WCC.

**Francois Hendrick - MAX-DOAS observations of NO\textsubscript{2} in NDACC: status and perspectives**

Presentation summary is reflected in Section 2.4.

**Ian Galbally - Experiences of measuring NO\textsubscript{xy} at Cape Grim, Australia**

Ian Galbally shared the experience of NO\textsubscript{x} and NO\textsubscript{y} measurement at Cape Grim, Australia. The first successful measurements of NO and NO\textsubscript{2} were made on a campaign basis in 1996. From 2009 onwards, continuous monitoring with a CLD NO with BLC and Mo NO\textsubscript{y} converter has been used. A single point calibration via standard addition to the ambient sample air and convertor conversion efficiency by gas phase titration are performed twice a day. Signal processing provides answers to the analyser’s good functioning and gives NO, NO\textsubscript{2} and NO\textsubscript{y} measurements results and their uncertainties. The daytime mole fractions observed with the CSIRO built instrument in February 1995 were NO at 5 pmol/mol and NO\textsubscript{x} at 10 pmol/mol in background conditions increasing to NO at 70 pmol/mol in air passing over land (Carpenter et al. 1997; Monks et al. 1998; Galbally et al. 2000). The new system (AQD CLD) appears to give higher NO and NO\textsubscript{2} values than the levels measured at Cape Grim in 1995 and 1996 by both CSIRO and UK UEA systems. The current observations at Cape Grim give an ambient NO at night (2 pmol mol\textsuperscript{-1}) during winter that is consistent with the expected zero NO. During the 2015 summer fire season around Cape Grim however this level was elevated by about 15 pmol/mol due to untitrated NO. This indicates the necessity of protocols for when night-time NO is considered a proxy zero measurement. Zero air was noted to have significant increased
signals (40 to 200 pmol/mol) for NOxy when compared with ambient NO zero. A possible confounding issue is that zero air contained very low water vapour and ambient measurements are in humid air. Discussions highlighted the following issues:

- Data processing requires expertise and editing and it is time-consuming.
- The principles/algorithms utilized in the data processing need to be documented.
- NOx mole fractions of order of 10 pmol/mol occur in southern hemisphere marine boundary layer air.
- Measurement artefacts are a significant issue for NOx measurements in southern hemisphere marine boundary layer air.

Christian Ehlers - Twenty years of ambient observations of nitrogen oxides and specified hydrocarbons in air masses dominated by traffic emissions in Germany

Christian Ehlers presented the results of twenty years of observations of NOx and specified hydrocarbons in mostly urban air masses dominated by traffic emissions in Germany. These measurements used a mobile laboratory (attached to an automobile) for Volatile Organic Compounds (VOC) and a CLD system for NOx (and CO, CO₂). Measurements were taken in quite urban environments to investigate traffic emissions. Good agreement was found between observed and modelled CO although peak concentration could not be covered by 1 km model resolution. Diesel cars are the dominant source of NOx and petrol cars are of VOC. Following the spread of catalytic converter, a much stronger reduction of VOC was observed than of NOx. While O₃ production has significantly reduced in urban areas, NOx and VOC need to both be included in future reduction schemes as O₃ production can move to a different regime otherwise (Ehlers et al., 2016).

Robert Holla - Measuring NOx with multiple instruments – the more information, the bigger the uncertainty?

Four instruments for NOx (and NOy) were used at Hohenpeissenberg. These included a CLD with BLC measuring NO and NO₂, a CLD with Au-converter for NO and NOy, a CLD with PLC for NO and NO₂ and a Cavity Attenuated Phase Shift (CAPS) direct NO₂ measurement instrument. Merging these measurements all following similar QA/QC and applying a night-time zero correction showed overlapping uncertainty ranges for 80% of the data (2-σ) for the year 2014. Parts of the deviations cannot be explained by the estimated uncertainty range due to unaccounted artefacts in the measurement techniques. However, it should be noted that when the night-time correction of NO is not applied and the zero is determined from zero air generator measurement, in 44% of the time the highest and lowest NO measurements had no overlap in the uncertainty ranges.

At many stations, only one instrument is operated and the uncertainty budget cannot be tested which potentially results in an underestimation of the uncertainty. To deal with this, several measures of how to determine appropriately the instrument zero were discussed and shall lead to corresponding recommendations in the NOx measurement guidelines. The need for regular station audits and parallel measurements to a reference instrument was highlighted.
References


Di Carlo, P. et al., 2013: Aircraft based four-channel thermal dissociation laser induced fluorescence instrument for simultaneous measurements of NO2, total peroxy nitrate, total alkyl nitrate, and HNO3, Atmospheric Measurement Techniques, 6, 971–980.


LIST OF EXPERT MEETING PARTICIPANTS
Expert Meeting on Nitrogen Oxides
University of York, York, UK, 12-13 April 2016

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EXPERT MEETING AGENDA
Expert Meeting on Nitrogen Oxides
University of York, York, UK, 12-13 April 2016

Tuesday, 12 April

09:00 Welcome James Lee
09:05 Introduction and meeting objectives Christian Plass-Duelmer

Session 1 - Overview of the observational network and requirements Chair: Oksana Tarasova

09:20 Measurements of NOx and NOy at Hohenpeissenberg Dagmar Kubistin
09:35 NOx observations in Arctic Detlev Helmig
09:50 NOx observations at Cape Verde Chris Reed
10:05 NOx observations at Auchencorth Moss, near Edinburgh, UK Mhairi Coyle
10:20 NOx measurements at Puy de Dome Aurélie Colomb
11:00 MAX-DOAS observations of NO2 in NDACC: status and perspectives Francois Hendrick
11:15 Experiences of measuring NOxy at Cape Grim, Australia Ian Galbally
11:30 Twenty years of ambient observations of nitrogen oxides and specified hydrocarbons in air masses dominated by traffic emissions in Germany Christian Ehlers
11:45 Discussion (1) - Application for aircraft measurements: recommendations, current issues Lead: Stéphane Bauguite
13:30 Discussion (2) - Recommendations for the network development & Review of the Data Quality Objectives Lead: Christian Plass-Duelmer

Session 2 - Measurement techniques Chair: James Lee

14:10 Measuring NOx with multiple instruments – the more information, the bigger the uncertainty? Robert Holla
14:25 New direct NO2 measurements (e.g. CAPS, LIF, QCL) Martin Steinbacher and James Lee
14:40 AQD BLCs James Lee and Chris Reed
15:30 Use of the small sensors for NOx measurements Martin Steinbacher, Stefan Gilge and James Lee

16:00 Discussion (3) - NO measurements: What is the current state of the technology? Issues around instrument operation, especially for low level measurements. Different manufacturers – best recommended for remote or continental measurements. Lead: Chris Reed

16:30 Discussion (4) - NO2 measurements: Photolytic converters, what is the current state of the technology, what type should we be using, what are the interference issues? Lead: Chris Reed
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<tr>
<td>17:00</td>
<td><strong>Discussion (5)</strong> - Role of the small sensors in the GAW network</td>
<td>Lead: Martin Steinbacher, Stefan Gilge and James Lee</td>
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<td>17:30</td>
<td>Meeting adjourned</td>
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**Wednesday, 13 April**

**Session 3 - Gas standards and calibration**

- 09:00 Underpinning measurements of NOx & Status of the CCL for NO  
  Chair: Martin Steinbacher  
  Paul Brewer

- 09:15 **Discussion (6)** - Zero air generation – current state of the Technology  
  Lead: Paul Brewer

**Session 4 - Quality Assurance**

- 09:35 Status of the MG NOx  
  Chair: Martin Steinbacher  
  Christian Plass-Duelmer and Stefan Gilge

- 09:55 Update on the activities of the WCC-NOx  
  Franz Roher and Christian Ehlers

- 10:10 **Discussion (7)** - NOx measurements guidelines: follow-up  
  Lead: Christian Plass-Duelmer and Stefan Gilge

- 11:00 **Finalization of the action list**  
  Lead: Alastair Lewis

- 11:30 Final remarks and meeting closure
EXTENDED ABSTRACTS

MEASURING NOX WITH MULTIPLE INSTRUMENTS – THE MORE INFORMATION, THE BIGGER THE UNCERTAINTY?

Robert Holla¹, Dagmar Kubistin¹, Christian Plass-Dülmer¹, Stefan Gilge¹,²

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² German Meteorological Service, Zentrum für Medizin-Meteorologische Forschung Freiburg, Germany

1. Long-term measurements of NOx and NOy at Meteorological Observatory Hohenpeissenberg (MOHp)

Continuous measurements of oxidised nitrogens are performed at the GAW station MOHp using three different measurement methods:

Three Ecophysics chemiluminescence detectors (CLDs) are used to monitor NOx and NOy. The three CLDs are equipped with different types of converters. The first of the two CLDs for the measurement of NO and NO₂ (CLD1) uses a so called “blue light converter (BLC)” with a blue LED as light source, the second one (CLD3) is equipped with a photolytic converter (PLC) using a Xenon gas emission lamp as light source for photolysis and the third one (CLD2) thermally decomposes NOy to NO by a self-built gold converter heated to 300° C.

NO₂ is measured additionally by two optical techniques: a CAPS (cavity attenuated phase shift spectrometer) yields additional independent in-situ time series of NO₂, whereas a MAX-DOAS (Multi-Axis Differential Optical Absorption Spectroscopy) device provides information on the vertical distribution of NO₂ by remote sensing of scattered sun light.

2. Discrepancies between different chemiluminescence instruments

For all three CLD instruments the calibration and zero gas procedure is conducted in the same way, as well as the determination of the converter efficiencies via gas phase titration (GPT), following the same time schedules.

However in the past we often recognized episodes where the error ranges of the individual chemiluminescence monitors did not overlap. This can be observed especially for NO as the calculated errors are several times smaller than those for NO₂.

*Figure 1- Example NO diurnal variation measured by the three CLDs. NO values were corrected for quenching of the chemiluminescence signal by water vapour and for the reaction of O₃ with NO inside of the inlet line according to the ACTRIS measurement guidelines*. The shaded areas indicate the ±1.96 sigma uncertainty ranges.
Figure 1 shows an example of a diurnal variation of NO, where the differences between the three CLDs are obvious. Especially CLD3 shows a large offset, even at night, when NO should be zero due to missing photolysis of NO$_2$. These discrepancies were observed although weekly zero gas measurements are taken into account. A possible reason for this might be interferences occurring while measuring ambient air caused by species which are not present in the zero gas.

\[
\Delta [NO] \quad (1.96 \, \text{sigma})
\]

\[
NO_{\text{diff}} = \max(\text{NO CLD1}, \text{NO CLD2}, \text{NO CLD3}) - \min(\text{NO CLD1}, \text{NO CLD2}, \text{NO CLD3})
\]

Figure 2 - Upper panel: Histograms of calculated 1.96 sigma uncertainties of NO for the individual chemiluminescence detectors (red, green and blue) compared to the observed maximum differences (NO$_{\text{diff}}$) between the individual instruments (cyan). The histograms contain data of the whole year 2014. Lower panel: After subtracting an offset, determined from night time NO where ozone is above 20 ppb, the calculated 1.96 sigma uncertainties and the observed maximum differences (NO$_{\text{diff}}$) are much better aligned. Embedded panel: Example diurnal variation of NO after subtracting the night-time offset of NO (cf. Fig. 1).
Following the recommendation by the World Calibration Center for NOx (Franz Rohrer, Research Center Jülich) a night-time offset of NO was determined for each day from the average NO between 00:00 and 02:00 UTC. A running mean with a width of 24 hours was used to close the gaps in between the night-time values. Once determined, the night-time offset of NO was subtracted from the original corrected NO mixing ratios. In general this procedure leads to a better agreement of the observed differences and 1.96 sigma uncertainties calculated from error propagation described below in Section 3 (cf. Fig. 2). However, the night-time corrected NO mixing ratios must be manually inspected afterwards, as in single cases fast changes of ozone or the offset itself may lead to negative NO mixing ratios. Unfortunately, for NO\textsubscript{2} this kind of correction is not possible, as NO\textsubscript{2} mixing ratios are not necessarily supposed to be zero at night.

### 3. Error propagation for chemiluminescence detectors compared to observed discrepancies

According to eq. i. the mixing ratio of NO $\text{[NO]}$ measured by a chemiluminescence detector is calculated from the difference of counts measured in main-chamber-mode $\text{Counts}\textsubscript{MC}$ and pre-chamber-mode $\text{Counts}\textsubscript{PC}$. The calibration factor or span factor $\text{spanF}$ is calculated from the signal measured with a nominal mixing ratio $\text{[NO]}\textsubscript{calib}$ generated by dilution of a standard cylinder gas (eq. ii.).

$$\text{[NO]} = \frac{\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC}}{\text{spanF}} \quad \text{(eq. i.)}$$

$$\text{spanF} = \frac{\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC}}{\text{[NO]}\textsubscript{calib}} \quad \text{(eq. ii.)}$$

Applying linear error propagation yields the error margin $\Delta[\text{NO}]$:

$$\Delta[\text{NO}] = \Delta(\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC}) \cdot \frac{1}{\text{spanF}} + \Delta\text{spanF} \cdot \frac{[\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC}]}{[\text{spanF}]^2} \quad \text{(eq. iii.)}$$

$\Delta(\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC})$ is given by

$$\Delta(\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC}) = \sqrt{\text{Counts}\textsubscript{MC}^2 + \text{Counts}\textsubscript{PC}^2} \quad \text{(eq. iv.)}$$

The error of spanF was determined in two different ways (cf. Fig. 3):

1) $\Delta\text{spanF}$ was assumed to be as large as the half difference between span factors of two consecutive measurements.

2) The standard deviation of $\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC}$ during the last span factor measurement was used for $\Delta\text{spanF}$.

Both methods yielded similar errors for NO and NO\textsubscript{2}.

In future, also the uncertainty of the standard gas cylinders $\Delta[\text{NO}]\textsubscript{calib}$ will be taken into account according to eq. v.:

$$\Delta\text{spanF} = \Delta(\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC}) \cdot \frac{1}{[\text{NO}]\textsubscript{calib}} + \Delta[\text{NO}]\textsubscript{calib} \cdot \frac{[\text{Counts}\textsubscript{MC} - \text{Counts}\textsubscript{PC}]}{[\text{NO}]\textsubscript{calib}^2} \quad \text{(eq. v.)}$$
The mixing ratio of NO₂ \([NO_2]\) is calculated according to:

\[
[NO_2] = \left( \frac{(Counts_{MC} - Counts_{PC})_{converted}}{spanF} - \frac{(Counts_{MC} - Counts_{PC})}{spanF} \right) \cdot \frac{1}{ConEff} \quad \text{(eq. vi.)}
\]

So, for NO₂ also the error of the converter efficiency \(\Delta ConEff\) needs to be taken into account. From the course of the measured converter efficiencies during 2014 it was assumed to be around 1%.

\[
\Delta [NO_2] = 2 \cdot \Delta (Counts_{MC} - Counts_{PC}) \cdot \frac{1}{spanF \cdot ConEff} \quad \text{(eq. vii.)}
\]

\[
+ \Delta spanF \cdot \frac{(Counts_{MC} - Counts_{PC})_{converted} - (Counts_{MC} - Counts_{PC})}{ConEff \cdot spanF^2} \quad \text{...}
\]

\[
+ \Delta ConEff \cdot \frac{(Counts_{MC} - Counts_{PC})_{converted} - (Counts_{MC} - Counts_{PC})}{ConEff^2 \cdot spanF} \quad \text{...}
\]

The resulting uncertainties for NO₂ are in good agreement with the observed maximum differences between the two CLDs measuring NO₂ (cf. Fig. 4).
Figure 4 - Histograms of calculated 1.96 sigma uncertainties of NO$_2$ for the individual chemiluminescence detectors (red, green and blue) compared to the observed maximum differences (NO$_{\text{diff}}$) between the individual instruments. The histograms contain data of the whole year 2014.

References

a. WP4- NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides Deliverable D4.2: Draft for standardized operating procedures (SOPs) for NOxy measurements
NOX AND NOY MEASUREMENTS AT HOHENPEISSENBERG, GERMANY

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1. Motivation

Long-term observations of nitrogen oxides in the troposphere are crucial for understanding the tropospheric ozone trends, the atmospheric self-cleaning capacity as well as having an independent measure on anthropogenic emission regulations, recently highlighted by the diesel exhaust scandal. However, the global coverage of GAW stations measuring NOₓ (NO + NO₂) and total reactive nitrogen NOᵧ is sparse demanding an extension of the global network worldwide.

![Figure 1 - Data availability in GAW from 07/04/2016. The red symbols denote that the data from the station has been updated in the last 365 days. Taken from the World Data Centre for Greenhouse Gases, http://ds.data.jma.go.jp/gmd/wdcgg/cgi-bin/wdcgg/map_search.cgi](image)

2. Observations at Hohenpeissenberg

Since 1996, continuous observations have been performed at the GAW station Hohenpeissenberg (47.8 N, 11.02 E, 985 m asl). The station is currently equipped with three chemiluminescence detectors (CLD) for NO measurements, one blue light converter (BLC), one photolytic converter (PLC), one CAPS (cavity attenuated phase shift spectrometer) for NO₂, one self-built gold converter for NOᵧ and one gas chromatograph (GC) for PAN (peroxyacetyl nitrate). The preliminary time series from 1997 till 2014 are presented in Fig. 2. PAN is shown for 2003 till 2009 only due to remaining finalization of the data. Strong seasonal cycles are observed for all nitrogen oxides species as well as for ozone (O₃). Whilst higher concentrations of NOₓ are observed in winter, ozone shows a maximum in spring/summer (Fig. 3). PAN, being photochemically formed via RO₂+NO₂, shows a similar behaviour as ozone, indicating photochemical production of both species in the warmer months. However, the maximum of the higher oxidised NOₓ species (NOₓ =NOᵧ - NOₓ = HNO₃ + HONO + N₂O₅ + NO₃ + PAN + higher nitrates) is shifted towards early spring with lowest values in winter.
The enhanced photochemical activity in spring/summer is also reflected by the larger fraction of NO\textsubscript{2} on the total NO\textsubscript{y} in these seasons (Fig. 4). The maximum of PAN is shifted towards summer, indicating a lower proportion of HNO\textsubscript{3} to NO\textsubscript{y}. Besides photochemical production, HNO\textsubscript{3} is strongly impacted by dry and wet deposition, most likely being enhanced in the more humid summer months. In contrast the primary emitted NO\textsubscript{x} by vehicles and combustion processes is the major contributor to NO\textsubscript{y} in winter months due to the slow photochemistry. Distinct diurnal cycles are observed for both winter and summer (Fig. 5). During the cold months, the Hohenpeissenberg observatory is generally situated above the nocturnal boundary layer which slowly rises during the day. Polluted air from the lower situated village is transported upwards causing a maximum in the late afternoon. In summer, the boundary layer rises earlier and leads to local maxima in the morning and late afternoon. Lower NO\textsubscript{x} during noon is a combination of dynamics and faster photochemistry, latter also corresponding to higher values for NO\textsubscript{2} at midday. PAN peaks at summer noon, contributing about 1/3 to total NO\textsubscript{y}.

Figure 5 - Diurnal cycle for winter (DJF) (dashed lines) and summer (JJA) (solid lines). Mixing ratios in ppb.
3. Impact on the oxidation capacity

NO\textsubscript{x} controls effectively the abundance of OH, the major cleaning agent during daytime. It determines the lifetime of many atmospheric pollutants on a global and local scale. Continuous observation of OH at the Hohenpeissenberg observatory shows a distinct maximum concentration for 1 to 2 ppb NO\textsubscript{x}. Being within the most common observed concentration range at the observatory, the self-cleaning capacity is in its optimum for this station, which on a larger scale is representative for many areas in central Europe.

![Figure 6 - OH, normalized to J(O\textsuperscript{1 D}) and NO\textsubscript{x} observations at Hohenpeissenberg. The OH maximum is centred around 1 to 2 ppb NO\textsubscript{x} being typical concentrations for this station.](image)

Acknowledgments

The authors are grateful to the Hohenpeissenberg team for their great support and for maintaining the instrumentation.
MAX-DOAS OBSERVATIONS OF NO₂ IN NDACC: STATUS AND PERSPECTIVES

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1. Introduction

The Network for the Detection of Atmospheric Composition Change (NDACC) is an international research network of remote sounding stations contributing to the World Meteorological Organization (WMO) GAW (Global Atmosphere Watch) programme and working under the auspices of United Nations Environment Programme (UNEP) and the International Ozone Commission (IO3C). It officially started operations in 1991 and at present time it includes ~90 sites distributed worldwide. The main objectives of NDACC are (1) observing and understanding the physical/chemical state of the stratosphere and troposphere, (2) assessing the impact of stratospheric changes on the underlying troposphere and on global climate, and (3) playing a key role in ground truthing of satellite and model data.

Like Dobson/Brewer, FTIR, LIDAR, microwave, and sondes, ground-based UV-visible Differential Optical Absorption Spectroscopy (DOAS) is part of the official NDACC remote sensing techniques. By exploiting the increase of the slant light paths in the stratosphere at twilight, stratospheric ozone and related trace gases such as nitrogen dioxide (NO₂), bromine monoxide (BrO), and chlorine dioxide (OClO) have been monitored for more than two decades using zenith scattered sunlight DOAS observations at about 30 stations. Since early 2000’s, a new technique called Multi-Axis DOAS (MAX-DOAS) has been developed for detecting absorbers present in the lowest few kilometres of the troposphere like NO₂, formaldehyde (HCHO), sulphur dioxide (SO₂), nitrous acid (HONO), glyoxal (CHOCHO), BrO, as well as aerosols. During the recent years, NDACC stations equipped with MAX-DOAS instruments are growing in number and the operational generation of quality-assessed tropospheric data products is being developed for progressive implementation in NDACC. This task is performed under the responsibility of the NDACC UV-vis Working Group (WG).

Here, we give an overview on the current status and perspectives of MAX-DOAS observations of tropospheric NO₂ in NDACC. Further details and results can be found in the corresponding presentation.

2. MAX-DOAS technique

2.1 Principles

MAX-DOAS is a passive DOAS technique consisting of measuring scattered sunlight radiance spectra at zenith and at different elevation angles towards the horizon (the so-called off-axis geometry; see Figure 1), increasing therefore the sensitivity to absorbers present close to the ground. The main principles of the DOAS method is extensively described in Platt and Stutz (2008) (see also Hönninger et al., 2004). In brief, it involves the following steps: (1) separation of the trace gas fine-scale absorption features from broad-band absorption due to
Rayleigh and Mie scattering and instrumental effects, (2) analysis of the remaining absorber narrow-band structures by least-squares spectral fitting on laboratory cross-sections; this step provides the so-called differential slant column densities (DSCDs) which are defined as the difference between the trace-gas concentration integrated along the effective light path and the amount of absorber in a measured reference spectrum, and (3) conversion of the DSCDs into vertical column densities (VCDs) and/or vertical profiles using appropriate radiative transfer calculations and profile inversion schemes (see e.g. Vlemmix et al., 2015). It should be noted that DOAS is recognized as a “self-calibrating” technique because differential absorptions are measured and therefore the impact of possible instrumental degradations can be largely removed by using appropriate reference spectra. For tropospheric studies, the zenith spectrum of the scan is frequently chosen as reference, in this way also removing the contribution of the stratosphere in off-axis DSCDs, which can be significant for a species like NO\textsubscript{2}.

![Figure 1](image.png)

**Figure 1 - Sketch illustrating the MAX-DOAS viewing geometries (off-axis and zenith). Typical elevation angle values used during a scan are given in the grey frame.**

### 2.2 Spatial representativeness

As for all remote sensing techniques, MAX-DOAS observations average over space and time providing integrated values representative over a certain volume (Richter et al., 2013). The vertical and horizontal extents of this volume depend strongly on the wavelength, viewing geometry (elevation and relative azimuth angles, solar zenith angle), and sky conditions (presence or not of clouds and/or aerosols). This effect is illustrated in Figure 2 where the effective horizontal light path length \( L_{\text{eff}} \) at 360, 450, and 560 nm is estimated from 2D-MAX-DOAS observations of the oxygen dimer \( \text{O}_4 \) performed by the University of Colorado in Mainz (Germany) during the MAD-CAT intercomparison campaign (http://joseba.mpch-mainz.mpg.de/mad_cat.htm).
Figure 2 - Azimuthal diurnal variation of the effective light path length $L_{\text{eff}}$ at 360, 450, and 560 nm estimated from 2D-MAX-DOAS observations of O$_3$ performed by the University of Colorado at Max-Planck Institute for Chemistry in Mainz on 17 June 2013 (cloud-free day). The corresponding NO$_2$ near-surface concentration appear in the lower plots (adapted from Ortega et al., 2015).

$L_{\text{eff}}$ is comprised between 5 and 10 km, 10 and 20 km, and 18 and 30 km at 360, 450, and 560 nm, respectively. Given the pixel size of the current and future satellite nadir air quality instruments like OMI (13x24 km$^2$) and TROPOMI (3.5x7 km$^2$), these horizontal path length values indicate that MAX-DOAS and satellite nadir measurements are sensitive to similar spatial domain. Therefore, MAX-DOAS is particularly suitable for validating satellite data and also for investigating NO$_2$ spatial inhomogeneities within a satellite pixel.

2.3 Error budget

The error budget associated with MAX-DOAS NO$_2$ VCD and near-surface concentration has been assessed in several studies (e.g. Vlemmix et al., 2010; Hendrick et al., 2014; Ortega et al., 2014). Uncertainty sources taken into account are those related to the DOAS spectral fit and to the conversion of DSCDs into VCDs and/or vertical profiles including the aerosol content retrieval which is needed prior to the trace gas retrieval (Friess et al., 2006). Total uncertainty ranges typically from 10-20% for VCDs and 10-30% for the near-surface concentration in clear-sky and thin clouds conditions. Larger values can be obtained in the presence of optically thick clouds and/or high aerosol loads since both are known to affect more strongly the quality of the MAX-DOAS retrievals (Wagner et al., 2014; Gielen et al., 2014).

3. MAX-DOAS Network

3.1 Current status

The geographical distribution of the (MAX-)DOAS network is depicted in Figure 3. About 50 MAX-DOAS instruments are currently deployed worldwide in addition to ~20 zenith-sky DOAS instruments.
So far, only the zenith spectrometers are officially part of NDACC. The main reason is that MAX-DOAS systems and algorithms are still under development, generally operated at scientific level by expert scientists. However, significant harmonization efforts regarding retrieval methods and settings, error and spatial representativeness characterization, data format (adoption of the GEOMS hdf format; see http://avdc.gsfc.nasa.gov/index.php?site=1876901039) have been carried out within the framework of the EU FP7 project NORS (2011-2014; http://nors.aeronomie.be) and are continuing within the EU FP7 project QA4ECV. One of the objectives of the latter is to generate harmonized and quality-assessed NO\(_2\) (and HCHO) MAX-DOAS data files at a selection of 12 sites for satellite validation purpose (see http://www.qa4ecv.eu/sites/default/files/QA4ECV_D3.8_v1.0_web.pdf). These data files will be made available on the NDACC database by end of 2016.

3.2 Applications of MAX-DOAS NO\(_2\) observations

Because they have similar spatial domain (see Section 2.2), MAX-DOAS is widely used to validate satellite nadir observations of pollutants like NO\(_2\), HCHO, and SO\(_2\). For instance, in the case of the GOME-2 instruments on board of the METOP-A and B platforms, the validation of trace gas operational products is done in the framework of the EUTMETSAT O3MSAF trace gases Validation and Quality Assessment Working Group (http://cdop.aeronomie.be/, see also Valks et al., 2011; Hassinen et al., 2016). Figure 4 shows the most recent validation results of GOME-2A tropospheric NO\(_2\) vertical columns (DLR/GDP4.8 operational product) at a selection of MAX-DOAS sites. As can be seen, the level of agreement strongly depends on the location of the station, with generally smaller satellite columns than ground-based MAX-DOAS. A better agreement is found at remote and suburban than at urban sites. A possible reason is that in urban conditions, the local pollution sources captured by the MAX-DOAS instruments are not adequately sampled at the coarser resolution of the satellite pixel.

Due to the harmonization efforts and progress towards a NRT delivery (MAX-DOAS NO\(_2\) data files are generated at some stations with a 24h latency) made during the EU FP7 project NORS, MAX-DOAS is now used as reference for the NRT and off-line validation of tropospheric NO\(_2\) vertical profiles and columns from the EU Copernicus Atmospheric Monitoring Service (CAMS) global and regional models (e. g. Inness et al., 2013). An example of NRT validation report
generated by the NORS validation server for the Xianghe station (Beijing suburban area) can be found at http://nors-server.aeronomie.be/report/?instrument_type=UVVIS.DOAS.OFFAXIS. One of the main advantages of the MAX-DOAS technique is that several trace gas species as well as aerosols can be simultaneously monitored on a long-term basis by the same instrument. This is illustrated in Hendrick et al. (2014) where HONO, NO$_2$, and aerosols vertical profiles and integrated columns have been measured in the Beijing area between June 2009 and December 2012. These multi-year data sets have allowed a better quantitative characterization of the HONO potential sources and sinks in high NO$_x$ conditions and provided additional constraints to modelling studies.

Figure 4 - Validation results (scatter plots) of the GOME2A DLR/GDP4.8 tropospheric NO$_2$ column operational product at a selection of MAX-DOAS stations (Left: suburban/remote sites; right: urban sites).

4. Conclusions and perspectives

MAX-DOAS instruments are currently monitoring tropospheric NO$_2$ year-round at about 50 sites worldwide, representative of urban, suburban, and remote conditions. This technique provides vertical column density as primary quantity but at most of the stations, information on the vertical distribution, especially the near-surface concentration, are also retrieved. This makes MAX-DOAS particularly suitable for the validation of satellite nadir observations of pollutants like NO$_2$ and for the assessment of 3D Chemistry Transport Models. The combination of vertical column density and surface concentration could be also potentially used to make the link between in-situ air quality networks and satellite observations. Further investigations are needed on this issue, requiring the simultaneous operation of in-situ and MAX-DOAS instruments at a selection of GAW/NO$_x$ reference sites.

In the last four years, significant efforts towards a harmonized and quality-assessed MAX-DOAS network have been carried out by the NDACC UV-vis WG within the framework of the EU FP7 projects NORS and QA4ECV. It will continue in the next couple of years with the ESA project FRM$_4$DOAS (Fiducial Reference Measurements for Ground-Based DOAS Air Quality Observations). The overall objective of this project is to develop a centralised operational system providing harmonised ground-based reference data from a network of MAXDOAS instruments within a short latency period (6-24h). FRM$_4$DOAS will support the NRT validation of satellite data products to be generated as part of the Copernicus Sentinel programme.
References


FIRST EXPERIENCES WITH ELECTROCHEMICAL GAS SENSORS

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1. Motivation

The Air quality department at DWD, RCHB mainly deals with air quality measurements and joined expert reports for health resorts in Germany. Since the respective measurement sites often have no electrical power nor internet access, and the so far used passive sampler techniques for ambient air quality measurements have limited temporal resolution, the below describe new electrochemical sensors sound promising.

2. Instrument description

- **AQMesh®**: developed and manufactured by Environmental Instruments Ltd (UK)
- electrochemical sensors (NO, NO₂, O₃, CO, SO₂ by diffusion)
- metering time period: 15 min, detection limit and accuracy at low ppb level
- range of operation: T: -30 to 40 °C; P: 800 to 1200 hPa; RH: 15 to 85 %
- tested & calibrated at manufacturer
- small, lightweight, battery driven, cloud based data server, connection via mobile network, some 10k€ per unit
- operating costs: some 2.5 k€/y

3. Test at urban site, provided by manufacturer

![Figure 1: Time series of NO data at an urban site in Barcelona in March 2015. Blue AQMesh, black: reference instrument. Chart provided by manufacturer.](image-url)
The accordance between AQMesh sensor and reference instrument in the mixing ratio range from LDL to some 140 ppb looks very promising.

4. Tests at GAW sites Schauinsland (SSL) and Hohenpeissenberg (HPB)

Tests at Schauinsland and Hohenpeissenberg showed sometimes similar behaviour, sometimes huge differences between AQMesh and reference instruments. The tests were very demanding since the mixing ratios especially for nitrous oxide are mainly below the given LDL of the AQMesh instrument. However, the two pods show very similar results.

![Figure 2. Time series of NO data at SSL site. Black: reference instrument, red and blue the two AQMesh pods, respectively, green dotted line: LDL of AQMesh given by the manufacturer.](image1)

![Figure 3. Time series of NO2 data at HPB site. Black: reference instrument, red and blue the two AQMesh pods, respectively.](image2)

5. Test at urban road site at Freiburg (Schwarzwaldstrasse)

Currently the two AQMesh pods are tested at the road site “Schwarzwaldstrasse”. Reference measurement data, performed by the “Landesamt für Umwelt, Messungen und Naturschutz Baden-Württemberg (LUBW)” aren’t available up to now. However, data of the two pods show, in contrast to the experiences at SSL and HPB, larger differences between each other.

6. Conclusion

- small, lightweight, not too expensive, needs no power socket, ....
- tests provided by manufacturer / distributor look very convincing
- too high LDL for remote and probably most rural sites in GAW (for NO and NO2)
manufacturer calibration not sufficient (depending on location ?)
good agreement between the two Pods at SSL & HPB, however not at Freiburg, “Schwarzwaldstrasse” (?)
sometimes good relative signal, sometimes not. Reasons ????
better results for O₃ und CO, however, no good results
lifetime of sensors should be about 24 month, at least 12 month. NO sensors have been changed twice up to now (6 month). – faulty batch ?
=> lot of work has to be done before instrument is usable for routine applications

Acknowledgments

The author is grateful to Envilyse, the German provider of AQMesh instruments, for lending two AQMesh instruments without any costs for extensive testing.
UNDERPINNING MEASUREMENTS OF NOX: STATUS OF THE CCL FOR NO

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The National Physical Laboratory (NPL) has a world class capability for the provision of static and dynamic reference standards of nitrogen monoxide and nitrogen dioxide. Since the formation of the Consultative Committee for Amount of Substance (CCQM) Gas Analysis Working Group (GAWG), NPL has demonstrated equivalence with leading National Metrology Institutes (NMIs) in international comparisons for 100 and 1000 µmol/mol NO in nitrogen (CCQM K1c) and 10 µmol/mol NO₂ in nitrogen (CCQM K74). NPL has also coordinated a key comparison in 2004 (CCQM K26a) involving 700 nmol/mol NO in nitrogen and a EURAMET comparison in 2013 (EURAMET 1183) involving 450 nmol/mol. In the latter, NPL used a state of the art dilution facility to generate dynamic reference standards of NO in nitrogen at 450 nmol/mol from a 10 µmol/mol primary reference gas mixture of NO in nitrogen. The dynamic facility was used to certify a suite of travelling NO in nitrogen standards. The travelling standards were certified before and after distribution to participants and over a period of more than a year. These measurements were used to provide the reference values and to determine accurate drift rates so that any change in the amount fraction during the distribution period could be corrected. The comparison included the Hohenpeissenberg Meteorological Observatory, DWD, Germany. As a result of NPL’s performance in these comparisons, the following Calibration and Measurement Capabilities (CMCs) published on the BIPM Key Comparison Data Base (KCDB) have been obtained:

- NO in nitrogen from 100 nmol/mol to 10 mmol/mol with relative expanded uncertainties from 0.6 to 0.1% respectively.
- NO₂ in nitrogen or air from 1 to 1000 µmol/mol with relative expanded uncertainties from 3.0 to 0.2%.

These are for providing static reference mixtures in cylinders and calibrated reference mixtures by comparison to NPL primary reference standards.

As stated in GAW Report 195, result of extended trials at several NMIs suggest that, mixtures of NO in nitrogen at amount fractions between 10 mmol/mol and 100 µmol/mol are stable over periods of many years when prepared using appropriate techniques. Figure 1 shows stability data for an NPL PRGM of NO in nitrogen prepared at 500 nmol/mol. The mixture was certified four times after preparation. A 10 µmol/mol NPL PRGM of NO in nitrogen was blended with high purity nitrogen (Air Products BIP) using the Molbloc dilution facility at NPL (Figure 2) to generate the dynamic reference standards for certification. The gravimetric amount fraction is shown with the dotted line. A first-order curve was fitted to the data using a generalised least squares method. This provides a degradation rate of $0.018 \pm 0.013 \text{ nmol mol}^{-1} \text{ day}^{-1}$ and represents a 0.013 % loss for a 50 µmol/mol mixture in a year.
Figure 1 - Stability measurements of an NPL NO in nitrogen PRGM with a nominal amount fraction of 500 nmol/mol, using a chemiluminescence analyser and the NPL Molbloc facility to generate the reference standard.

Experiments have been performed to validate the Molbloc facility. An example involves diluting three different PRGMs of NO in nitrogen (with amount fractions of 9.95, 9.90 and 10.14 µmol/mol) using the Molbloc facility. The flow rates of the PRGM and the balance gas were the same in all experiments. The mixture in each case was used to certify a 495 nmol/mol PRGM.
of NO in nitrogen. A chemiluminescence analyser (Eco Physics CLD 66) was used as a comparator and the mean difference between the analytical and gravimetric values for each experiment is shown in Figure 3. The bars represent one standard deviation of the data. The mean amount fractions are shown to agree with the gravimetric amount fraction to better than 0.5%. These data further supports the accuracy claims of the dilution system (1 %) and provide further evidence for the accuracy of the static standards.

Figure 3 - The certified amount fraction of an NPL PRGM of NO in nitrogen mixture, using the dilution system with three different NPL PRGMs of NO in nitrogen with amount fractions of 9.95, 9.90 and 10.14 µmol/mol (shown as 1, 2 and 3, respectively).

Further evidence to support NPL’s capability is the results from international comparisons. Figure 4 shows results from three comparisons coordinated by NPL (CCQM-K26a, EUARMET 1084 and EURAMET 1183) involving NO at 700, 200 and 450 nmol/mol respectively. These comparisons were underpinned by NPL’s capability to provide static and dynamic reference standards of NO in nitrogen.
In March 2016, NPL was appointed as the Central Calibration Laboratory (CCL) for NOx in accordance with the terms of reference set out in the memorandum of understanding between NPL and the WMO GAW programme. This establishes provision of stable and accurate primary standards for nitrogen monoxide or equivalent transfer standards, to the WMO/GAW Programme. This standard will be used as primary standard for the assessment of global ambient levels of NOx. As CCL, NPL will support a stable and accurate gas standard for nitrogen monoxide that defines the scale and maintain the infrastructure for dissemination. Reference standards will be prepared initially at a nominal amount fraction of 50 µmol/mol. These gas mixtures will be prepared in aluminium gas cylinders of 10 litre internal volume with the internal surfaces treated with a proprietary process called “Spectraseal” applied by BOC. These will then be made available to the WMO/GAW-VOCC WCC. Static gas standards at other amount fractions and for NO2, as requested by the WMO/GAW, will be researched for stability feasibility and developed based on the research results.
TWENTY YEARS OF AMBIENT OBSERVATIONS OF NITROGEN OXIDES AND SPECIFIED HYDROCARBONS IN AIR MASSES DOMINATED BY TRAFFIC EMISSIONS IN GERMANY

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During the past 20 years the number of violations of ozone alarm threshold values decreased to nearly zero in Germany. This air quality improvement was achieved through the reduction of traffic related emissions in urban areas. We analyse ambient observations of nitrogen oxide and hydrocarbon (VOC) concentrations since the early Nineties.

Diesel vehicles can be identified as the dominating source of nitrogen oxide emissions. Detailed hydrocarbon composition measurements identify temporarily reduced catalyst efficiency of petrol cars as the major source of VOC emissions in urban areas.

Taking the reactivity of the individual hydrocarbons with the OH radical into account, the total VOC reactivity \( R_{\text{VOC}} = \sum (k_{\text{OH}+\text{VOC}_i}[\text{VOC}_i]) \) can be calculated from the measured VOC concentrations. Taking also into account the reactivity of nitrogen dioxide with the OH radical \( R_{\text{NO}_2} \) the ratio of \( R_{\text{VOC}}/R_{\text{NO}_2} \) can be used to describe the local ozone production instead of considering the full details of the hydrocarbon mixture.

While traffic related VOC emissions have been significantly reduced in line with emission inventories, the inventory reports approximately constant VOC emissions from solvent use, being the dominating source of VOC in Germany. This is in contrast to our observations in cities where solvent use seems to be a minor VOC source.

Our observations show a decrease in the \( R_{\text{VOC}}/R_{\text{NO}_2} \) ratio by a factor 7.5 during the period from 1994 to 2014. The analysis revealed that the reduction of the local ozone production rate was mainly caused by a large VOC reduction combined with a small \( \text{NO}_x \) reduction at the same time.

Further details have been published: Faraday Discussions, 2016, DOI: 10.1039/C5FD00180C
LIST OF RECENT GAW REPORTS*


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