

GAW Report No. 195

WMO/GAW Expert Workshop on Global
Long-term Measurements of Nitrogen Oxides and
Recommendations for GAW Nitrogen Oxides Network

(Hohenpeissenberg, Germany, 8-9 October 2009)

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WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH



No. 195

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(Hohenpeissenberg Meteorological Observatory, Germany, 8-9 October 2009)

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Table of Contents

FOREWORD.....	i
1. BACKGROUND TO THE MEASUREMENT OF OXIDISED NITROGEN COMPOUNDS WITHIN GAW	1
1.1 Atmospheric chemistry of nitrogen oxides and their relevance for the GAW Programme	1
1.2 Scientific and policy reasons for NO _x measurement	4
1.3 Implementation procedure	5
1.4 Potential products and services	6
2. ESSENTIAL COMPONENTS OF A GAW GLOBAL NO_x OBSERVATIONAL NETWORK.....	6
2.1 Criteria for the GAW NO _x network design	6
2.1.1 Geographic considerations	6
2.1.2 Use of existing programmes and infrastructure	8
2.2 Monitoring platforms.....	9
2.2.1 Continuous measurements at surface stations	9
2.2.2 Mobile Platforms	9
2.2.3 Remote sensing	10
2.3 Measurement techniques and measurement guidelines.....	10
2.3.1 Recommendations for measurement of NO by ozone induced chemiluminescence detection (O ₃ -CLD)	11
2.3.2 Recommendations for measurement of NO ₂ by photolytic conversion of NO ₂ to NO followed by chemiluminescence detection (PLC-O ₃ -CLD).....	12
2.4 Outlook, future measurement techniques for NO and NO ₂	13
3. QUALITY ASSURANCE.....	14
3.1 Data Quality Objectives (DQOs) for NO _x measurements.....	14
3.2 Role of the Central Calibration Laboratory (CCL)	16
3.2.1 Scope of the CCL.....	16
3.2.2 Structure of the CCL	16
3.2.3 Preparation, value assignment and stability of primary standards for NO	16
3.2.4 Preparation, value assignment and stability of primary standards for NO ₂	17
3.3 Role of the World Calibration Centre (WCC)	17
3.4 Implementation of QA system on site	18
4. DATA ARCHIVING	18
5. OUTLOOK, FURTHER NETWORK DEVELOPMENT	19
References.....	21
ANNEX I - Abbreviations and Acronyms.....	23
ANNEX II – List of Participants	24
ANNEX III – Agenda	26

FOREWORD

The WMO/GAW Expert Workshop on Global Long-term Measurements of Nitrogen Oxides was held at the Hohenpeissenberg Meteorological Observatory, Germany from 8 to 9 October 2009. The Workshop was organized to support the reactive gases component of the Global Atmosphere Watch Programme. The aim was to integrate and harmonize measurements of nitrogen oxides to achieve a sustainable and reliable high-quality observation network for nitrogen oxides within the GAW Programme. The workshop was jointly organized by Stefan Gilge, Christian Plass-Duelmer (both at Hohenpeissenberg Meteorological Observatory, DWD, Germany), Stuart Penkett (University of East Anglia, UK, and the chair of Scientific Advisory Group for Reactive Gases, SAG-RG), Liisa Jalkanen and Oksana Tarasova (both at WMO/GAW secretariat, WMO, Geneva, Switzerland).

This report, as a product of the Workshop, forms the basis of the GAW strategy of supporting measurements of nitrogen oxides into the future.

The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) serves as an international framework aimed at providing reliable long-term observations of the chemical composition and physical properties of the atmosphere which are relevant for understanding atmospheric chemistry and climate change. 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 are a component of a group of reactive gases required to be measured in the GAW Programme. The reactive gases group focuses on gases known to be intimately involved in various aspects of the chemistry of the troposphere and includes surface ozone (O_3), carbon monoxide (CO), volatile organic compounds (VOCs), and sulphur dioxide (SO_2), as well as oxidized nitrogen species. The sum of nitric oxide (NO) and nitrogen dioxide (NO_2) has traditionally been called NO_x . 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_2O) is obviously an oxide of nitrogen but it is not dealt with in this report because it is inert in the troposphere. It is measured separately by another component in the GAW Programme because of its role as a greenhouse gas.

The focus of this report is on NO and NO_2 mostly because their measurements are presently more extensive and it is thus easier to establish high quality measurements with a fully implemented quality assurance system. Measurements of total NO_y are presently undertaken in the GAW framework but the measurement quality control and calibration methodology is deemed not mature enough at present to recommend the inclusion of total NO_y measurements for GAW.

Measurement of NO_x in the global atmosphere is important since it has a large influence on both tropospheric ozone and on the hydroxyl radical (OH). NO_x has been measured at a number of sites continuously, but often using equipment which does not specifically measure NO_2 and thus gives a measurement not accurately representing NO_x . NO_x has been measured regularly in most air-borne programmes and NO_2 is now being measured globally from satellites (column amounts only) although the measurements are presently limited mostly to continents due to sensitivity and other considerations. All these measurements suggest that substantial mixing ratios of NO_x are present over most of the continents although this remains to be confirmed by in-situ measurements of the type proposed by GAW. As NO and NO_2 are highly reactive, they should be measured by in-situ or remote active methods which are personnel demanding and constrain the expansion of the network. There are efficient *in situ* measurement techniques for NO, and to a lesser extent for NO_2 ; these are discussed in this report and recommendations for GAW measurements by particular methods are given.

In order to establish credibility within the world community studying many molecules of significance in the atmosphere, GAW operates a common system designed to collect data in an established network which is supported by a comprehensive quality assurance system. This ensures data comparability and compatibility within the network and provides high-quality assessments of the long-term variability and trends of molecules being measured. The structure of the GAW quality assurance system with its essential components and linkages is shown in Figure 1.

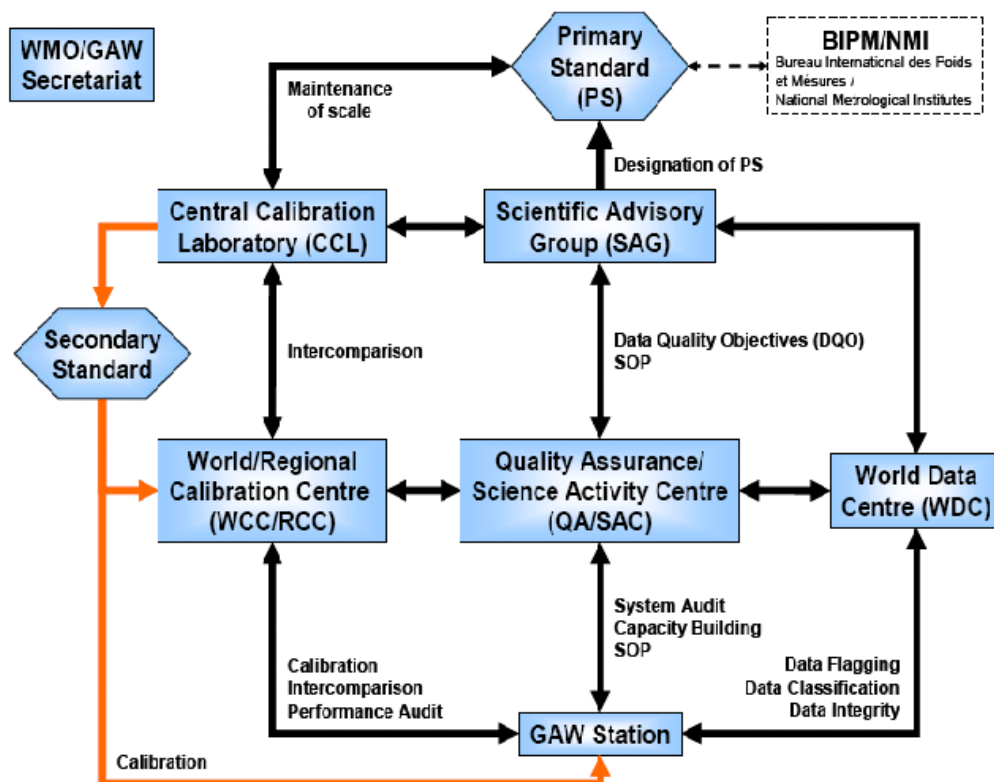


Figure 1 - Conceptual framework of the GAW quality assurance system

This system has been discussed in detail in “The WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008-2015” (WMO, 2008). Before the workshop most of the elements shown in Figure 1 were absent for oxidised nitrogen compounds. In particular:

- The GAW Central Facilities and infrastructure for NO_x including Quality Assurance/Scientific Activity Center (QA/SAC), Central Calibration Laboratory (CCL), World Calibration Center (WCC) are not assigned
- Data Quality Objectives (DQO) are not formulated
- Standard Operating Procedures (SOPs) required to reach the set DQO and standardizing the measurements within the network are not developed
- A network has not yet been designed and the number of stations currently reporting data is very small
- The only central facility currently assigned to accept measurement data is the World Data Centre for Greenhouse Gases (WDCGG) in Japan

Against this background the workshop was held to develop a comprehensive plan for the setting up of a global network for measurements of NO_x within GAW, possibly expanding to include specific forms of NO_y in the future, supported by the essential components shown in Figure 1.

This report summarizes the rationale, strategy for implementation, recommendations on measurement techniques and an outline of a quality control system for in-situ NO_x measurements in GAW. A more technically oriented NO_x Measurement Guidelines (MG) will follow including description and recommendations on procedures for sampling, analysis, calibration, quality assurance and control, and data flagging and reporting, as well as descriptions of the tasks of the central facilities, the CCL and the WCC. The current report consists of chapters on the present state of knowledge of nitrogen oxides chemistry in the atmosphere and the reasons for the establishment of a GAW global network for NO_x measurements; on the components of a GAW NO_x observational network including network design, on monitoring platforms and measurement techniques; on quality assurance; on data archiving; and on further developments beyond a basic NO_x network.

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1. BACKGROUND TO THE MEASUREMENT OF NITROGEN OXIDES WITHIN GAW

1.1 Atmospheric chemistry of nitrogen oxides and their relevance for the GAW Programme

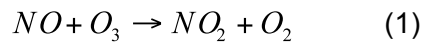
Oxidised nitrogen occurs in many forms in the atmosphere reflecting the reactivity of fixed nitrogen and its many oxidation states. It differs from other groups of compounds measured by GAW in that nearly all the individual species are interconvertible by chemical processes occurring in the atmosphere. A brief outline is presented here. A fuller discussion is given in various recent texts including Penkett et al. (2003) and Jenkin (2006). Most of the important molecules of the oxidised nitrogen family present in the atmosphere are shown in Table 1 along with their atmospheric lifetimes and their importance for atmospheric chemistry. This is also discussed in the text below.

Table 1 - The main forms of oxidised 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).

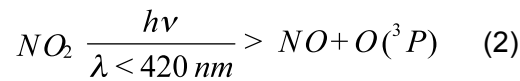
The importance of its measurement to atmospheric chemistry is also shown

Molecule	Formula	Lifetime	Importance to atmospheric chemistry
Nitric oxide	NO	h	Controls OH and O ₃ in the troposphere
Nitrogen dioxide	NO ₂	h-d	Only source of O ₃ in the troposphere
NO _x (nitrogen oxides)	NO + NO ₂	h-d	Dominant form of oxidised nitrogen in regional atmosphere
Nitrate radical	NO ₃	s-h	Important oxidant in nighttime chemistry. Rapidly lost by reaction with NO and red light in daytime
Dinitrogen pentoxide	N ₂ O ₅	h	Nighttime source of nitric acid. Reservoir for nitrate radical and NO _x
Nitrous acid	HNO ₂	min-h	Alternative source of hydroxyl radicals to O ₃ chemistry
Nitric acid	HNO ₃	d	Important acidifying agent and major sink for oxidised nitrogen
Peroxy nitric acid	HNO ₄	min-d	Reservoir compound in upper troposphere
Nitrate aerosol	NO ₃ ⁻	d	Important component of regional aerosol
Organic nitrates	RO-NO ₂	w	Major component of oxidised nitrogen in remote marine atmosphere. Higher nitrates (4+) are tracers for tropospheric photochemistry
Peroxyacyl nitrates (PANs)	R-CO ₃ NO ₂	h-w	Reservoir compound for NO _x . Tracer for tropospheric photochemistry
NO _y	all above		NO _y is the dominant form of oxidised nitrogen in the remote atmosphere
Nitrous oxide	N ₂ O	>100 years	Important gas controlling ozone concentrations in the stratosphere. Unreactive in the troposphere. Significant greenhouse gas.

Nitric oxide (NO) and nitrogen dioxide (NO₂), the sum of which is referred to as NO_x, exert a major influence on oxidation processes in the troposphere. Figure 2 shows how the major atmospheric forms of oxidised nitrogen (listed in Table 1) are chemically connected. Nitrogen oxides are mostly emitted as NO, by both anthropogenic processes (e.g. fossil fuel combustion) and natural processes (e.g. soil emissions and lightning). NO rapidly reacts with ozone to form NO₂.



NO_2 absorbs light in the near UV and breaks down into NO and ground state oxygen atoms ($O(^3P)$), see Figure 2:



This photochemical process is one of the most important occurring in the troposphere since it is responsible for virtually all ozone formation occurring there via the reaction of $O(^3P)$ with oxygen molecules:

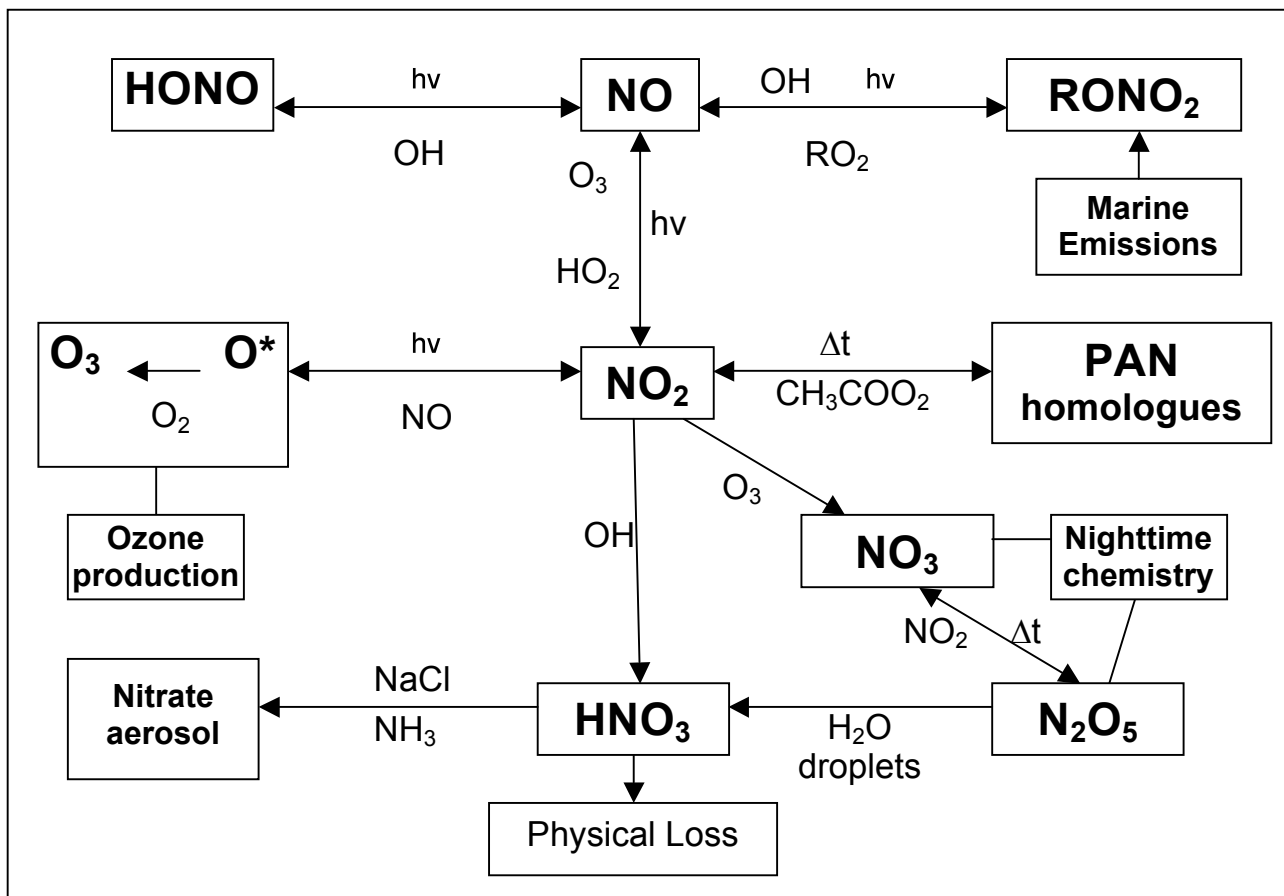
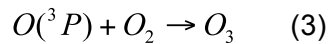


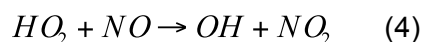
Figure 2 - Chemical connectivity of oxidised nitrogen compounds in the troposphere. Emissions are mostly in the form of NO and NO_2 , loss processes are dominated by rain-out/wash-out of HNO_3 and nitrate aerosol along with dry deposition. R is an organic group; PAN is peroxyacetyl nitrate, Δt means thermal decomposition, $h\nu$ is photodissociation

Reactions (1), (2) and (3) constitute a photochemical equilibrium in daylight such that

$$[O_3] = j_2[NO_2]/k_1[NO], \quad (A)$$

where j_2 and k_1 are photolysis and thermal rate constants for reactions (2) and (1) respectively. This equilibrium is disturbed by peroxy radicals such as HO_2 and RO_2 which convert NO to NO_2 without consuming ozone (see Figure 2) and it therefore allows ozone to accumulate in the troposphere by altering the ratio of NO to NO_2 (see expression (A), known as the Leighton relationship, above).

Reaction (4) shown below also allows chain reactions involving OH and peroxy radicals (HO_2 and RO_2) to propagate, e.g.



The resultant NO_2 is available again for more ozone production and the hydroxyl radical is reformed to react with more trace substances in the atmosphere producing further peroxy radicals and ultimately cleansing the atmosphere by physical processes. Accordingly, in this simplified picture NO and NO_2 are closely related to each other in a photo-stationary state and their ratio depends on the levels of O_3 , UV light and peroxy radicals. In remote areas of the global atmosphere, however, the mixing¹ ratios of nitrogen oxides decrease to very low levels, often below 10 ppt. Under these conditions, the atmospheric chemistry changes with two major consequences:

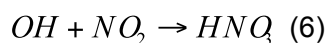
- First, the recycling of OH radicals is reduced due to lack of NO to participate in the reaction presented in equation (4)
- Second, the reaction of ozone with peroxy radicals competes with reaction (4) and at low NO mixing ratios becomes dominant:



with the result that ozone is depleted in very remote areas.

Thus, at NO_x mixing ratios above about 50 ppt, ozone will be made in a very efficient chain reaction involving OH and HO_2 with a chain length of the order of 100. At NO_x mixing ratios of the order of 20 ppt range, ozone will either be maintained or destroyed, particularly at the high water vapour mixing ratios (because of enhanced OH radical production) typical of the marine boundary layer in the tropics and temperate latitudes (Ayers et al., 1992). This simple reaction sequence shown above holds the key to much of the oxidation chemistry occurring in the atmosphere and explains why global measurements of NO and NO_x are important.

Figure 2 also shows other forms of oxidised nitrogen as well as NO_x which are present in the atmosphere; together they are referred to in atmospheric chemistry parlance as NO_y (see Table 1 for individual molecules). Each form has specific functions. Thus nitrous acid (HNO_2) can be photolysed and acts as a direct source of OH, in addition to the OH source from ozone photolysis in the presence of water vapour. The nitrate radical (NO_3) is a significant oxidant at night in much of the continental boundary layer; it is in thermal equilibrium with nitrogen pentoxide (N_2O_5) which is readily taken up in water droplets to make nitric acid (HNO_3). The main source of HNO_3 in the atmosphere, however, is the reaction of OH with NO_2 .



This is a radical-radical recombination reaction (since both NO and NO_2 are stable free radicals) and is the main termination step in the chain reaction producing ozone from NO_2 photolysis described above. It is the principal sink for oxidised nitrogen since HNO_3 is resistant to chemical change in the lower troposphere and is rapidly lost by rain-out/wash-out or by deposition to the Earth's surface; it also forms a nitrate aerosol by interaction with ammonia (NH_3) over land and sodium chloride (NaCl) over the ocean. Peroxynitric acid (not shown in Figure 2 but made by reaction of NO_2 and HO_2 radicals) is only stable in the cold conditions experienced in the mid to upper troposphere. Nitrous oxide is inert in the troposphere and is therefore not shown in Figure 2 but it exerts a controlling influence on stratospheric ozone.

Both NO and NO_2 react with organic radicals to form organic nitro compounds, the most important being peroxyacetyl nitrate (PAN) and organic nitrates (RONO_2) which both act as

¹ Two units are used in this document to describe atmospheric content of the species, namely mixing ratio (ppt, ppb or ppm) and mole fraction (nmol/mol, $\mu\text{mol/mol}$). 1ppb = 1 nmol/mol, 1 ppm = 1 $\mu\text{mol/mol}$.

reservoirs for NO_x . PAN is formed by the reaction of NO_2 with the peroxyacyl radical (CH_3COO_2) (see Figure 2), which in turn is derived from the oxidation of acetaldehyde, a common product of the oxidation of many nonmethane hydrocarbons, by hydroxyl radicals in the presence of oxygen or through photolysis of some aldehydes or ketones. PAN is relatively stable to attack by hydroxyl radicals and photolysis by solar radiation. Thus it is longer lived than NO_x (depending on temperature) and can be transported into the background atmosphere where it can act as a source of NO_x by undergoing thermal decomposition, especially in warm conditions close to the earth's surface. Higher homologues of PAN are formed from higher aldehydes which in turn result from oxidation of longer-chain hydrocarbons.

Organic nitrates of differing chain length from C_2 to C_8 have been observed in the atmosphere and they result from reaction of the respective peroxy radical (RO_2) with NO (see Figure 2). Methyl nitrate is not formed efficiently by this reaction but has a major source in the ocean along with ethyl and propyl nitrate. Reaction of these short chain organic nitrates with OH or photolysis may act as an important source of NO_x in very remote regions such as the marine boundary layer of the tropical Pacific Ocean (Neu et al., 2008). This process could act to moderate ozone loss at low NO_x due to the processes described above. In much of the world atmosphere oxidised nitrogen is mostly present in an organic form and this presents a major challenge to GAW since there are no established GAW measurement programmes for PAN and organic nitrates in place at present.

Because of the absence of regular measurements of organic nitrates etc on a global scale the current report focuses on the setting up of a network for high quality global NO and NO_2 measurements as a first step. Measurements of other specific NO_y components should follow at a later date.

1.2 Scientific and policy reasons for NO_x measurement

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

A substantial part of the oxidised nitrogen which ends up in the atmosphere is due to the anthropogenic contribution to global emissions of NO_x . According to a recently published review (Reis et al., 2009), in 2005 anthropogenic emissions of NO_x amount to 28 Tg N yr^{-1} with the highest contribution from energy production and transport. Natural sources of NO_x include about $5 \pm 3 \text{ Tg N yr}^{-1}$ produced by lightning (Schumann et al., 2007) and about 11 Tg N yr^{-1} produced by soils and biomass burning (Martin et al., 2003). Moreover, there is a positive contribution to the troposphere by stratosphere-troposphere exchange (Galloway et al., 2004) mainly in the form of nitric acid. The anthropogenic contribution has grown substantially since the pre-industrial period in comparison with the natural emissions, mainly due to growing energy demand and development of various forms of motorized transport. The overall impact of these increasing emissions of oxidised nitrogen is to spread their influence much wider across the continents and into the surrounding marine atmosphere. The main regions of emissions on the continents are also changing such that Southeast Asia and South Asia are replacing Europe and North America as the areas where most anthropogenic emissions occur. This has various implications for atmospheric chemistry and related policy considerations. Global monitoring of many NO_y compounds in the atmosphere is required to understand these issues.

Several specific scientific reasons can be identified to justify this statement.

- (a) NO_x compounds have a central controlling role in free radical chemistry and photochemical oxidation processes in the troposphere. Many gases are oxidised by both hydroxyl and nitrate radicals including, for instance, sulphur dioxide which produces a sulphuric acid aerosol on oxidation or halocarbons (which otherwise can contribute halogens for the destruction of ozone in the stratosphere). In addition, through the set of reactions described above, NO_x regulates the lifetime of methane (e.g. through OH recycling due to

reaction (4)), and the production of tropospheric ozone through reactions (1-4) with subsequent modification of the NO to NO₂ ratio by free radicals. Both CH₄ and tropospheric ozone are greenhouse gases hence NO_x indirectly influences radiative forcing.

Ozone formed in the polluted regions is a dangerous air pollutant and directly affects vegetation growth and human health. Ozone produced in the background atmosphere by NO_x chemistry provides a base level of ozone upon which pollutant ozone is superimposed. Also products of the NO_x oxidation chain contribute to the formation of a secondary aerosol, which has an important role to play in the greenhouse effect and in local air quality.

- (b) NO_x compounds in the atmosphere can be oxidized to acidic species, forming an acid aerosol and acid precipitation, which in some locations can acidify lakes and soils, causing harm to living organisms. Acid deposition has been identified as a major environmental problem in Europe and eastern North America since the 1960s and 1970s. Concerns focused on the adverse effects of acid rain on the environment, including acidification of fresh waters and terrestrial ecosystems, and forest damage. Overload of the soil environment with nitrate leads to its transportation to inland water bodies and the ocean and may trigger blooms of microscopic plants that consume oxygen as they decompose leading later to so-called dead zones (eutrophication). On land, excess of nitrogen is a threat to biodiversity. For example, grasslands across much Europe have lost a quarter or more of their plant species after decades of human-created nitrogen deposition from the atmosphere (Townsend and Howarth, 2010).

Current research into the critical loads of N deposition both for acidification and eutrophication (see Hettelingh et al., 2008) has led to the establishment of more stringent critical loads, with dynamic modelling approaches being explored to assess the timescales of ecosystem damage and recovery. The problems identified on the European and North American continents will undoubtedly become apparent in various parts of Asia as emissions in these latter regions increase.

- (c) The atmospheric transport and transformations of nitrogen compounds is an essential component of the cycle of life (or biogeochemistry) on the planet, where fixed nitrogen is a major and essential plant nutrient. All natural emission processes have taken place for millions of years and, through the atmospheric nitrogen cycle, they ultimately lead to a redistribution of fixed nitrogen in the biosphere. How important these processes are to those parts of the biosphere that are N limited (including large ocean areas) is unknown, but needs to be determined to properly understand the impact of anthropogenic emissions of NO_x on the Earth's biosphere both on land and in the ocean.

1.3 Implementation procedure

The meeting noted, that it is quite clear that the contributors to the GAW Programme should measure oxidised nitrogen compounds. However, taking into account the limited resources available, it was recommended that the initial phase of the nitrogen programme should focus on high quality measurements of NO and NO₂ in as many locations as possible. Thus a rational sequence for oxidised nitrogen measurements within GAW is recommended by the meeting to be as follows:

- Begin with in-situ NO and NO₂ measurements using equipment which matches the requirements listed in this report at surface sites (with the primary focus to establish such measurements at GAW Global and Regional sites).
- Proceed towards measurement of specific NO_y components in the future. Measurement of total NO_y is not recommended since no reliable calibration procedure can be set up with suitable standards.
- Work towards an integrated approach, which will include measurements from different platforms, starting with surface in-situ and air-borne measurements with subsequent extension to satellite and ground-based remote sensing.

In order for these measurements to be fully incorporated into GAW it is necessary to:

- Ensure that surface measurements made by different laboratories are compatible within the data quality objectives described below.
- Expand the spatial and temporal distributions of NO and NO₂ on a global scale.
- Provide in-situ measurement data to validate satellite and ground-based NO₂ column and profile measurements.

1.4 Potential products and services

If the GAW Programme is successful in setting up an extensive global network for high quality measurements of both NO_x and specific forms of NO_y, then various products and services, as defined by the GAW Strategic Plan, will result. These will enable users to do the following:

- Combine surface and remote measurements with numerical models of the atmosphere to better define the NO_x budget.
- Characterize the impact of NO and NO₂ on the oxidative capacity of the atmosphere, the ozone budget, and aerosol formation and composition.
- Assess the impact through all the above processes on climate change.
- Characterize the impact of NO_x on air quality and the composition of precipitation.
- Detect and understand NO_x trends in comparison with emission inventory data.
- Quantify deposition of oxidized nitrogen to ground and ocean surfaces.

2. ESSENTIAL COMPONENTS OF A GAW GLOBAL NO_x OBSERVATIONAL NETWORK

2.1 Criteria for the GAW NO_x Network design

The purpose of the NO_x network within GAW is defined by the rationale discussed above. The measurements described here are mainly focused on the measurements representative for remote and regional atmosphere. Measurements in cities and in regions that are downwind of cities or major urban/industrial complexes fit into the EMEP and WMO GURME programmes. There are also several observational programmes in North America, which focus on NO_x measurements as a part of air pollution monitoring, including NAPS and CAPMoN in Canada, and EPA networks in the US. Initially a major emphasis of the NO_x activity in the GAW Programme is to achieve better data coverage for NO_x measurements in the relatively unpolluted atmosphere.

The expected NO_x mixing ratios at a site directly define the requirements towards the measuring system (see Section 3); e.g. at locations where the mixing ratios of NO determines whether ozone is made or destroyed by free radical chemistry it is necessary to be able to measure NO down to 1 ppt and NO₂ down to 5 ppt.

2.1.1 Geographic considerations

The geographical location of measurement stations should consider the Earth's diverse distribution of climate zones, ecosystems, land use forms and human populations. Observations are needed in: (a) marine and continental environments; (b) polar, mid-latitude and equatorial locations in both hemispheres, and (c) in the boundary layer and the free troposphere. Southern hemispheric sites are of importance for understanding more marine-dominated and pristine conditions compared with those experiencing the impact on air composition of higher population density and industries in the northern hemisphere. Transects from coastal to continental locations will yield information about continental emission sources. Coastal sampling stations, in particular on the western coasts of North America, Europe and Australia will yield data on trans-oceanic transport and processing of air pollutants in the marine boundary layer. Data from monitoring at high elevation observatories will generally better represent free tropospheric air composition and also captures the influence of long-range transport.

The distribution of NO₂ in the global atmosphere has recently become available from satellite retrievals, particularly GOME and SCIAMACHY (see Figure 3). There are three main regions with high mixing ratio (actually, the map presents tropospheric column) of NO₂ in the continental boundary layer, North America, Europe and Southeast Asia (mostly China and Japan). However, most of the land mass shows NO₂ mixing ratios which are detectable by the SCIAMACHY satellite. The only regions where the mixing ratios approach those shown over the oceans are northern Canada and Alaska, Siberia, the Sahara Desert, the Tibetan Plateau and the centre of Australia. Mixing ratios are also lower over the Polar Regions. The satellite map also shows areas over the oceans with high mixing ratios of NO₂. Some of these are associated with shipping lanes but others may be influenced by the proximity of large emission sources on nearby continents. Most of the observations over world oceans show very low NO₂ mixing ratios and the major form of oxidised nitrogen present is organic one which is not detected at present by satellite.

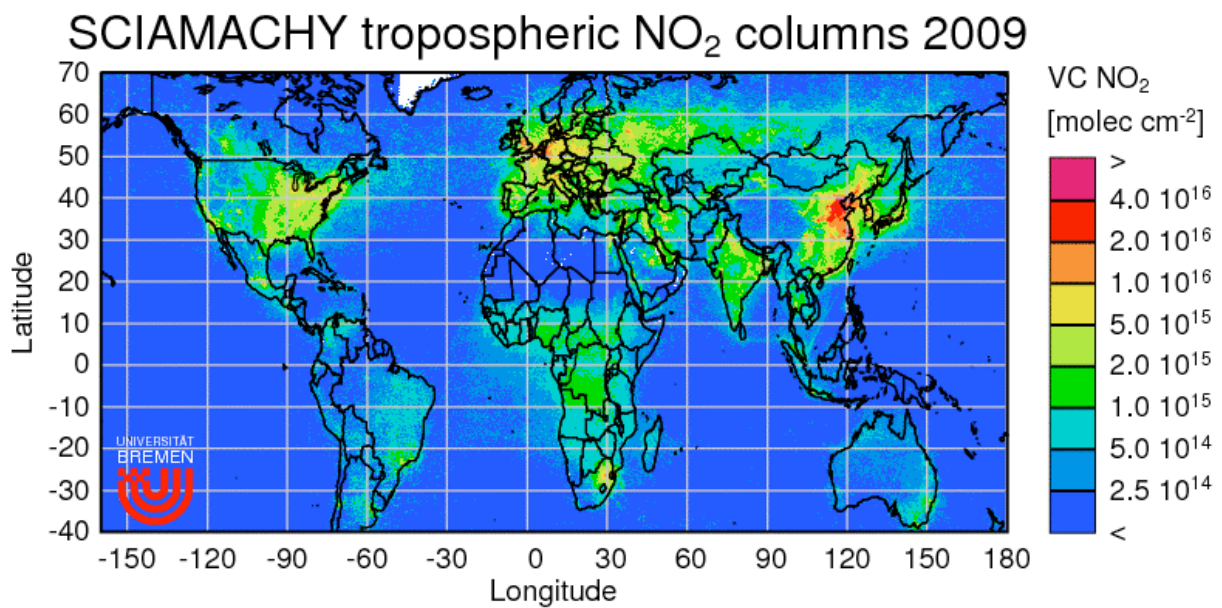


Figure 3 - Satellite map of the global distribution of tropospheric NO₂ in 2009
(Courtesy of Andreas Richter, University of Bremen)

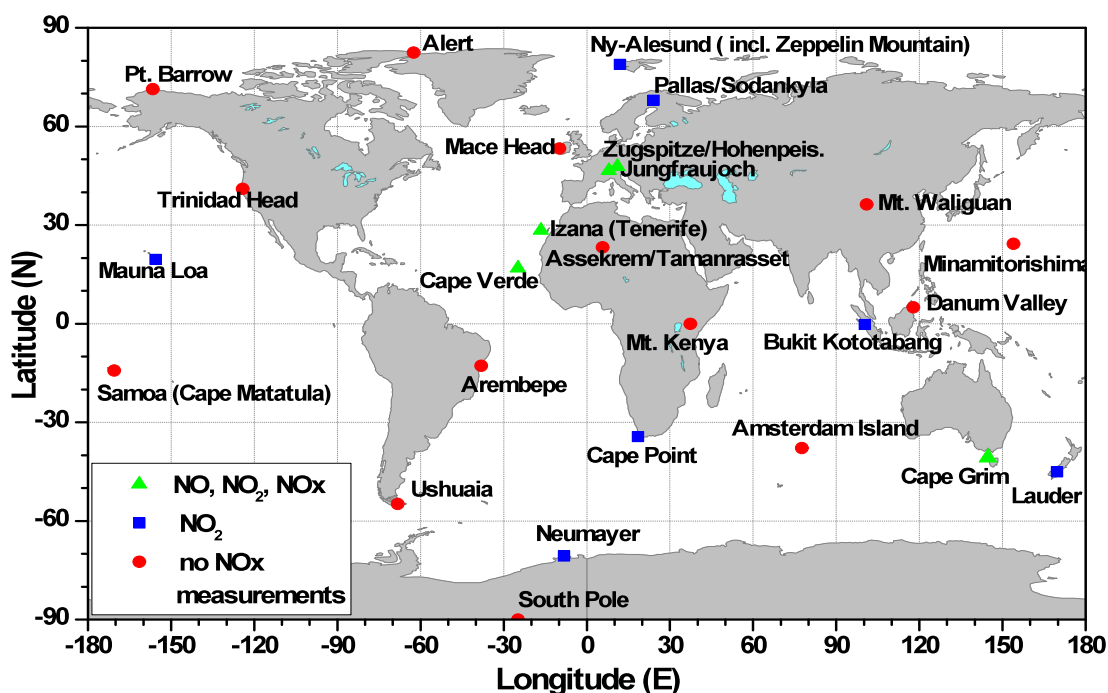


Figure 4 - Global GAW stations operational at the end of 2009.

Measurements of different oxidised nitrogen compounds are marked by different symbols. Information on measurements programme is extracted from GAWSIS (GAW Station Information System). Among all GAW Global stations, only Jungfraujoch, Hohenpeissenberg and Cape Verde submit NO_x data to the data centre (WDCGG). (Cape Grim has ongoing NO_x measurements since June 2009, they will be submitted to WDCGG in due course)

2.1.2 Use of existing programmes and infrastructure

WMO/GAW has a well-established global network of sites which record the concentrations of many gases and aerosols, including greenhouse gases such as CO₂, CH₄ and N₂O (overview is regularly published as an Annual Greenhouse Gas Bulletin, available at the GAW webpage), reactive gases such as CO and ozone and in some cases selected VOCs (Helmig et al., 2009). Ideally all sites which perform continuous in situ measurements of CO, ozone or VOCs should also measure NO and NO₂ but unfortunately very few report any data at present.

Based on information available in GAWSIS measurements of NO are/were performed at 18 stations (14 European), and 7 stations (all European) submitted their NO data to the officially assigned World Data Centre (World Data Centre for Greenhouse Gases, WDCGG) within the last 3 years. GAWSIS has 100 fully operational stations registered as performing NO₂ measurements and 21 stations submitted the data to WDCGG within the last three years (all European). It should be stressed, however, that the quality of these data is often not well known and generally not in line with the DQO's described in Section 3. Generally, data of non-specified quality are not acceptable for inclusion in the GAW database.

Many of the reporting stations are under the influence of anthropogenic NO_x emissions, and only a handful of these stations give data representative of the regional atmosphere. The measurements of NO and NO₂ are relatively easy to perform in most continental locations given the necessary resources and expertise; it is far more difficult to accurately measure NO and, to a greater extent, NO₂, at remote locations especially in the pristine, marine environment. The only truly marine NO_x data submitted to the WDCGG is from the GAW Global station at Cape Verde located in the marine boundary layer in the tropics, see Figure 4.

Examples of existing locations where GAW NO and NO₂ measurements are made on a routine, long term basis with GAW specified technology include Cape Verde in the boundary layer of the tropical Atlantic Ocean off the west coast of Africa, Hohenpeissenberg in southern Germany in the European boundary layer and both Zugspitze and Jungfraujoch in the Alps at high altitude over Europe. In the Southern Hemisphere measurements have been made at the GAW stations at Cape Grim, Tasmania (Galbally et al., 2000) and in Antarctica. Measurements at these latter locations are very demanding because of the extremely low concentrations experienced. There are other locations where NO_x measurements have been performed but mostly on a research basis including e.g. Niwot Ridge (Colorado, USA) and Egbert (Ontario, Canada). However, these measurements are not associated with GAW and data are not reported to the World Data Centre. Where it is possible, it would be desirable to affiliate such measurements to the GAW Programme.

There are many good reasons to link together the GAW Programme with existing programmes designed to measure oxidised nitrogen compounds, at least the common skills required to both make and interpret such measurements.

Because of the role of NO_x in photochemistry and ozone production, NO and NO₂ are measured and their emissions are controlled in Europe. This monitoring is conducted by the *co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP)*, which is part of the United Nations Convention on Long Range Transport of Air Pollution. EMEP has approximately 100 stations that measure NO_x in Europe, but mostly using integrating methods with daily samples. EMEP stations are classified according to 3 levels. The Level 3 National Background Sites, that measure NO, NO₂, PAN and Organic nitrates, are relevant to the GAW Programme and constitute the basic part of NO_x observation for the GAW Programme in Europe. Extensive experience has been gained by EMEP in building a NO_x observational network. As many EMEP stations are regional or global stations in GAW, there is a vital, synergetic interest of EMEP in the establishment of the GAW-NO_x network, e.g. to use the same measurement techniques and QA among the networks. A particular point of note here is that both EMEP and this report recommend the use of a photolyc converter rather than a hot molybdenum converter for NO₂ measurements.

2.2 Monitoring platforms

The initial goal for the global NO_x observations programme is to obtain continuous, surface-based, in-situ measurements. In the longer run, the synergistic use of three types of platforms (surface stations, mobile platforms and remote sensing) provides the best opportunity for assessment of both the spatial and temporal NO_x distribution.

2.2.1 Continuous measurements at surface stations

In-situ monitoring at atmospheric observatories allows for long-term, frequent (minute resolution) sampling of atmospheric NO_x. Such measurements are valuable to study the influence of diurnal and seasonal changes in local and regional meteorology, long-range transport and atmospheric photochemistry on NO, NO₂ and NO_x. Furthermore, these stations will serve as an important resource for testing and future deployments of new NO_x and speciated NO_y measurement techniques, and ground-truthing for aircraft and satellite based programmes.

2.2.2 Mobile platforms

Aircraft, ships and trains are increasingly being utilized as mobile atmospheric research platforms. Such platforms provide unique opportunities for the study of horizontal and vertical distributions of NO_x. These data are important for research on transport and identification of NO_x sources and sinks. Several long-term monitoring initiatives from mobile platforms offer opportunities for meeting GAW's objectives. These include, for example, the European airborne CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) programme, and the rail based TROICA (Trans-Siberian Observations into the Chemistry of the Atmosphere, www.troica-environmental.de and www.troica.ru) experiment in Russia with mobile observations at the ground. The IAGOS programme (Integration of routine Aircraft measurements into a Global Observing System, <http://www.fz-juelich.de/icg/icg-2/iagos>) is especially designed to fulfil the needs of IGACO and GAW. IAGOS currently prepares the

transition from the former MOZAIC project into a sustainable infrastructure with enhanced measurement capabilities, global coverage, and real-time data transmission from aircraft.

2.2.3 Remote sensing

Satellite measurements are able to provide information on NO₂. Column density for NO₂ is provided from GOME and SCIAMACHY with a global coverage. Surface based MAX-DOAS has the potential to measure the local vertical profile and column of NO₂. MAX-DOAS has been used mainly in research applications and for monitoring at selected locations, e.g. the GAW Global stations Neumayer and Hohenpeissenberg. Experience with using this new technique, MAX-DOAS, for long-term monitoring, has to be gained and its suitability for GAW purposes with respect to data quality has to be tested. These local vertical profile measurements may ultimately be a vital link between continuous point measurements and satellite regional coverage.

2.3 Measurement techniques and measurement guidelines

It was agreed at the workshop that the species nitric oxide (NO) and nitrogen dioxide (NO₂) can be measured at all surface locations with the equipment, calibration standards and protocols available at present. The following is a discussion which ultimately will lead to a set of measurement guidelines (MGs) or standard operating procedures (SOPs) to be published later.

Figure 5 gives an overview of the existing measurement techniques for detection of nitrogen oxides. They could be separated into three main groups: passive, active and remote sensing techniques. Principally, active techniques draw the air sample through the detector or sampling device by a pump, whereas passive techniques use the diffusion of air to the sampling device. In remote sensing techniques, e.g. satellite, FTIR or MAX-DOAS, sampled air and detector are at different locations.

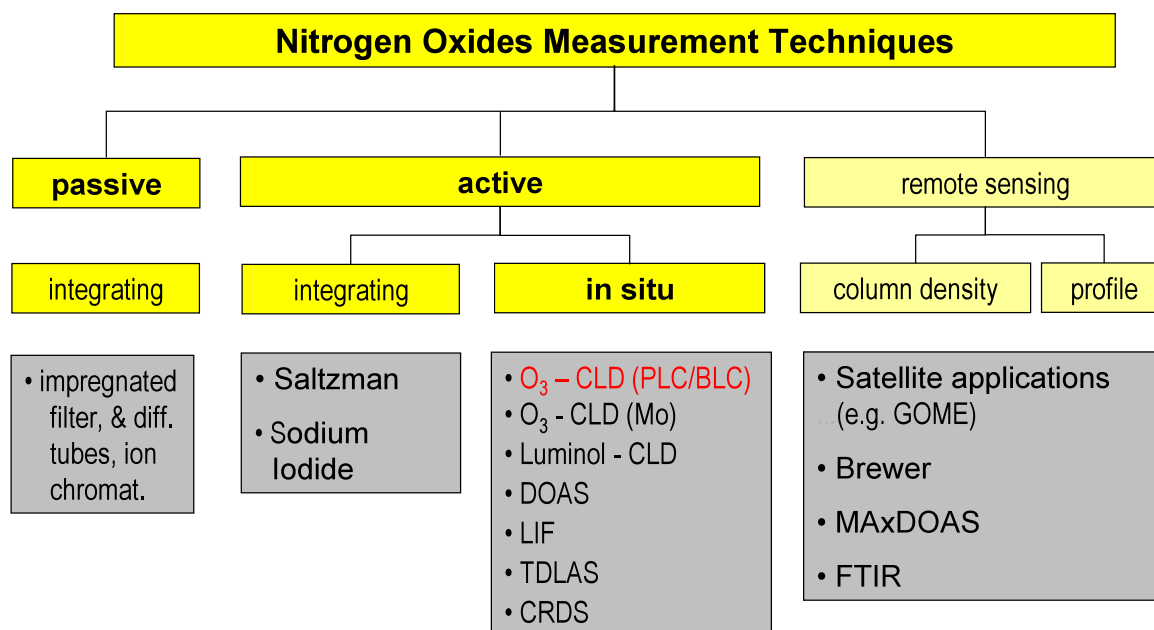


Figure 5 - Summary of NO_x measurement techniques

The active techniques can be divided into integrating and “in-situ” techniques, with the integrating techniques consisting of a sampling step usually involving liquid-phase sample collection and off-line analysis, whereas in-situ (continuous) measurements directly analyse the sample air. Passive methods are always integrating. Active integrating methods comprise the well known Saltzman method and related methods like the Griess or Sodium Iodide method. The latter is being used for example in the EMEP network. Due to the high reactivity of NO_x, flask sampling is impossible.

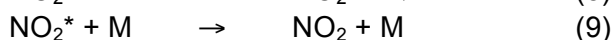
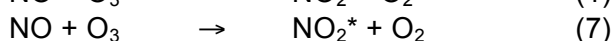
“In-situ” techniques comprise the ozone chemiluminescence detection (CLD), which detects NO directly and NO₂ after suitable conversion to NO with a photolysis converter (PLC) or blue light converter (BLC). The Luminol-CLD measures NO₂ directly and NO indirectly after oxidation. Also, very selective and partly new optical absorption techniques for NO₂ detection have been developed including tuneable diode laser absorption spectroscopy (TDLAS), differential optical absorption spectroscopy (DOAS), laser induced fluorescence (LIF), Fourier-transformed infrared absorption spectroscopy (FTIR) and cavity ring down spectroscopy (CRDS).

A brief discussion of active in situ methods which are well established and suitable for GAW is given below. At present, there is no other mature technique that can compete with ozone-induced chemiluminescence NO detection (CLD) measurement of NO. Recent developments in cavity ring-down spectroscopy (CRDS) for measurement of NO₂ and of NO as NO₂ after oxidation by ozone were promising, if the uncertainties in the zero level could be reduced. Passive and active integrating methods are not accepted in the GAW Programme for their inappropriate selectivity and time resolution.

2.3.1 Recommendations for measurement of NO by ozone induced chemiluminescence detection (O₃-CLD)

The meeting recommended to focus on NO measurements by CLD as the best way to begin a GAW NO_x network of sufficient sensitivity and selectivity, at reasonable instrumental cost, and with a large number of experienced operators worldwide.

For analysing the NO amount in ambient air, the gas phase chemiluminescent reaction of nitric oxide with ozone according to reactions (1) and (7)-(9) is used:



Most of NO oxidation leads to ground-state NO₂ according to reaction (1), only a fraction leads to NO₂ molecules in excited state (7). By far the largest portion of NO₂^{*} returns to ground-state without light emission by collision with molecules M (e.g. N₂, O₂) according to reaction (9) and a steady-state analysis of the above set of equations leads to the expression (B)

$$[\text{NO}_2^*] = k_7[\text{NO}][\text{O}_3] / k_9[\text{M}] \quad (\text{B})$$

The radiation emission due to reaction (8) takes place at wavelengths between 600 and 3000 nm, with an intensity maximum at 1200 nm. The emitted light is detected with a photomultiplier tube (PMT). In order to minimize the noise contributed to the signal by the detector, the PMT temperature is stabilized, typically below 0°C. The sensitivity of the instrument is dependent on many variables, including the pressure of the reaction chamber (lower pressures are better to minimize reaction (9)), the temperature of PMT (dark current), the ozone mixing ratio in the reaction chamber and the mass flow of the sample air through the chamber. All these variables must be kept constant to provide a stable instrument response. Ozone is generated by silent electrical discharge. Since the reactions take place with a high excess of O₃, the chemiluminescence reaction is directly proportional to the NO mixing ratio in the sample gas.

At low nitric oxide mixing ratios a chemiluminescence signal caused by reaction of ozone with gases other than NO could be a significant disturbance of the measuring signal (interference). However, typically these molecules react with O₃ at a much slower rate than the reaction of NO with O₃. The interferences can be corrected by making a “zero” measurement on the signal, i.e. a measurement of the instrument signal when **no** NO is present in the sample air. One way of doing this is by using a prechamber. In this “zero measurement mode the mixture of ambient air and ozone passes a prechamber (without a PMT). The NO/O₃ reaction takes place to completion in this prechamber before the sampled gas passes into the main chamber where only the

chemiluminescence of the slower reactions of the interfering molecules with O_3 is counted. In the ambient measurement mode, ambient air and ozone are led directly in the measuring chamber, and the chemiluminescence of both the reactions of NO and the interfering molecules with O_3 are detected. To determine the ambient mixing ratio of NO, the signal from the zero mode is subtracted from the signal from the ambient mode and the difference is multiplied by the calibration factor. Zero mode measurements are made at least every hour or during every measurement cycle, depending on how fast mixing ratios of interfering components are expected to change.

There are instrument artefacts associated with the zero signal. These in part arise because the physical and chemical conditions in the reaction chamber are not identical in the zero and measurement modes. Regular tests to quantify these instrument artefacts may be made using an external supply of NO_x free zero air. There are also variations in instrument response due to varying water vapour in the sample air. This is an issue more for aircraft sampling rather than fixed stations, provided regular calibrations are undertaken. As a general rule, the systems require calibration with at least one standard gas in regular intervals, and the linearity should be confirmed by different dilutions of standard with zero gas or using a suite of standards with different mixing ratios. Measurements of zero artefacts and calibration at one mixing ratio should be performed daily or every few days. Full multipoint calibrations should be performed at least every 6 months.

2.3.2 Recommendations for measurement of NO_2 by photolytic conversion of NO_2 to NO followed by chemiluminescence detection (PLC- O_3 -CLD)

The CLD instruments measure only NO. Thus, NO_2 must be converted to NO before detection. The instrument makes measurements in an NO mode and then an $NO+NO_2$ mode and the difference in these two measurements, when calibrated, gives the NO_2 mixing ratio. Thus, a high time resolution (<10 min) is recommended to ensure sampling of the same air mass during subsequent NO and NO_x measurements. The conversion of NO_2 to NO is achieved by photolysis of NO_2 at wavelengths <420 nm, as previously described in equation (2) using a photolytic converter (PLC).

In NO_2 mode, ambient air is drawn through a photolysis cell where it is irradiated with light from an appropriate light source, in most applications either mercury (Hg) or Xenon (Xe) arc lamp or UV-LEDs. A major fraction of NO_2 is photolysed with a conversion efficiency which depends on the intensity of irradiation. This conversion efficiency needs to be calibrated, and from the yield of NO the initial NO_2 mixing ratio can be calculated. The intensity of UV radiation decreases with increasing age of the light source, and so regular calibrations of the NO_2 to NO conversion efficiency are required as discussed below. Minimizing sample residence time in the photolysis cell minimizes undesired dependence on variations in ambient levels of oxidants (O_3 , RO_2 , etc.) which lead to back-reaction with the NO produced from NO_2 photolysis. Use of reduced pressure immediate after the photolysis chamber is one way of reducing the residence time.

A new approach for NO_2 to NO conversion is afforded by the use of UV light-emitting diodes (LEDs) instead of an arc lamp. Advantages of UV-LEDs are the substantially longer source lifetime and corresponding nearly constant conversion efficiencies, the mechanical simplicity, and the simple on/off characteristic of the LEDs. New LED-based converters provide sensitivity equal to or greater than traditional arc-lamp systems. The use of UV-LED converters is recommended for GAW NO_2 measurements.

NO_x monitors applied for NO_x observations in polluted environments frequently use heated molybdenum converters. Such instruments are **not recommended** for GAW sites since these surface converters are not selective to NO_2 but also convert oxidized nitrogen compounds such as nitric acid (HNO_3), peroxyacetyl nitrate (PAN), and other organic nitrates to NO at undetermined efficiencies, leading to overestimated NO_2 signals especially under clean air conditions (Steinbacher et al., 2007, Winer et al., 1974). The “ NO_2 signal” in this case is therefore some unknown fraction of NO_y rather than NO_2 .

To meet the requirements of data quality objectives and depending on stability of the conversion efficiency, a calibration of the photolytic converter should be carried out in appropriate time intervals. For calibration, NO₂ produced by gas-phase titration (GPT) of an NO-in-N₂ gas standard with added ozone is recommended. The GPT ozone source must be very stable over time, and irradiation of zero air with the 185 nm UV output from a temperature-controlled Hg pen-ray lamp has proved to be suitable. Silent electrical discharge is not appropriate for ozone production because it is not stable enough for GPT and generates small amounts of NO₂.

The PLC-O₃-CLD instrument calibration procedure is as follows:

- i) A known NO mixing ratio in zero air is produced, passed through the darkened PLC (UV light source extinguished or shuttered), and the CLD response to NO is determined: [NO]₍₁₎. This initial measurement is sufficient to determine the CLD sensitivity to NO.
- ii) The PLC is then illuminated by the UV source and a measurement is made (this gives the CLD signal due to NO in the standard gas, plus NO from any NO₂ impurities in the standard gas and/or zero air): [NO.c]₍₁₎.
- iii) The PLC UV source is extinguished, the ozone source of the GPT unit is energized, allowed to stabilize, and adjusted so that 80-90% of the NO is titrated to NO₂. The extent of titration is determined by the ensuing decrease in CLD NO signal with the GPT unit energized and the PLC extinguished: [NO]₍₂₎.
- iv) The PLC is then illuminated and the resulting CLD signal measured: [NO.c]₍₂₎.

The conversion efficiency of the PLC, *E*, is then calculated from:

$$E = 1 - \frac{\{[NO.c]_{(1)} - [NO.c]_{(2)}\}}{\{[NO]_{(1)} - [NO]_{(2)}\}} \quad (C)$$

2.4 Outlook, future measurement techniques for NO and NO₂

The development of new monitoring techniques for GAW depends on initial trial programmes being set up at one or more GAW stations with experimental instruments and the instruments and techniques being investigated for applicability to GAW long term monitoring. This applies equally to the development of improved measurement techniques for existing measurement programmes, and to the development of measurement techniques for new measurement programmes.

Other techniques that are under development and could supplement the newly developing GAW NO and NO₂ measurement programme at a future date include:

- Tuneable diode laser absorption spectroscopy (TDLAS)
- Differential optical absorption spectroscopy (DOAS)
- Laser-induced fluorescence (LIF)
- Absorption in high-finesse cavities using either narrow (CRDS) or Integrated Cavity Output Spectroscopy (ICOS) or broad-band (BBCEAS) light sources

While all NO₂ measurement techniques have limitations, and some have undesirable interferences (e.g., LIF and CL detectors show some dependence on ambient water vapour; UV photolysis can convert HONO as well as NO₂, etc.), these future techniques have been shown to provide high-quality NO₂ data (e.g. Fuchs et al., 2010), and all except DOAS could measure NO via its oxidation to NO₂ under controlled conditions. Stable long-term operation should be possible for most of the mentioned techniques. Participating GAW stations with adequate resources are encouraged to gain long-term experience with the use of these techniques and their comparison in background conditions with the standard NO and NO₂ techniques. An overriding consideration is

that it is much better to use techniques which specifically measure the molecule in question rather than use converters and measurement in some other form.

3. QUALITY ASSURANCE

The quality assurance (QA) system plays a key role in the establishment of the global observations for each compound, which is measured in the GAW Programme. The aim of the QA system is to ensure data comparability and compatibility within the network and to provide reliable assessments of the long-term variability and trends.

Main principles of the GAW QA system:

- Network-wide use of only one reference standard or scale (primary standard). In consequence, there is only one institution (assigned as a Central Calibration Laboratory, CCL) responsible for this standard.
- Full traceability to the primary standard (provided and supported by CCL) of all measurements made by Global, Regional and Contributing GAW stations. This activity is usually assigned to the World or Regional Calibration Centres (WCC/RCC).
- The definition of data quality objectives (DQOs), which indicate the acceptable level of uncertainty for the network measurements.
- Establishment of guidelines on how to meet these quality targets, i.e., harmonized measurement techniques based on Measurement Guidelines (MGs) and/or Standard Operating Procedures (SOPs).
- Use of detailed log books for each parameter containing comprehensive meta information related to the measurements, maintenance, and calibrations.
- Regular independent assessments (system and performance audits).
- Timely submission of data and associated metadata to the responsible World Data Centre as a means of permitting independent review of data quality by a wider community.

3.1 Data Quality Objectives (DQOs) for NO_x measurements

Data quality objectives (DQOs) define qualitatively and quantitatively the type, quality and quantity required of primary data and derived parameters to yield information that can be used to support decisions. In particular, DQOs specify tolerable levels of uncertainty in the data, required completeness, comparability and representativeness based on the decisions to be made (WMO, 2007).

Usually DQOs are developed by an expert community taking into consideration the objectives for observations of any particular compound. These recommendations take into consideration the efforts by different programmes and projects and present a community consensus accepted with the GAW Programme. In the case of nitrogen oxides and VOCs the efforts of the GAW community are coordinated with the CEC programme (ACTRIS project in FP7, starting in 2011) which will also work on DQOs and SOPs/Measurement Guidelines for both nitrogen oxides and VOCs.

In case of NO and NO₂ the DQOs presented in Table 2 constitute a compromise between the scientific need, the physical and chemical properties of the studied compounds and the instrumental accessibility. The scientific needs are seen in either or a combination of (i) long-term monitoring to derive changes and trends in the atmospheric composition, (ii) monitoring to enable analyses of source-receptor relationships and transport processes, (iii) photochemical process-studies at the respective GAW sites making use of all available GAW data (see Section 1 for a more extensive description of scientific needs):

- For long term measurements, trends exceeding 1% per year should be discernable, hourly measurements with a minimum 66% coverage and appropriate accuracy (see Table 2) are required.
- Examination of source-receptor relationships and transport processes need a time resolution of at least one hour since air mass change occurs in this time frame.

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

Taking into account the typical lifetime of nitrogen oxides, and the remoteness of the station with respect to distance from source areas, it is useful to set 3 different levels of DQOs according to the site characteristics, e.g. the typically encountered mixing ratios of NO_x.

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

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

¹ whichever is the larger, e.g. for level 2 “enhanced” at NO₂ of 1 ppb an uncertainty of 50 ppt is required (5% of 1 ppb), at 0.2 ppb an uncertainty of 15 ppt would be required.

² assuming that the random uncertainties are negligible compared to the calibration uncertainty

Table 2 summarises the scientific goals, instrumental techniques, and sensitivity requirements for GAW NO_x sites with different characteristics, including continental, continental background, and pristine marine locations. It should be recognized that Table 2 presents initial DQO requirements to be achieved in the NO_x network. These are expected to evolve in time for each site depending on the available technologies and the experience gained particularly in the early phase of GAW NO and NO₂ monitoring.

Commercial instruments are available with the necessary characteristics to cover both basic (Level 1) and enhanced (Level 2) situations but only research instruments developed by skilled investigators are capable of providing real measurements in pristine conditions (Level 3).

In spite of a clear scientific need to establish the data quality objectives, the above formulated requirements will indeed present a difficult measurement challenge given the low levels of NO and NO₂ expected at many of the potential GAW NO_x sites. Further, the need to quantify trends accurately over time at low ambient levels of NO and NO₂ places an additional burden on even the best measurement techniques, so that careful operation and thorough attention to detail

will be required to achieve the DQOs necessary to make atmospherically relevant measurements of NO and NO₂.

3.2 Role of the Central Calibration Laboratory (CCL)

3.2.1 Scope of the CCL

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

In the first instance, it is proposed to establish a primary standard of NO in nitrogen, at an amount fraction that will enable the uncertainty requirements for NO_x measurements in the network to be met. This will be diluted at point of use and used for calibration of NO measurements such that these meet the Data Quality Objectives (DQOs). It will also be used with ozone titration for calibration of NO₂ measurements.

Subsequently a primary facility and standards for NO₂ will be developed for use as an audit standard to validate NO₂ measurements directly. This is particularly important for the calibration of systems that measure NO₂ directly for which the use of ozone titration with an NO standard may introduce unnecessary complexity.

3.2.2 Structure of the CCL

In 2006, the Gas Analysis Working Group (GAWG) of the CCQM (Consultative Committee for Quantity of Matter) was invited to develop a model for a coordinated CCL for the GAW global long-term VOC monitoring network (WMO, 2007; Helmig et al., 2009). This is now achieved through collaboration between NPL, NIST, VSL and KRISS. In addition, the programme of international comparisons organized by the GAWG is planned to take account of the need for regular comparisons to continue to demonstrate the integrity and stability of the primary standards required by the GAW network.

CCL for NO_x will be organized in collaboration and using the experience of the metrological community.

3.2.3 Preparation, value assignment and stability of primary standards for NO

Pure NO is unstable with respect to decomposition to nitrous oxide, nitrogen dioxide and nitrogen at high pressures except in the presence of sufficient balance gas. Consequently, it is only stored after dilution in pure nitrogen to an amount fraction of 10 mmol/mol or less, which reduces this decomposition reaction to a negligible rate at room temperature. A further difficulty in handling NO at amount fractions above 1 µmol/mol that can limit the stability of NO standards is the oxidation reaction to NO₂. This reaction is eliminated by the use of extremely pure balance nitrogen with levels of oxygen below 10 nmol/mol.

When stored at high-pressure in cylinders, the polarity of the nitrogen monoxide molecule and its radical nature lead to some physisorption and chemisorption into a layer on the surface of the cylinder. Since this effect leads to the development of a surface layer, the amount of nitrogen monoxide absorbed depends on the chemical reactivity and size of the surface and is largely independent of the amount fraction of the nitrogen monoxide in the gas phase. Therefore, the effect is most observable at amount fractions below 10 µmol/mol. Consequently; cylinders with proprietary passivated coatings are used for these amount fractions and below.

Results 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. Standard mixtures at 50 µmol/mol have been shown to have decay rates of between 0.2 and 0.02% per year (Wielgosz et al., 2008). Hence, it is proposed to maintain a stable hierarchy of NO/N₂ mixtures at amount fractions of 50 µmol/mol, which will be refreshed over a time-period of several years. Dilutions will be made from this stable

hierarchy on a six-monthly basis in order to provide mixtures between 1 and 10 $\mu\text{mol/mol}$ with validated uncertainties and rates of drift. Research will quantify the performance of standards between 0,5 and 1 $\mu\text{mol/mol}$.

3.2.4 Preparation, value assignment and stability of primary standards for NO_2

Standards of NO_2 are generally prepared by NMIs by gravimetric dilution of NO in a balance of nitrogen. The NO is then converted to NO_2 by the subsequent addition of an excess of oxygen.

The current state of comparability of national standards for NO_2 at a nominal amount fraction of 10 $\mu\text{mol/mol}$ has been studied within the international comparison CCQM-K74, coordinated by the BIPM (the final report is expected in 2011.) The comparison used reference values measured for each cylinder with respect to a NO_2 permeation facility using continuous on-line weighing developed by the BIPM. This facility has been thoroughly validated and has shown a capacity to assign NO_2 value to amount fractions with relative standard uncertainties of 0.15%. Preliminary results from the comparison show that the most experienced NMIs are able to produce independent standards of NO_2 in nitrogen (with 1000 ppm O_2) that agree to within better than 0.5%.

A complication in the preparation of NO_2 standards can be caused by the presence of trace amounts of water vapour, which lead to the conversion of NO_2 to HNO_3 . At present, HNO_3 amount fractions of less than 300 nmol/mol are often present within nominally 10 $\mu\text{mol/mol}$ NO_2 standards, although careful selection of passivation for the cylinder in some NMIs can give standards with less than 50 nmol/mol of HNO_3 present. Successful extension of this research should support the extension of permeation and cylinder standard facilities to NO_2 mole fractions down to 500 nmol/mol.

The WMO/GAW Secretariat is working on an agreement with NMIs within the CCQM/GAWG for provision of the CCL for NO.

3.3 Role of the World Calibration Centre (WCC)

The World Calibration Centre (WCC) constitutes a second important component of the QA system. One of the main tasks of WCC is to assist the GAW stations to link in-situ observations to the GAW primary standard. This should be done through regular calibrations and audits at the GAW sites using transfer standards, possibly in co-operation with Regional Calibration Centres which would need to be established in future. Facing the extreme requirements for NO_x measurements in remote and pristine conditions with respect to the sensitivity and selectivity of the applied methods it is highly recommended to perform side-by-side comparisons under controlled atmospheric conditions, e.g. to use an atmospheric simulation chamber for tests under such low and controlled mixing ratios of NO_x .

The Research Centre Jülich (represented at the meeting by Franz Rohrer) has volunteered to operate the World Calibration Centre for NO_x (WCC- NO_x). This intention has been approved by the administration of the Research Centre Jülich and is supported by the QA / SAC hosted by the German Federal Environment Agency. The German Federal Environmental Agency has confirmed its interest in the establishment of the NO_x World Calibration Centre at Jülich which will be coordinated and financially and logistically supported in the framework of QA/SAC Germany.

WCC- NO_x will also perform conventional audits (to check the complete set-up on-site and followed by a side-by-side comparison at the station (if feasible)) and will improve the international compatibility by implementing an audit system for NO and NO_2 measurements at global sites of the GAW Programme. These audits are part of the quality assurance (QA) system requested in the GAW Strategic Plan (WMO, 2008). An audit involves representatives from WCC- NO_x evaluating the overall conformity of a station with the principles of the GAW QA system, as well as performing an on-site comparison of reference gases and instruments. They usually require 2-3 days. Results of the audits are provided to the participants and discussed, audit reports are made available through the internet. A more detailed description of the audit procedure can be found in the WMO

Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance (WMO, 2009b).

In addition, WCC-NO_x will make use of the “SAPHIR” chamber facility that is operated at the Research Centre Jülich. It has proven its capability in an intercomparison of 4 different measurement techniques for NO₂ namely, chemiluminescence (CLD), laser induced fluorescence (LIF), cavity enhanced absorption spectroscopy (CEAS) and broadband cavity ringdown spectroscopy (BCRDS). The SAPHIR chamber with ultra pure air can produce low ppt NO and NO₂ mixing ratios. This condition can be used to check the minimum detection limit and sensitivity of different techniques. The SAPHIR chamber is a very good facility for comparisons under controlled conditions (Fuchs et al., 2010)

3.4 Implementation of QA system on site

To ensure quality of the measurements at the GAW stations the elements of QA should be implemented on site. It is required that GAW stations:

- Adopt and follow the GAW Measurement Guidelines and SOPs and give feed-back on these documents to the WCC
- Establish quality control procedures by following the guidelines as documented by the GAW-scientific advisory group for reactive gases and WCC
- Use the recommended GAW primary standard for calibration of measurements
- Participate in instrument comparisons at central facilities and during station audits. Results from these comparisons need to be properly documented and archived. If disagreement between measurements is larger than the data quality requirements, further tests and investigations need to be undertaken to resolve and mitigate disagreements. The WCC should coordinate these activities

Due to complexity of the measurements it is important to follow these procedures and keep in contact with the respective Central Facilities (WCC and Scientific Advisory Group on Reactive Gases) and be up to date with the development of the gas standards by CCLs, it is important that the experience of participating stations be shared at regular expert meetings to ensure that the best approaches are implemented by the network.

A Measurement Guidelines document for NO_x will be published separately. It is foreseen that this document will be adjusted from time to time to take into account any substantial changes in measurement technology and with respect to experience gained in GAW-NO_x measurements.

4. DATA ARCHIVING

The global data archive for *in situ* nitrogen oxide data is the World Data Centre for Greenhouse Gases (WDCGG) maintained by the Japan Meteorological Agency (JMA, <http://gaw.kishou.go.jp/wdcgg>). All NO_x 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. WDCGG accepts irregularly spaced data (such as events/campaign) and continuous data. Of the latter, hourly data as well as higher aggregates are archived. In addition to the NO_x data, WDCGG also encourages submission of meteorological data.

The format used by WDCGG for the data is plain ASCII encoded text in tabular form, preceded by a section containing metadata. Quality checks performed by WDCGG currently include consistency checks as well as checks on data integrity. WDCGG uses ‘-9(99...)’ – with a different number of digits depending on the field – to indicate missing values. Data submitters are advised to consult the WDCGG data submission guidelines [WMO, 2009a] or to contact WDCGG prior to data submission.

Presently there are very few stations submitting data on a regular basis to WDCGG, see Section 2.1.2.

5. OUTLOOK, FURTHER NETWORK DEVELOPMENT

There was consensus at the workshop that the logical first step in implementing the GAW NO_x-NO_y network is focusing on NO and NO₂ measurements. As part of the establishment of a NO and NO₂ monitoring programme in GAW several steps are required. These include:

- Establishment of a World Calibration Centre (WCC)
- Establishment of a Central Calibration Laboratory (CCL)
- Establishment of comprehensive global NO and NO₂ observations with GAW stations as backbone
- Development of measurement guidelines, standard operating procedures and data quality objectives
- Finalising and propagation of primary and secondary standards
- Establishment of a programme of station audits
- Archiving and analysis of the resultant data

The Reactive Gases SAG has developed the concepts and much of the basic work required to implement a NO and NO₂ monitoring programme at GAW stations. These concepts will be delineated in a separate report on Measurement Guidelines. Some of the criteria put forward will evolve in time and depend substantially on the available technologies and the experience gained particularly in the early phase of GAW NO and NO₂ monitoring.

There was also consensus that the GAW network should facilitate the future measurement of other oxidised nitrogen species including peroxy acetyl nitrate (PAN) and PAN-type compounds, nitric acid (HNO₃), nitrous acid (HNO₂), and monofunctional alkyl nitrates (RONO₂). As indicated previously in Chapter 1 the rationale for such observations would be to achieve long-term monitoring and trend evaluation of the reservoir substances for NO_x in remote areas, in order to understand the role of nitrogen oxide compounds in photochemistry. Individual objectives include the role of NO_x on free radical chemistry, on acidification and exchange with land surfaces, and on aerosol properties. Alkyl nitrates can be measured from stainless steel canister samples (up to C5), as currently performed on a long-term basis for Pacific samples by the University of Irvine (Blake, 2010) and PAN can be measured using commercially available GC equipment with some modification. Additional funding would be necessary to fully integrate measurement of these molecules into the GAW nitrogen programme with its comprehensive requirements for calibration and auditing etc.

There was debate about whether a reliable measurement of total NO_y in the background atmosphere can be developed, or whether speciated NO_y measurements is the only reliable method. Adding total NO_y measurements themselves, with all the attendant uncertainties of calibration, interferences, stability over time, measurement implementation throughout a global network, and indeed lacking a definition appropriate to GAW, was considered to be less promising at this point. Again, further detailed measurements in background air are required to resolve this issue.

It was agreed at the meeting that individual nitrogen-containing compound measurements should be made using existing technology as research activities. In this way, GAW NO_{xy} stations are encouraged to add, or continue existing, measurements of PAN, HNO₃, RONO₂ etc. to demonstrate the capability of these measurements in the context of a global network. The expertise developed by station operators should ultimately lead to later inclusion of these measurements into the GAW nitrogen programme. Realistic DQOs and SOPs particularly for PAN and organic nitrates will need to be developed formally in the GAW NO_x-NO_y network in the future.

The most important issue at present concerns the global coverage of NO and NO₂ measurements within the GAW network. The current network is very limited as noted in Section 2.1.2. A major task for the Reactive Gases SAG is to find the ways to expand the number of stations reporting measurements especially of a global nature, and stimulate measurement programmes that can lead to true global coverage. It is particularly important to collect quality assured data in regions with low NO_x mixing ratios such as remote continental, pristine oceanic and polar regions, and the free troposphere.

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Abbreviations and Acronyms

BBCEAS	Broad Band Cavity Enhanced Absorption Spectroscopy
BLC	Blue Light Converter
CAPMoN	Canadian Air and Precipitation Monitoring Network
CCL	Central Calibration Laboratory
CCQM	Consultative Committee for Amount of Substance
CLD	Chemiluminescence Detection
CMDL	Climate Monitoring and Diagnostics Laboratory, NOAA (now Global Monitoring Division of the Earth System Research Laboratory, NOAA ESRL)
CSIRO	Commonwealth Scientific & Industrial Research Organisation
DBMS	Data Base Management Strategy
DOAS	Differential Optical Absorption Spectroscopy
DQO	Data Quality Objectives
DWD	National Meteorological Service of Germany
ECD	Electron Capture Detector
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
Empa	Swiss Federal Laboratories for Materials Testing and Research
ESRL	Earth System Research Laboratory, NOAA
FID	Flame Ionisation Detector
FTIR	Fourier-transformed infrared absorption spectroscopy
GAW	Global Atmosphere Watch (WMO Programme)
GAWG	CCQM Gas Analysis Working group
GAWSIS	GAW Station Information System
GG or GHG	Greenhouse Gases
GMD	Global Monitoring Division (as part of NOAA ESRL)
GURME	GAW Urban Research Meteorology and Environment project
ICOS	Integrated Cavity Output Spectroscopy
ICP	InterComParison experiment
ISO	International Organization for Standardization
KRISS	Korean Research Institute of Standards and Science
LIF	Laser-Induced Fluorescence
MG	Measurement Guidelines
NAPS	Canadian National Air Pollution Surveillance programme
NIST	National Institute of Standards and Technology
NMI	National Metrology Institute, National Measurement Institute
NOAA	National Oceanic and Atmospheric Administration (USA)
NPL	the National Physical Laboratory
PLC	Photolytic Conversion
QA	Quality Assurance
QC	Quality Control
QA/SAC	Quality Assurance/Science Activity Centre
RG	Reactive Gases
SAG	Scientific Advisory Group
SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedure
SRM	Standard Reference Material
TDLAS	Tunable Diode Laser Absorption Spectroscopy
UV	Ultraviolet radiation
VSL	the National Metrology Institute of the Netherlands
WCC	World Calibration Centre
WDCGG	World Data Center for Greenhouse Gases
WMO	World Meteorological Organization

**WMO/GAW Expert Workshop on
Global Long-term Measurements of Nitrogen Oxides**
(Hohenpeissenberg Meteorological Observatory, Germany, 8-9 October 2009)

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**WMO/GAW Expert Workshop on
Global Long-term Measurements of Nitrogen Oxides**
(Hohenpeissenberg Meteorological Observatory, Germany, 8-9 October 2009)

Agenda

Thursday, 8 October

09:00	Welcome Welcome and Introduction Introductory note WMO-GAW	Wolfgang Fricke Christian Plass-Dülmer Liisa Jalkanen
09:10	Purpose of Meeting and Background to NO _{xy} Measurements in the Troposphere	Stuart Penkett
09:30	Short presentations from programmes and stations	Chair: L. Jalkanen
09:35	NO _{xy} measurements: instrumentation depending on concentration level and time resolution	Tom Ryerson
09:50	Ground-based in-situ observations of oxides of nitrogen: experience from the Swiss National Air pollution Monitoring Network	Martin Steinbacher
10:00	The Pic du Midi station: instrumentation, results and planned NO _{xy} measurements	Francois Gheusi
10:10	NO _{xy} Measurements at Cape Verde Observatory	James Lee
10:35	NO _x measurements in the Antarctic	Neil Brough
10:45	Measurements of NO _{xy} at the Cape Grim Station	Ian Galbally
10:55	Methods for long term NO _{xy} measurements at CARE (Egbert) station	Jan Bottenheim
11:05	NO _{xy} at Hohenpeissenberg	Stefan Gilge
11:15	Special aspects	Chair: O. Tarasova
11:20	NO _{xy} measurements in China: surprising results concerning the present theory of photochemistry	Franz Rohrer
11:35	Interesting results of START and ARCTAS	Frank Flocke
11:50	High sensitivity airborne NO ₂ at 10 Hertz: advances in solid-state UV sources	Tom Ryerson
12:00	The Cabauw Intercomparison campaign of Nitrogen Dioxide measuring Instruments	A. Pieters/U. Friess
12:10	NO ₂ profiles with MAXDOAS	Udo Friess
12:25	Satellite Remote Sensing of NO ₂	Steffen Beirle
13:45 till 15:30	A General Discussion to approve/decide on Agenda, structure of Report and responsibilities	Chair: C. Plass-Duelmer Rapporteur: Holger Gerwig
	GAW- Structure, Groups and Central Facilities	Oksana Tarasova

Friday, 9 October

09:00	Nature of the GAW NO_{xy} Network, rationale, locations and species	Chair: Stuart Penkett Rapporteur: Ian Galbally
09:05	status of NO _{xy} measurements in EMEP and possible links / joint activities with GAW	Kjetil Tørseth

09:20	Discussion Rationale, Networks, Stations, species, DQO, Ground-based in situ, airborne, Remote, including a contribution by M. Schultz (MACC) on data needed for models	
10:30	Instrumentation and SOPs	Chair: Stefan Gilge Rapporteur: Tom Ryerson
10:35	Possible structure of SOPs, results of Intercomparisons as introduction to the	Stefan Gilge
10:50	Discussion Instruments and SOPs; NO ₂ conversion: PLC, BLC, Mo ; NO _y : Au/Mo converter; Comparison: CLD – NaI (EMEP); Passive sampling NO ₂ ; Uncertainties / artefacts	
Objective of this session: Recommendation for GAW concerning defined measurement methods, propose and agree on SOPs, contribution to meeting report.		
13:00	Quality Assurance and WCC	Chair: Franz Rohrer Rapporteur: M. Steinbacher
13:35	DISCUSSION QA-SAC with contribution by H. Gerwig, QA-SAC Germany; Round robins Intercomparison at WCC; Audit with reference instrument MONEY? ; WHAT is feasible?	
Objective of this session: propose and agree on WCC, evaluation of QA/QC procedures, contribution to meeting report.		
14:15	CCL and primary standards	Chair: Martin Milton Rapporteur: Oksana Tarasova
14:20	The role of NMIs through the CCQM-GAWG in the CCL for VOCs	Martin Milton
14:35	Gas standards and comparisons for NO ₂ , NO and HNO ₃ covered by BIPM-CCQM-GAWG	Robert Wielgosz
14:55	Comparability of standards for ambient NO _x and dynamic methods	Martin Milton
15:05	Discussion Standards compatible with DQO's; Availability and costs; round robin test gases	
Objective of this session: propose and agree on scale, standards and CCL, contribution to meeting report.		
15:30	Contributions to Meeting Report and Its Structure Outlook	
16:30	End of Meeting followed by Guided tour through the Observatory for interested participants	

GLOBAL ATMOSPHERE WATCH REPORT SERIES

1. Final Report of the Expert Meeting on the Operation of Integrated Monitoring Programmes, Geneva, 2-5 September 1980.
2. Report of the Third Session of the GESAMP Working Group on the Interchange of Pollutants Between the Atmosphere and the Oceans (INTERPOLL-III), Miami, USA, 27-31 October 1980.
3. Report of the Expert Meeting on the Assessment of the Meteorological Aspects of the First Phase of EMEP, Shinfield Park, U.K., 30 March - 2 April 1981.
4. Summary Report on the Status of the WMO Background Air Pollution Monitoring Network as at April 1981.
5. Report of the WMO/UNEP/ICSU Meeting on Instruments, Standardization and Measurements Techniques for Atmospheric CO₂, Geneva, 8-11; September 1981.
6. Report of the Meeting of Experts on BAPMoN Station Operation, Geneva, 23-26 November 1981.
7. Fourth Analysis on Reference Precipitation Samples by the Participating World Meteorological Organization Laboratories by Robert L. Lampe and John C. Puzak, December 1981.
8. Review of the Chemical Composition of Precipitation as Measured by the WMO BAPMoN by Prof. Dr. Hans-Walter Georgii, February 1982.
9. An Assessment of BAPMoN Data Currently Available on the Concentration of CO₂ in the Atmosphere by M.R. Manning, February 1982.
10. Report of the Meeting of Experts on Meteorological Aspects of Long-range Transport of Pollutants, Toronto, Canada, 30 November - 4 December 1981.
11. Summary Report on the Status of the WMO Background Air Pollution Monitoring Network as at May 1982.
12. Report on the Mount Kenya Baseline Station Feasibility Study edited by Dr. Russell C. Schnell.
13. Report of the Executive Committee Panel of Experts on Environmental Pollution, Fourth Session, Geneva, 27 September - 1 October 1982.
14. Effects of Sulphur Compounds and Other Pollutants on Visibility by Dr. R.F. Pueschel, April 1983.
15. Provisional Daily Atmospheric Carbon Dioxide Concentrations as Measured at BAPMoN Sites for the Year 1981, May 1983.
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192. Guidelines for the Measurement of Atmospheric Carbon Monoxide (WMO TD No. 1551), 44 pp, July 2010.
193. Guidelines for Reporting Total Ozone Data in Near Real Time (WMO TD No. 1552).
194. 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Jena, Germany, 7-10 September 2009) (WMO TD No. 1553).