GAW World Calibration Centre for Nitrous Oxide (WCC-N_2O)

Report 2009 - 2011

FZK: 351 01 069

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KIT - University of the State of Baden-Württemberg and
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Summary

The World Calibration Centre for Nitrous Oxide (WCC-N_2O) is operational since 2002 and ranges among the central facilities of the World Meteorological Organization (WMO) / Global Atmosphere Watch (GAW) Programme. Its main purpose is the improvement of the data quality of N_2O measurements in the troposphere. The WCC-N_2O is operated by the Karlsruhe Institute of Technology (KIT), Institute of Meteorology and Climate Research, IMK-IFU, and is funded by the German Federal Environment Agency (UBA) through its Quality Assurance/Science Activity Centre (QA/SAC Germany).

The activities of the WCC-N_2O during 2009 - 2011 were related to:

- laboratory analyses, notably comparisons of N_2O gas mixtures serving for calibrations or as travelling standards,
- participation in national and international intercomparison experiments,
- conducting audits at GAW stations,
- contributions to GAW documents,
- participation in national and international workshops,
- lectures held at the GAW Training and Education Centre (GAWTEC).

The main calibration standards employed by the WCC-N_2O are directly linked to the GAW N_2O scale maintained by the responsible Central Calibration Laboratory. Audits comprised a general inspection of the individual GAW station and a data quality check, in particular based on a comparison experiment involving five travelling standards of the WCC-N_2O, containing different N_2O concentrations. Important details in the context of audits were related to the quality of the analytical procedure, notably the characteristics of the detector performance, and compatibility of the N_2O measurements within the GAW network.

The audits conducted since the inception of the WCC-N_2O have revealed significant differences in the performance of the gas-chromatographic systems, even if equipped with similar instrumentation. In most cases, there are no obvious parameters of the instrumentation for major improvements in the near future. However, important progress at individual stations has been achieved, notably regarding the overall goal of the requested network compatibility of N_2O measurements. Nonetheless, the fulfilment of the N_2O Data Quality Objectives still remains a challenge.

Zusammenfassung

Das "World Calibration Centre for Nitrous Oxide (WCC-N_2O)" (Weltkalibrierzentrum für Lachgas) existiert seit 2002 und gehört zu den zentralen Einrichtungen des Messprogramms "Global Atmosphere Watch (GAW)" der Weltorganisation für Meteorologie (WMO). Seine Hauptaufgabe besteht in der Verbesserung der Datenqualität von N_2O-Messungen in der Troposphäre. Das WCC-N_2O wird vom Institut für Meteorologie und Klimaforschung, IMK-IFU, des Karlsruher Instituts für Technologie (KIT) betrieben und vom Umweltbundesamt (UBA) durch dessen Zentrum für Qualitätssicherung und wissenschaftliche Tätigkeiten (QA/SAC Germany) finanziert.

Die Aktivitäten des WCC-N_2O im Berichtszeitraum 2009 - 2011 umfassten hauptsächlich:

- Laboranalysen, insbesondere Vergleichsmessungen von N_2O-Gasmischungen, die zu Kalibierzwecken und Qualitätstests dienen,
- Teilnahme an nationalen und internationalen Vergleichsexperimenten,
- Durchführung von Audits (Begutachtungen) an GAW-Stationen,
- Beiträge zu GAW-Dokumenten,
- Teilnahme an nationalen und internationalen Workshops,
- Schulungsvorträge in Rahmen des GAW-Ausbildungszentrums (GAWTEC).

Die im WCC-N_2O vorhandenen Laborstandards sind direkt auf die GAW N_2O-Kalibrierskala rückführbar, die im zentralen Kalibrierlabor für das GAW-Programm gepflegt wird. Die durchgeführten Audits umfassten eine allgemeine Besichtigung der betreffenden Station und eine Überprüfung der Datenqualität mittels Vergleichsmessungen von fünf Gasgemischen des WCC-N_2O mit unterschiedlichen N_2O-Konzentrationen. Wichtige Einzelpunkte im Rahmen der Audits betrafen die Qualität der eingesetzten Analysemethode, insbesondere die Detektorcharakteristik, sowie die Kompatibilität der N_2O-Messergebnisse im Rahmen des GAW-Netzwerks.

Die seit der Errichtung des WCC-N_2O durchgeführten Audits haben wesentliche Unterschiede in der Leistung der eingesetzten gaschromatischen Systeme erkennen lassen, sogar bei Verwendung des gleichen Gerätetyps. In den meisten Fällen gibt es keine offensichtlichen Parameter, deren Veränderung deutliche Verbesserungen erwarten lässt. Insgesamt sind jedoch wichtige Fortschritte an einzelnen Stationen zu verzeichnen, insbesondere im Hinblick auf die angestrebte Vergleichbarkeit der N_2O-Messungen innerhalb des GAW-Netzwerkes. Dennoch bleibt die Erfüllung der GAW-Datenqualitätsziele weiterhin eine Herausforderung.

1 Introduction

The implementation of the World Meteorological Organization/Global Atmosphere Watch (WMO/GAW) World Calibration Centre for N_2O (WCC-N_2O) began in 2001, when this GAW facility was built up at the Fraunhofer Institute IFU in Garmisch-Partenkirchen, Germany. From 2002 onwards, the activities of the WCC-N_2O, which was now hosted by the Forschungszentrum Karlsruhe, IMK-IFU (Garmisch-Partenkirchen), were conducted under supervision and through funding by the Quality Assurance/Science Activity Centre (QA/SAC) Germany, operated by the German Federal Environment Agency (UBA) at its facilities in Langen. After formal approval as a GAW central facility by WMO/GAW in November 2002, the WCC-N_2O became officially operational. In October 2009, the Forschungszentrum Karlsruhe (FZK) and the University of Karlsruhe were merged to form the Karlsruhe Institute of Technology (KIT). On the web, the WCC-N_2O presents itself under www.imk-ifu.kit.edu/wcc-n2o/.

Previous project periods were described by WCC-N_2O Reports for 2003-2004, 2005, 2006, 2007-2008 as well as by reports in German for 2009, 2010, and 2011, respectively. The time under consideration in this project report spans the period from January 2009 to December 2011. Therefore, several items previously addressed in the individual reports for 2009, 2010, and 2011, respectively, are compiled here, and for the first time described in an English version of the project reports.

During this period 2009 - 2011, the WCC-N_2O was again funded by the German Federal Environment Agency (UBA) – under the Contract # FZK 351 01 069. This forms part of Germany's contribution to the GAW Programme. Since not all activities of the WCC-N_2O originally scheduled for the 3-year period could be terminated until 31 December 2011, in addition remaining work was done during the first months of 2012. This is also reported here.

2 N_2O Measurements within GAW

2.1 N_2O in the Atmosphere

Basic information about nitrous oxide (N_2O) and the scope of its global monitoring has been summarized in the GAW Atmosphere Watch Guide (WMO GAW Report No. 143). Moreover, the recent global picture is presented in the WMO Greenhouse Gas Bulletin (WMO 2011). From these references, part of the following information has been taken.

N_2O is a gas that has both natural and anthropogenic sources, such as oceans, fossil fuel, biomass burning and agricultural fertilisers, with anthropogenic contributions constituting about 40 % of all emissions (WMO 2011). It contributes about 6 % to the enhanced greenhouse effect. As such, nitrous oxide is currently the third-most important contributor to the radiative forcing of long-lived greenhouse gases. N_2O in the troposphere has increased from about 270 ppb in pre-industrial times to a global abundance of 323 ppb in 2010 with a mean growth rate of 0.75 ppb yr^{-1} over the past 10 years (WMO 2011).

N_2O is inert in the troposphere, and its major sink is its photochemical transformation in the stratosphere. Because of its long atmospheric lifetime (~ 120 years), background levels of nitrous oxide can be representatively determined at GAW global stations. Regional stations, however, may also give useful new insights into the global N_2O budget. N_2O concentration trends are used in climate models and for describing the nitrogen cycle in the atmosphere.

Since N_2O is one of the atmospheric constituents related to issues of both stratospheric ozone and climate, it is included in the measurement programme recommended for global GAW stations (WMO/GAW Report No. 80, p. 33). Flask sampling of air is an alternative method of monitoring N_2O concentrations. Flasks would be returned to a central laboratory for analysis. Typical frequencies are weekly or bi-weekly sampling.

The Data Quality Objectives (DQOs) for N_2O monitoring of background concentrations have to be based on requirements of the scientific community. As an example for the data quality needed to describe N_2O in the atmosphere correctly, the interhemispheric difference of 1 - 1.5 ppb is mentioned here. When comparing data from different sites and networks, possibly based on calibration scales of different institutions, the bias plus uncertainty must be significantly smaller than this difference in order to achieve meaningful results. The current DQOs for the GAW network are presented in section 2.5 below.

2.2 N_2O Measurement Sites

2.2.1 Overview

Contributions to global N_2O data come from different sources. These can be roughly divided into three major categories: (i) Global networks, such as NOAA/ESRL GMD (formerly CMDL) (www.esrl.noaa.gov/gmd/) and AGAGE (Prinn et al., 2000; http://agage.eas.gatech.edu/); (ii) other stations, of which some are part of GAW, with either global or regional status; and (iii) a number of laboratories and sampling sites. Fig. 1 shows the GAW Global Stations as of 2011. The global stations are listed by regions in 2.2.2.

Fig. 1: Map showing the global stations of the GAW network (source: WMO/GAW)

2.2.2 List of WMO/GAW Global Stations as of 2011

Information taken from the GAW web site:
http://www.wmo.int/pages/prog/arep/gaw/GAW_Global_st.html
Stations where nitrous oxide is measured in situ are marked with "N_2O"

GAW Global stations

GAW Global stations have the most extensive measurement programme in at least three of the six GAW focal areas. In many cases, the stations are supported by more than one agency, have strong scientific supporting programme, and provide facilities for intensive campaigns.
GAW Global stations are listed below:

Africa

1) Assekrem /Tamanrasset (Algeria)	
2) Cape Verde Atmospheric Observatory (Cape Verde)	N_2O
3) Amsterdam Island (France)	
4) Mt. Kenya (Kenya)	
5) Cape Point (South Africa)	N_2O
6) Izaña (Tenerife, Spain)	N_2O

Asia

7) Cape Grim (Australia)	N_2O
8) Mt. Waliguan (China)	N_2O
9) Bukit Kototabang (Indonesia)	
10) Minamitorishima (Japan)	
11) Danum Valley (Malaysia)	
12) Nepal Climate Observatory - Pyramid (Nepal)	
13) Lauder (New Zealand)	N_2O
14) Mauna Loa (United States)	N_2O
15) Samoa (United States)	N_2O

South America

16) Ushuaia (Argentina)	
17) Arembepe (Brazil)	

North/Central America

18) Alert (Canada)	N_2O
19) Barrow (United States)	N_2O
20) Trinidad Head (United States)	N_2O

Europe

21) Pallas/Sodankylä (Finland)	N_2O
22) Zugspitze/ Hohenpeissenberg (Germany)	N_2O
23) Mace Head (Ireland)	N_2O
24) Monte Cimone (Italy)	N_2O
25) Ny Ålesund/Zeppelin Mountain (Norway)	
26) Jungfraujoch (Switzerland)	N_2O

Antarctica

27) Neumayer (Germany)	
28) South Pole (United States)	N_2O

2.2.3 Station Information

Detailed information about GAW stations, both global and regional, is available from GAWSIS, the Station Information System of WMO/GAW (http://gaw.empa.ch/gawsis/). Based on GAWSIS and other sources (http://agage.eas.gatech.edu/; www.esrl.noaa.gov/gmd/), some basic information about N_2O measuring stations, such as coordinates, altitude, in-situ vs. grab sampling, is listed in a table of the Annex.

N_2O data are archived at the WMO World Data Centre for Greenhouse Gases (WDCGG), operated by the Japan Meteorological Agency in Tokyo (http://ds.data.jma.go.jp/gmd/wdcgg/) Guidelines for the submission of data are available as WMO/GAW Report No. 174: WDCGG Data Submission and Dissemination Guide (2007).

2.3 Role of the World Calibration Centre for N_2O

Because N_2O was included in the Global Atmosphere Watch (GAW) measuring programme recommended for global stations, the establishment of a World Calibration Centre for Nitrous Oxide (WCC-N_2O) became necessary, as outlined in the WMO/GAW Strategic Plan 2001-2007 (WMO/GAW Report No. 142): "No systematic inter-laboratory calibration scheme for standard reference gases exists. This makes it difficult to compare and combine measurements from different monitoring programmes in order to increase global coverage." (p. 34).

The recommended basic GAW QA principles are: to use internationally accepted methods and vocabulary to describe the uncertainty of measurement (ISO standards); to harmonise measurement methodology at all stations using measurement guidelines (MGs) and standard operating procedures (SOPs); to conduct regular performance and system audits aimed at checking the conformity of a station with principles of the GAW QA system.

The schematic of Fig. 2 shows the relationships of the WCC-N_2O within the GAW network. In spite of its name, the WCC-N_2O is not supposed to maintain its own calibration scale, but is linked to the WMO/GAW N_2O scale maintained by the Central Calibration Laboratory (see 2.4).

Similar to other WCCs, the tasks of the WCC-N_2O within GAW are:

- Development of quality control procedures (in co-operation with the respective QA/SAC and SAG)
- Maintaining laboratory and transfer standards that are traceable to the reference standards
- Conducting performance and system audits at stations[1)]
- Conducting round-robin experiments (intercomparisons)
- Supporting network-wide quality review (in co-operation with the respective QA/SAC)
- Providing training and long-term technical help for station scientists and technicians

[1)] Based on the WMO/GAW Report No. 142, a Performance Audit is defined as a voluntary check for conformity of a measurement where the audit criteria are the Data Quality Objectives (DQOs) for the specific parameter. In the absence of formal DQOs, an audit will at least involve ensuring the trace-

ability of measurements to the Reference Standard. A System Audit is more generally defined as a check of the overall conformity of a station with the principles of the GAW system.

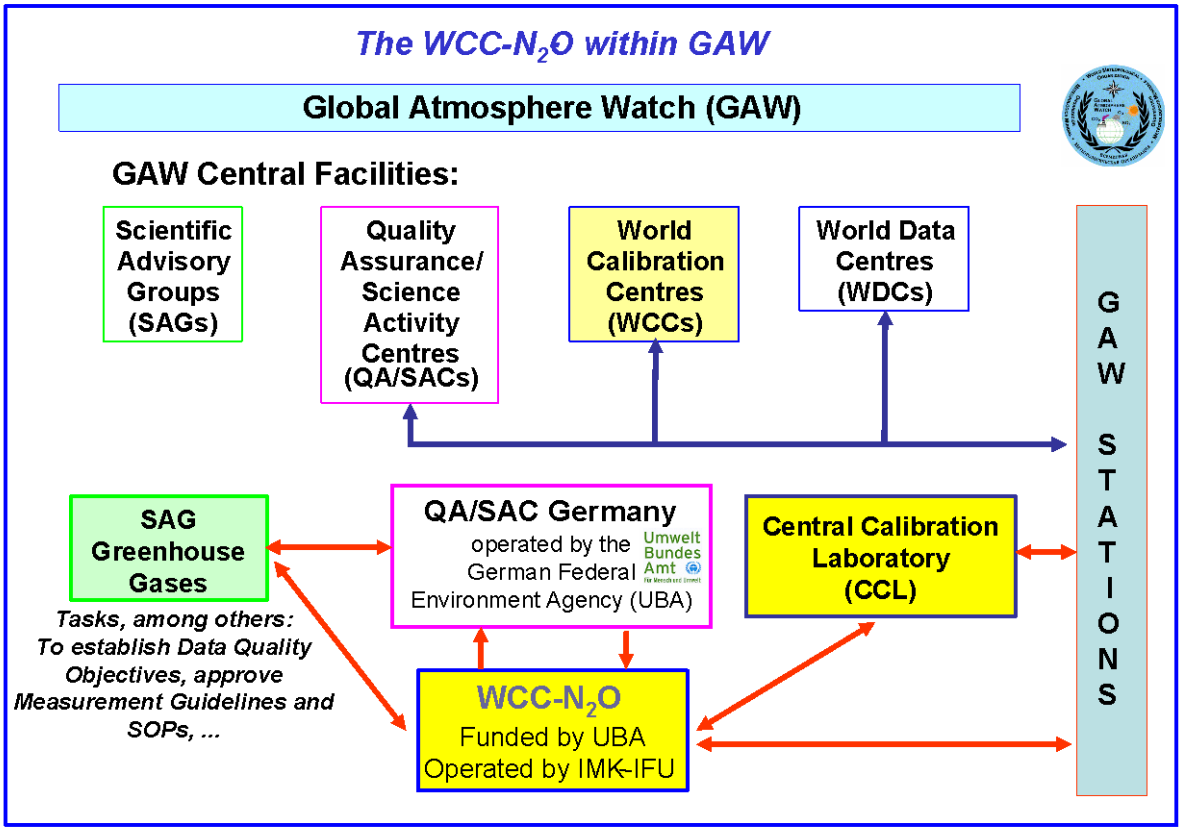


Fig. 2: Schematic showing how the WCC-N_2O is imbedded in the organisational structure of the Global Atmosphere Watch system. Top: Overview on GAW facilities, bottom: specific relationships of the WCC-N_2O.

In summary, the work of the WCC-N_2O contributes to improving the data quality in the network, harmonising the results from different stations, and – going beyond GAW – also from different global monitoring programmes. In this way, the WCC-N_2O will help to increase the overall N_2O data coverage. A priori, stations of regional status are not in the focus of the WCC activities. Exceptions, however, are prominent regional stations, such as Schauinsland (Germany) and Baring Head (New Zealand).

2.4 Standard Scale

There are two slightly different standard scales that have been in use by the two major networks, AGAGE and NOAA. One scale was developed at the Scripps Institution of Oceanography (Weiss, 1981) and has been primarily used within the AGAGE network, but also by university institutes and at other stations. Over the years the scale has been released in different versions, the currently relevant one being SIO-1998, which is related to the previous SIO-1993 according to SIO-1998 = SIO-1993 *1.0058 (Prinn et al., 2000).

The other important N_2O scale is the NOAA scale (Butler et al., 1988, 1989, 1998; Thompson et al., 2004; Hall et al., 2007). For the most recent information on the scale see http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html.

The internal consistency of this scale has been improved over the years. Because of the relatively wide range of mole fractions covered by the scale and the possibility of easy distribution of standards to GAW participants, the NOAA scale has been designated as the standard scale for the GAW network (WMO/GAW Report No. 142 and - in more detail - Report No. 161, p. 8-9). Therefore, NOAA has been assigned as the Central Calibration Laboratory (CCL). For current details of the CCL see http://www.esrl.noaa.gov/gmd/ccl/.

In recent years, the 2006 version of the NOAA scale has been developed (Hall et al., 2007), and its adoption is strongly recommended to all GAW participants. All N_2O mole fractions reported by the WCC-N_2O since January 2007 have been expressed in the NOAA-2006 scale.

In 2006 the CCL has conducted an informal intercomparison with SIO and found good agreement between the two scales over the range 298 – 319 ppb. Furthermore, the NOAA-2006 scale was found to be 0.23 % higher than the NIST scale (Hall et al., 2007).

Mole fractions expressed in the previously used NOAA-2000 scale can be converted to the NOAA-2006 scale by using the following polynomial (Hall et al., 2007):

$$Y = -2.20205 \cdot 10^{-7} * X^3 + 1.20704 \cdot 10^{-4} * X2 + 0.98343 * X,$$

where Y is the mole fraction [ppb] on the 2006 scale and X is the mole fraction on the 2000 scale. The 2006 scale is 0.19 ppb lower than the 2000 scale at 320 ppb N_2O. Note that the coefficients given in the 2006 WCC-N_2O report were slightly different, since those constituted a first version on the web, which was later corrected.

According to information given in earlier versions of the ESRL GMD web site, the above relationship is valid over the range 260 - 370 ppb. The reproducibility of N_2O calibrations was evaluated by measuring a 313.4 ppb standard every 2-3 weeks for 2 years. The standard deviation of all measurements was 0.09 ppb and nearly all results were consistent within 0.2 ppb. Therefore, the reproducibility of N_2O analyses at the CCL is estimated to be 0.2 ppb or better. According to the WMO/GAW Report No. 194, p. 14 (WMO, 2011), the reproducibility of NOAA N_2O calibrations (2 sigma) is assumed at 0.16 nmol mol^{-1} at the 95% confidence level.

The N_2O scale issues have become more complicated due to a scale update by the CCL in 2010, which resulted in the NOAA-2006A scale. As described in detail under http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html, the update was made after a drift of one of the five secondary standards used to calibrate the N_2O instrument in the CCL had been noticed. In detail, the following information is provided by the web site (as of April 2012):

> *"This drift not only impacted calibrations performed when this secondary standard was in use, but it also affected the transfer of the scale from one set of secondaries*

(used from Jan. 2006 to Jul. 2010) to a new set (in use since Jul. 2010). A new method of drift correction was implemented December 2011 and all data were re-processed. In addition, curve fitting routines have been updated from "ordinary least squares" to "orthogonal distance regression". These changes resulted in small (0.05-0.1 ppb) changes in assigned N_2O values. Because the scale is still based on the same 2006 primary standards, the scale has been renamed 2006A. Further, because the new curve fitting routines are applied on a monthly basis, it is not possible to determine a single formula to relate the 2006 and 2006A scales. For updated N_2O results, see the GMD CCL Reference Gas Calibrations page (http://www.esrl.noaa.gov/gmd/dv/ccg/refgas/).

In practice, this means that each GAW participant has to look up the most recent mole fractions for his/her laboratory standards at the above address (by input of cylinder number). From the individual processing of the respective values, corrections of previously obtained own results can be calculated (for details see 3.1.2.1). Unfortunately, the modification of the mole fraction calculation introduced by the CCL temporarily contained an error, which could lead to significantly different mole fraction values for some cylinders. The problem was only fixed in May 2012, after a few GAW participants – including the manager of the WCC-N_2O – had contacted the CCL.

The traceability chain foreseen for GAW is shown in the schematic of Fig. 3. The overall goal is to establish traceability of measurements to a single scale. In order to help achieving this aim, the WCC-N_2O has been implemented as a GAW facility.

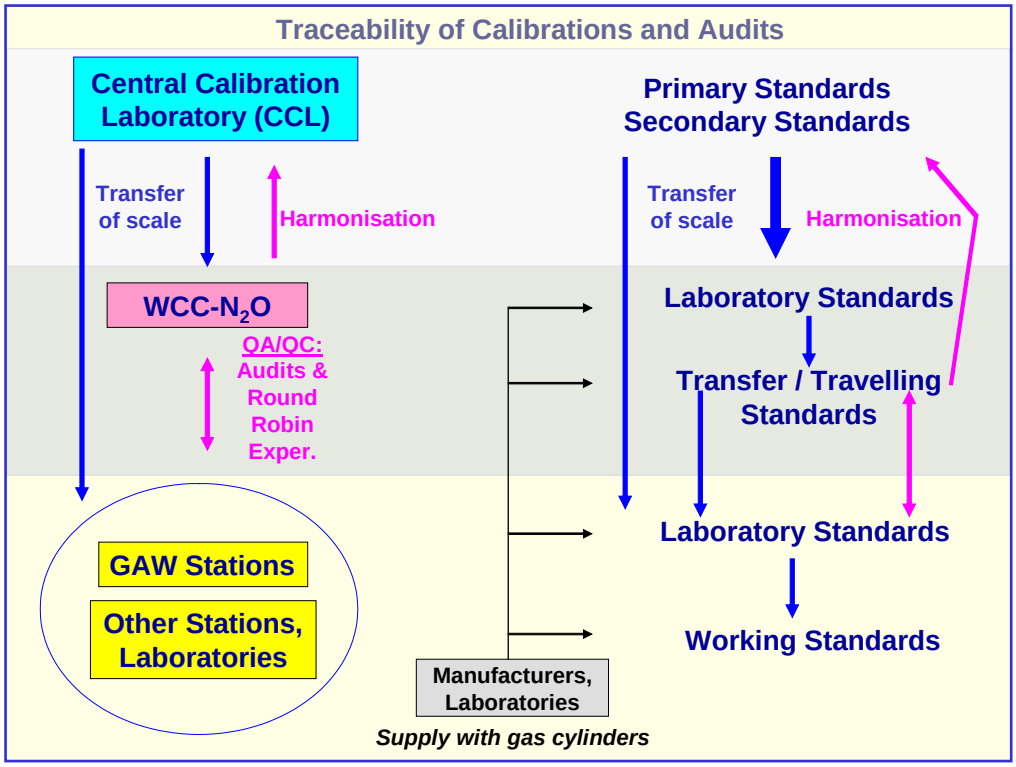


Fig. 3: Concept for traceability of the N_2O scale, in terms of institutions (left) and hierarchy of standards (right). The concept for the calibration is based on the NOAA standard scale for N_2O. NOAA-calibrated gas mixtures constitute the secondary standards to which all laboratory and transfer standards of the WCC (tertiary level) will be related to.

2.5 Data Quality Objectives (DQOs)

Data Quality Objectives are fundamental to QA/QC activities of the WCC-N_2O. The target objectives are driven by the requirements of the scientific community. As such, future targets may go beyond the current analytical capabilities. In a first approach, DQOs for N_2O were defined by the Scientific Advisory Group for Greenhouse Gases (SAG GG) during its meeting in Toronto (September 2003). Based on several discussions, notably during the 13th and 14th Experts Meetings and the subsequent meeting of the SAG GG in September 2005 and September 2007, respectively, several modifications to the earlier version of the DQOs were made. The most recent version of the DQOs is briefly summarised here as follows:

Relevant range of N_2O mole fractions: For basic calibrations of the analytical system and for intercomparisons, five (or better even six) different N_2O mole fractions ranging between 290 and 350 ppb should be used. This will determine the response curve of the ECD for N_2O. For ambient measurements, the most important range is between 310 and 330 ppb, for which more stringent objectives are set out than for the upper and lower wings.

Instrumental precision: The repeatability, expressed in terms of relative standard deviation, should be determined from multiple, interspersed analyses of a gas of constant N_2O mole fraction (e.g. working standard) during routine operation. The target value, as driven by scientific requirements, is 0.1 ppb (1 standard deviation), equivalent to 0.03% at ambient levels.

Uncertainty of ambient N_2O measurements: The uncertainty associated with ambient N_2O measurements can be separated into contributions related to instrumental precision, uncertainty associated with the standard scale, uncertainty of the working standards employed at a specific site as well as systematic analytical deficiencies. A small bias of the CCL N_2O scale is not relevant. It is the ability of the CCL to propagate the CCL N_2O scale to participating GAW laboratories that is important, as long as all laboratories are on the WMO/GAW scale. Uncertainty will be estimated by intercomparisons with standards provided within a round-robin experiment, intercomparisons as part of an audit or systematic intercomparisons of measurements of the same discrete samples with another lab. Such exercises will determine if measurements at different sites and from different institutions are on the GAW N_2O standard scale.

With respect to the resulting uncertainty, the following Data Quality Objectives have been defined and approved by the SAG GG. Target Data Quality Objectives are: Maximum standard uncertainty 0.1 ppb for the entire range of 290 to 350 ppb (cf. WMO/GAW Reports No. 161 and 168). Uncertainties (coverage factor = 1) larger than 0.5 ppb in the range 310 - 330 ppb, and 0.8 ppb for the upper and lower wings can be included in the database, but should be flagged. The above-defined intercomparison objectives will determine the network or interlaboratory compatibility of N_2O measurements.

3 Activities of the WCC-N_2O

3.1 Laboratory

The main tasks of the laboratory operated by the WCC-N_2O are to

- maintain analytical equipment for N_2O measurements that fulfils the quality objectives of GAW,
- keep an appropriate number of laboratory standards that were directly calibrated by the CCL,
- keep an appropriate number of travelling standards for audits and/or round-robin experiments,
- make comparisons between gas mixtures, which will usually be contained in high-pressure cylinders.

3.1.1 Gas Chromatograph

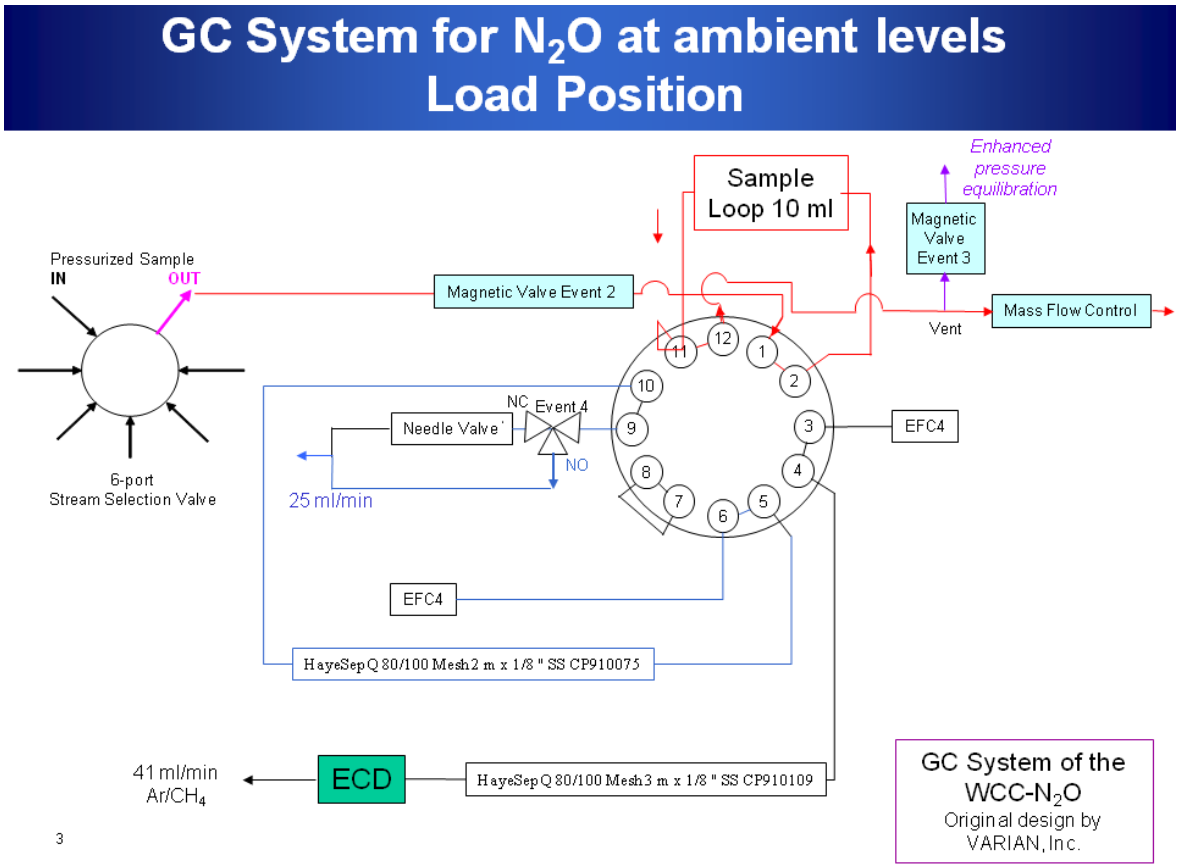
The classical technique for quantifying N_2O mole fractions at ambient levels is based on a gas chromatographic (GC) system with packed column and electron capture detector (ECD). After the fine-tuning of instrumental parameters during 2005, no major changes were made thereafter. Minor variations of GC parameters practically yielded the same overall precision. Noteworthy details are described under 3.1.1.1.

3.1.1.1 Instrumental Setup and Gas Flows

The instrumental parameters of the Varian GC 3800 and the gas flow configuration as used during recent years are given below:

Oven:	55 °C
Column:	HayeSep Q (80/100 mesh), 1/8" x 3 m main column
	HayeSep Q (80/100 mesh), 1/8" x 2 m backflush
Carrier gas:	Ar/CH_4 (95/5 %)
ECD:	Varian, 390 °C
Make-up gas:	Ar/CH_4 (95/5 %), 5 mL min^{-1}
	no makeup gas flow since July 2010
Gas sampling valve:	Valco 10-port (in separate oven at 50 °C)
Sample loop:	10 mL

Experiments with various flows of make-up gas in 2010 showed that the previously used small flows, notably 5 mL min^{-1}, were no longer essentially needed. Since minor leaks in the supply line could be a source of baseline noise, the make-up gas flow was set to zero in the CG methods file in July 2010.



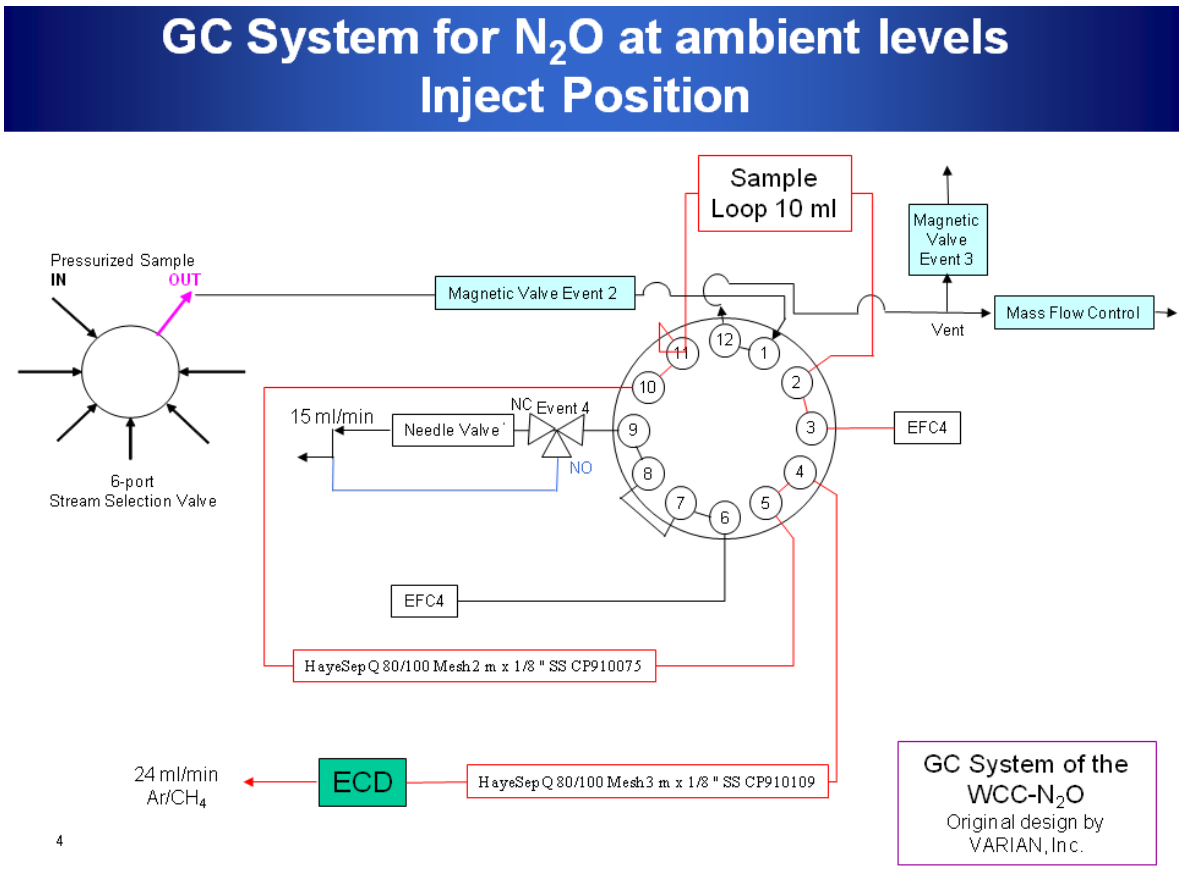


Fig. 4: Gas flow schematic of the gas chromatographic system in the laboratory of the WCC-N_2O for LOAD (top) and INJECT position (bottom).

With the aim of enabling a faster equilibration of the pressure in the sample loop after its flushing with sample air (Load position in Fig. 4), an additional valve was installed in July 2010. In this way it is possible to adjust the sample pressure in a wider range (ca. 0.5 – 1.5 bar) without need of careful adjustment to guarantee a complete equilibration in the sample loop to ambient pressure after the flushing is stopped. As a result, the repeatability (in %) of the analysis results was slightly improved by a value of about 0.01 %.

3.1.1.2 Performance of the Gas Chromatographic System

A typical chromatogram as obtained in the laboratory of the WCC-N_2O is shown in Fig. 5. At present, the retention time is at 6.85 minutes. It is very stable, with a standard deviation over 30 runs of 0.0005 min. Important features to enable good-quality analysis results are the full separation of the N_2O peak from the preceding CO_2 signal and from the subsequent small SF_6 peak. With the settings for pre-integration data bunching used for routine analyses, the baseline noise band typically amounts to 25 µV (peak-to-peak). The N_2O peak for ambient levels is typically ≥ 25 mV, which means a signal-to-noise ratio of 1000 or better. Due to the non-linearity of the ECD response, either 2-level calibration at appropriate levels or use of a separately determined response curve is necessary.

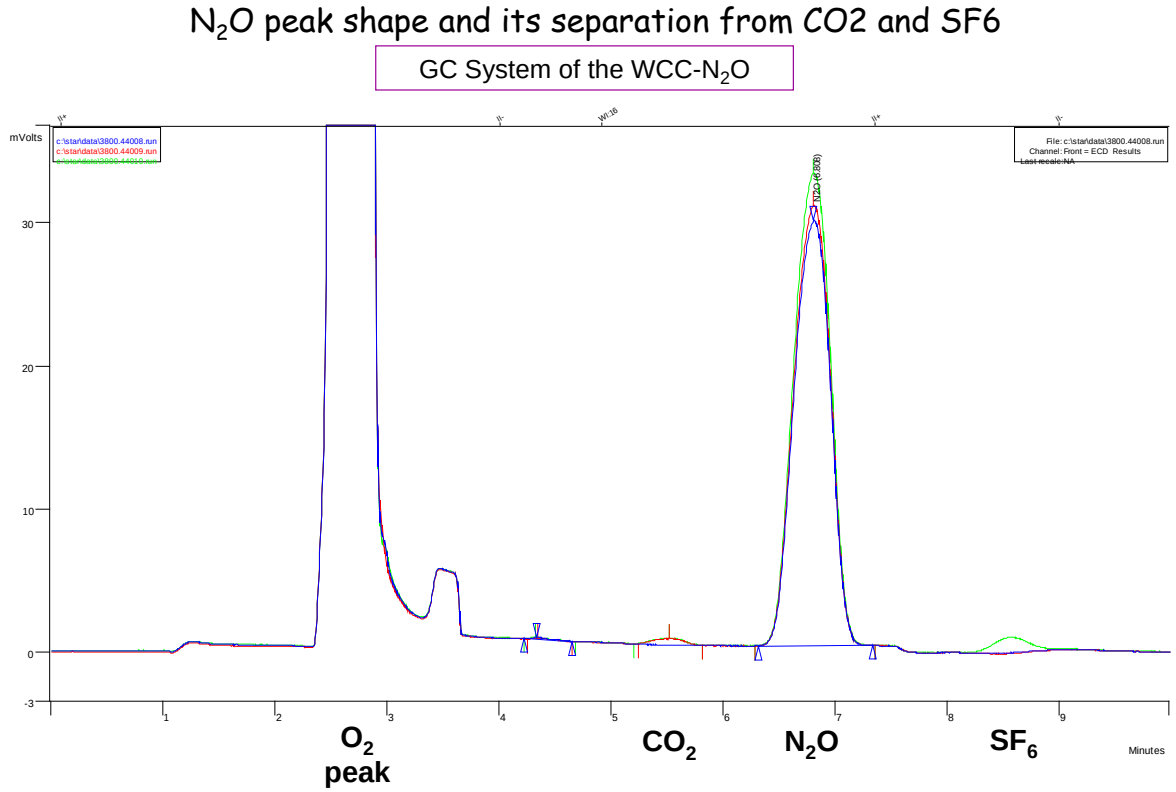


Fig. 5: Overlay of three typical chromatograms of N_2O at about ambient levels as obtained in the WCC-N_2O laboratory. Two of the samples contain CO_2, one sample also SF_6.

The typical repeatability of the N_2O mole fractions is slightly improved compared to the situation in 2006. It now ranges between 0.05 and 0.07 % (1 std. dev.); i.e. 0.15 - 0.2 ppb at ambient levels of N_2O (around 320 ppb). These numbers refer to analysis runs comprising a 2-

level calibration scheme and 14 injections of the unknown sample (u). With the standards S1 and S2, the routinely used sequence consists of S1, S1, S2, S2, u, u, S1, S1, S2, S2, u, etc. Assuming a 0.2 ppb standard deviation and n = 14, the standard uncertainty of the sample mean (std / √n) is 0.05 ppb, and the expanded uncertainty (coverage factor 2), corresponding to about the 95% confidence level, would be 0.1 ppb. The typical reproducibility, as estimated from the statistics over different series of comparisons of individual standards, is between 0.03 and 0.05 %.

While usually a carrier gas (Ar / CH_4), quality of 4.5 / 3.8 is employed, in the recent years an improved quality of the type 6.0 / 4.5 was used with the aim of guaranteeing an optimal performance of the GC system. It is noted that no obvious improvement could be quantified.

It is characteristic for the gas chromatographic technique that part of the analytical performance cannot be fully controlled by the operator. This refers particularly to the signal-to-noise ratio of the ECD. Moreover, the performance of the separation columns, such as peak resolution and tailing, can vary significantly between columns of the same type. Both components of the system strongly affect the resulting repeatability. In conclusion, there are only limited possibilities of improving the GC analysis in the future with respect to the final targets set out by GAW. As a result of the development of laser-based gas analysers in the recent years, in 2011 it actually became obvious that such new types of instruments will be capable to replace the GC technique for N_2O analysis in the near future.

According to the above considerations, a gas chromatographic system should be viewed as a complex unit for which the quality can only be characterised based on statistics of the analytical results. A quantification of the performance of individual components is not meaningful. For systems as the one considered here, the N_2O mole fraction range is limited by the suite of calibration standards available in the laboratory. For GAW applications, the range is prescribed by GAW documents, notably the Measurement Guidelines (WMO/GAW Report No. 185), and is set to 290 – 350 ppb.

3.1.1.3 Quality Assurance

Quality assurance as practiced in the laboratory of the WCC-N_2O comprises a suite of individual steps, which are tailored to the specific requirements. In detail these are:

- Laboratory logbook

- Archiving of all files generated by the computer for control and data processing with back-up on external media. The main file types comprise (i) files for methods and system control, (ii) GC raw data, which can be reprocessed, (iii) files with summary results of analysis sequences, (iv) data processing and result files in Excel format.

- The essential step of the quality assurance of the N_2O results is related to comparisons of different standards. By analysing a standard with well-quantified N_2O mole fraction as unknown sample, the analytical performance of the GC system can be assessed.

3.1.2 Standards

According to the traceability chain (Fig. 3) and the recommended GAW terminology (cf. the web-based Glossary (http://gaw.empa.ch/glossary/glossary.html), the standards of highest rank kept at the WCC-N_2O are Laboratory Standards (LS). Since both primary and secondary standards are exclusively located at the Central Calibration Laboratory (CCL), the LS are at the tertiary level within the entire hierarchy. These are gas mixtures that were calibrated by the CCL. The Laboratory Standards are used to calibrate a suite of Transfer Standards or Travelling Standards (TS). These are intended for audits and intercomparisons by the WCC-N_2O.

3.1.2.1 Laboratory Standards

Although this project report is focussed on the period 2009 – 2011, it is interesting to review the entire history of the WCC-N_2O laboratory standards and their assigned mole fractions as related to the different versions of the NOAA scale in the course of time.

The set of laboratory standards initially comprised seven 30-L cylinders containing N_2O in ultra-pure air. These were prepared by Scott-Marrin Inc. (Riverside, CA, USA; http://www.scottmarrin.com/) in 2001 and 2005, respectively, and subsequently calibrated by the CCL (NOAA/ESRL GMD (formerly NOAA CMDL), Boulder). They cover the range of mole fractions between 250 and 350 ppb. In the second half of 2008 another gas mixture was purchased from Scott-Marrin and calibrated by the CCL. This eighth standard was acquired to close a gap of mole fraction values at the upper end.

A recalibration of the seven initial laboratory standards took place in June 2005. According to an earlier version of the Measurement Guidelines for N_2O, a recalibration in the Central Calibration Laboratory would be due every five years. However, later recommendations as given in WMO/GAW Report No. 185 (WMO, 2009) request a 3-yearly recalibration. While this report is written (early 2012), considerations are underway in the GAW community to extend the period to four years. The requested 3-year period implied that the cylinders should be sent to the CCL in 2008 already. Due to urgent needs of the standards in the laboratory, this was only initialised towards the end of 2008, and the recalibrations were performed in February 2009.

The cylinder numbers and mole fractions assigned by the CCL in 2005 are shown in Table 1.The recent recalibration has confirmed the previously assigned values. According to WMO/GAW Report No. 161, p. 9, the consistency for assigning values to standards by the CCL could be guaranteed at ± 0.3 ppb at that time. Meanwhile these limits have been narrowed to ± 0.2 ppb (Hall et al., 2007) or even better. At the beginning of 2007 the mole fractions of the laboratory standards kept by the WCC-N_2O have been converted to the NOAA-2006 scale using the conversion formula provided at that time (Table 1). The absolute uncertainty of the scale is estimated at ± 1.06 ppb by the CCL (Brad Hall, NOAA ESRL GMD, personal communication, Nov. 2009).

Table 2 shows the mole fractions of the eight standards in the NOAA-2006A scale. The values taken from the CCL web site(an example is shown in Fig. 6) in October 2011 differ

slightly from the most recent ones resulting from an additional revision of the calculation scheme by the CCL (as described in 2.4). It is important to note that the NOAA-2006A scale has not been used for the operational work of the WCC-N_2O during the project period under consideration here. Thus, all results of comparisons and audits presented below are related to the NOAA-2006 scale, however, with the exception of the audit of Baring Head / NIWA laboratory conducted in October 2011. In this case the responsible scientist reported the comparison results in the NOAA-2006A scale (see 3.3.7.3).

For the conversion of mole fractions for WCC-N_2O cylinders that were not analyzed by the CCL, such as travelling standards, the WCC-N_2O is using correction terms obtained from a fit of "new" versus "old" mole fractions of the laboratory standards. When taking the values of October 2011 (see Table 2), a straight line indicates a subtraction of 0.08 ppb over the entire range from 290 to 350 ppb (Fig. 7). In contrast, the values for the laboratory standards as provided by the CCL in May 2012 yield a second order relationship (Fig. 7). Thus, to convert the mole fraction numbers of gas mixtures kept by the WCC-N_2O from NOAA-2006 to NOAA-2006A, the following formulas should be applied:

$$[\text{NOAA-2006}\mathbf{A}] = 7.4356\text{E-}05 * [\text{NOAA-2006}]^2 + 0.95730 * [\text{NOAA-2006}] + 5.922$$

or alternatively:

$$[\text{NOAA-2006}\mathbf{A}] = [\text{NOAA-2006}] - (-7.43556\text{E-}05 * [\text{NOAA-2006}]^2 + 0.0427035 * [\text{NOAA-2006}] - 5.922)$$

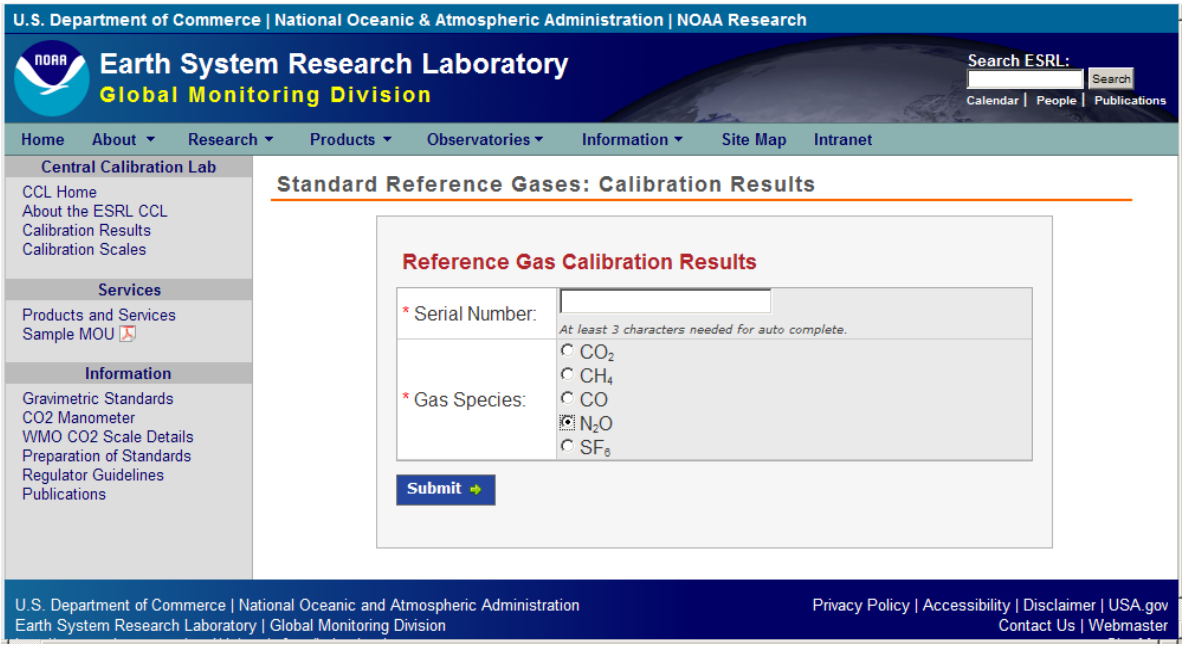


Fig. 6: Screen shot of the web-based tool to grab the current mole fractions of cylinders that have been analyzed at the CCL (http://www.esrl.noaa.gov/gmd/dv/ccg/refgas/).

Table 1: Laboratory standards of the WCC-N_2O. (1) N_2O values [ppb] of the Central Calibration Laboratory as of 2005 based on the NOAA-2000 scale; (2) values converted to the NOAA-2006 scale according to the formula of Hall et al. (2007); (3) values determined by the recalibration in early 2009 together with standard deviations given by the CCL. The new standard of 2008 was directly calibrated in the NOAA-2006 scale.

Cylinder	N_2O [ppb], 2005 NOAA-2000 scale	N_2O [ppb] NOAA-2006 scale	**N_2O [ppb], 2009** NOAA-2006 scale	Standard deviation [ppb]	Rel. std. dev. [%]
CA 04787	253.77	253.74	253.34	0.15	0.06%
CA 04785	312.53	312.42	312.26	0.08	0.03%
CA 04800	326.15	325.95	325.84	0.09	0.03%
CA 04743	333.50	333.23	333.36	0.14	0.04%
CA 04752	358.68	358.10	358.12	0.14	0.04%
CA 06234	293.60	293.27[a)]	293.34	0.11	0.04%
CA 06246	320.83	320.67	320.58	0.11	0.03%
CA 08456	---	---	350.79	0.09	0.03%

a): Based on results of the CCL for five WCC-N_2O travelling standards in 2007, the number has been lowered by 0.3 ppb, which means that an assigned value of 293.27 is used.

Table 2: Laboratory standards of the WCC-N_2O. (1) N_2O values [ppb] of the Central Calibration Laboratory determined by the recalibration in early 2009, NOAA-2006 scale, together with standard deviations; columns 2,3,4. (2) Values expressed in the NOAA-2006A scale according to the CCL web site as of October 2011; column 5. (3) Values expressed in the NOAA-2006A scale according to the CCL web site as of April 2012, column 6; and May 2012 or later, column 7.

Cylinder	**N_2O [ppb], 2009** NOAA-2006 scale	Standard deviation [ppb]	Rel. std. dev. [%]	**NOAA-2006A scale**, CCL web site, **Oct 2011**	***NOAA-2006A scale,*** *CCL web site,* ***Apr 2012***	**NOAA-2006A scale**, CCL web site, **May 2012**
CA 04787	253.34	0.15	0.06%	253.28	*253.15*	253.22
CA 04785	312.26	0.08	0.03%	312.18	*312.03*	312.11
CA 04800	325.84	0.09	0.03%	325.76	*325.69*	325.76
CA 04743	333.36	0.14	0.04%	333.28	*333.22*	333.29
CA 04752	358.12	0.14	0.04%	358.05	*358.23*	358.30
CA 06234	293.34	0.11	0.04%	293.24	*293.03*	293.11
CA 06246	320.58	0.11	0.03%	320.51	*320.40*	320.47
CA 08456	350.79	0.09	0.03%	350.74	*350.78*	350.86

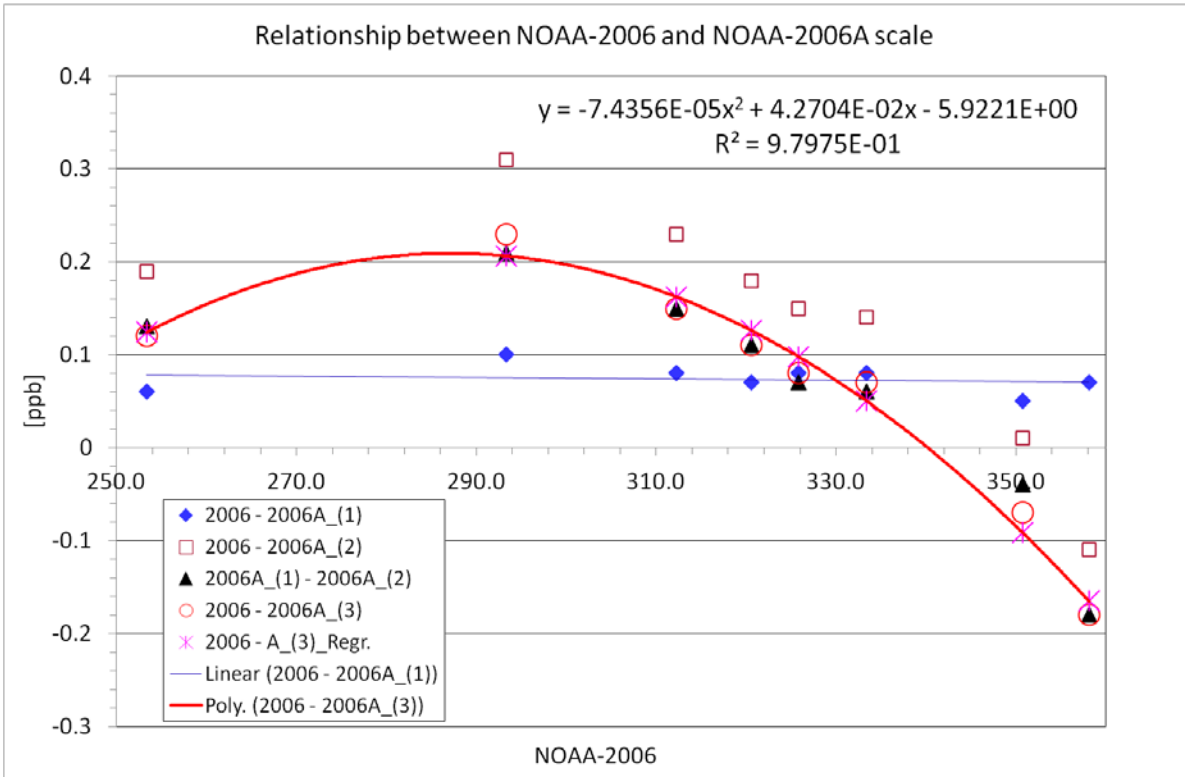


Fig. 7: Corrections for conversion from the NOAA-2006 scale to the current NOAA-2006A scale. The figure is based on the N_2O values for the 8 laboratory standards of the WCC-N_2O listed in the columns 2, 5, 6 and 7 of Table 2. The terms 2006_(1), _(2), and _(3) refer to mole fractions of October 2011 (col. 5), April 2012 (col. 6) and May 2012 (col. 7), respectively. The values taken from the CCL web site of October 2011 yielded a linear relationship (blue symbols and line). The values of April were erroneous. The most recent ones (May 2012) follow a second order relationship (red circles and regression curve).

While the text on the web page says that the scale changes amounted to about 0.05 to 0.1 ppb, greater changes are seen here. When looking at the differences for the WCC-N_2O laboratory standards (last calibrated in 2009), the differences are up to 0.23 ppb at 293.11 ppb, while they change sign and are at -0.18 ppb at 358.3 ppb (Fig. 7). Thus, in total the changes are spanning an interval of 0.41 ppb. In conclusion, the above adjustments obtained for the laboratory standards of the WCC-N_2O are not easy to explain since the corrections were assumed by the CCL to be caused by the drift of one secondary standard at a rate of about 0.12 ppb within five years, as taken from the CCL web site. Therefore, discussions with the CCL were still ongoing while this report was being finalized.

3.1.2.2 Travelling Standards

The first series of five standards consist of 10-L aluminium cylinders with mixtures of N_2O in synthetic air manufactured by Deuste Steininger, Mühlhausen, Germany. According to an earlier version of the DQOs, a range from 250 to 350 ppb should be covered by intercomparisons. Their assigned mole fractions were given in the 2006 Report of the WCC-N_2O.

This first series of 10-L cylinders (short names DS1 – DS5), originally also intended as travelling standards, were kept in the laboratory and serve as backup for the calibration scale. Because of the absence of other species in the mixture, which are of interest in N_2O quality control, notably CO_2 and SF_6, these standards are less suited for external intercomparisons, including audits. Results of recent reanalyses of these five standards are reported below under Laboratory Activities.

The present travelling standards account for a reduced testing range. As prescribed by the current DQOs, the relevant N_2O range for intercomparisons is only 290 - 350 ppb. Moreover, according to recent GAW requirements, standards used for N_2O should contain atmospheric levels of N_2, O_2, and CO_2, and in addition, preferably also SF_6. The presence of CO_2 and SF_6 is requested in order to assess possible interference of these species with the N_2O peak in the gas chromatogram. Table 3 gives an overview on the composition of the gas mixtures used as travelling standards.

Based on the currently available gas mixtures, two sets of 5 cylinders each can be combined for external comparisons or audits within the requested range of approximately 290 to 350 ppb N_2O.

Table 3: List of gas mixtures from which cylinders are selected to serve as travelling standards. 17 standards (DS6 – DS22) contain at least one other trace gas in addition to N_2O for testing purposes. The Cyl ID shows the short names, the cylinder numbers are listed in Table 4.

Cyl ID		**N_2O**	**SF_6**	**CO_2**	**CH_4**	**CO**
DS1		+				
DS2		+				
DS3		+				
DS4		+				
DS5_2		+				
DS6		+		+		
DS7		+		+		
DS8		+		+		
DS9		+		+		
DS10		+		+		
DS11		+	+	+		
DS12		+	+	+		
DS13		+	+	+		
DS14		+	+	+		
DS15		+	+	+		
DS16		+	+	+		
DS17		+	+	+	+	+
DS18		+	+	+	+	+
DS19		+	+	+	+	+
DS20		+	+	+	+	+
DS21		+	+	+	+	+
DS22		+	+	+	+	+

In order to provide an overview on the development of the mole fractions assigned to the travelling standards of the WCC-N_2O, the following information is given here: Five travelling standards were directly intercompared with the CCL at the beginning of 2007 (Table 4). The values determined by the CCL were reported in the new NOAA-2006 scale. The related standard deviations at the CCL were less than 0.15 ppb, number of data = 32. As previously described, according to Hall et al. (2007) and more recent information, the NOAA scale can now be maintained to within 0.2 ppb or even better.

For four out of the five standards, the agreement between CCL and WCC-N_2O was within a range of about 0.1 ppb. This comparison has defined the uncertainty associated with the mole fractions assigned to the travelling standards.

The mole fractions presently used for the travelling standards are presented in Table 5. Current values as related to the NOAA-2006 scale and mole fractions converted to the NOAA-2006A scale by way of the formula given above are listed. In addition, the results of comparisons with the CCL are shown. Results of 2007 (*in italic*) are listed for three cylinders only, since the other two cylinders also took part in the 2011 comparison. More information on the comparison between WCC-N_2O and CCL employing five travelling standards is provided in section 3.2.4.

Table 4: Gas mixtures in 10-L cylinders serving as Travelling Standards of the WCC-N_2O. Overview on mole fractions as assigned prior to 2009.

Cylinder		Additional gases in mixture		N_2O [ppb] as assigned by WCC-N_2O		CCL results (intercomparison 2007) [ppb]	Diff.: WCC – CCL [ppb] (2007)
Number	Short name	CO_2	SF_6	Based on NOAA-2000 scale	Converted to NOAA-2006 scale	NOAA-2006 scale	
4600	DS 6	+		253.40	253.37		
4556	DS 7	+		305.56	305.49		
4585	DS 8	+		315.29	315.16		
4588	DS 9	+		330.45	330.21		
4594	DS 10	+		347.90	347.47	347.35	0.12
6061	DS 11	+	+	296.30	296.26	295.89	0.37
4618	DS 12	+	+	326.59	326.38		
4563	DS 13	+	+	332.91	332.65	332.77	-0.12

4616	DS 14	+	+	306.03	305.95	305.89	0.06
4586	DS 15	+	+	319.12	318.97	318.90	0.07
4590	DS 16	+	+	332.59	332.33		
481362	DS 17	+	+		284.67 [a)]		
481310	DS 18	+	+		305.60 [a)]		
481454	DS 19	+	+		313.71 [a)]		
481333	DS 20	+	+		317.10 [a)]		
481356	DS 21	+	+		336.87 [a)]		
481319	DS 22	+	+		346 [a)]		

a) Provisional value assigned by the WCC-N_2O.

Table 5: Gas mixtures in 10-L cylinders serving as Travelling Standards of the WCC-N_2O. Current mole fractions as related to the NOAA-2006 scale and mole fractions converted to the NOAA-2006A scale by way of the formula given above. In addition, the results of comparisons with the CCL are shown (*of 2007 in italic*).

Cylinder		N_2O [ppb] currently assigned by WCC-N_2O		CCL results (intercom-parisons *2007* and 2011) [ppb]	Diff.: WCC – CCL [ppb]
Number	Short name	Based on NOAA-2006 scale	Converted to NOAA-2006A scale	NOAA-2006A scale	
4600	DS 6	253.40	253.28	–	
4556	DS 7	305.56	305.38	–	
4585	DS 8	315.29	314.82	–	
4588	DS 9	330.45	330.37	–	
4594	DS 10	347.90	347.50	*347.34*	*0.16*
6061	DS 11	296.30	295.89	*295.89*	*0.00*
4618	DS 12	326.59	326.08	–	
4563	DS 13	332.91	332.84	332.65	0.19
4616	DS 14	306.03	305.95	*305.86*	*0.09*

4586	DS 15	318.96	318.82	318.77	0.05
4590	DS 16	330.98	330.90		
481362	DS 17	284.94	284.74		
481310	DS 18	305.55	305.37	305.42	-0.05
481454	DS 19	313.04	312.88	312.73	0.15
481333	DS 20	316.97	316.82	–	
481356	DS 21	336.67	336.62	–	
481319	DS 22	347.28	347.34	346.97	0.37

3.1.3 Laboratory Activities

3.1.3.1 Overview

The laboratory of the WCC-N_2O was operated throughout the years 2009 – 2011. The analytical work in the laboratory was primarily related to

- comparisons of different standards kept by the WCC-N_2O,
- intercomparisons with other laboratories/institutions,
- tests of pressure regulators with respect to artefacts or contamination,
- detection of analytical problems related to the GC system,
- performance tests of the analytical instrumentation.

In total, about 346 result files were generated from the analysis sequences conducted. With 133 of them comprising 46 analyses per sequence (32 runs of standards, 14 samples), and 213 of 88 runs each, this amounts to 24862 individual chromatograms. All chromatograms were archived in the data format generated by the software of the GC and can be re-processed if any need should arise.

3.1.3.2 Analytical Problems

Challenges with temporary deterioration of the analytical quality had already been reported in the previous Report 2007-2008. They had been traced back to the fittings of the carrier gas supply at the rear wall of the GC, which developed a leak and thus caused a deterioration of the ECD signal (noisy baseline) as shown in Fig. 8.

In November 2009 again major problems occurred. Besides a noisy baseline of the detector signal, also poor reproducibility of the analysis results hampered the routine comparisons. Moreover, due to unidentified reasons the assigned values of standards were not reproduced precisely enough in the course of comparisons conducted as performance tests.

As part of the tests made in this context, in December 2009 the composition of the make-up gas of the ECD (flow of 5 mL min^{-1}) was changed from the normally used carrier gas Ar/CH_4 (95% / 5%) to a gas mixture of 0.25% CO_2 in argon. The analytical results were significantly

improved, however, it is uncertain if some changes to the plumbing had contributed to the success. Further tests for clarifying the details were postponed due to urgent other tasks. In consequence, the problems encountered caused a major delay of the scheduled comparison of standards, notably within the context of a WMO round-robin experiment.

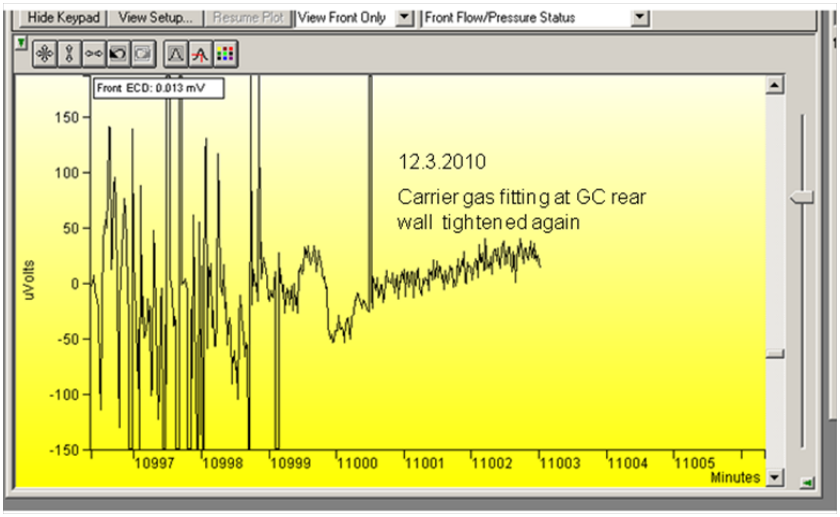


Fig. 8: Noisy baseline of the detector (ECD) and effect of tightening of a fitting in the carrier gas supply line. The baseline noise should be within a band of 25 µV only.

Unfortunately, the problems with minimal leaks causing a noisy baseline continued during the first months of 2010. Substantial progress was achieved at the end of May by inserting a piece of 1/16" stainless steel tube into the 1/8" carrier gas line (Fig. 9). This was made with the aim of avoiding possible resonance vibrations of the carrier gas tubing caused by the ventilator in the GC housing. In fact, the stability of the baseline was much better during the second half of 2010.

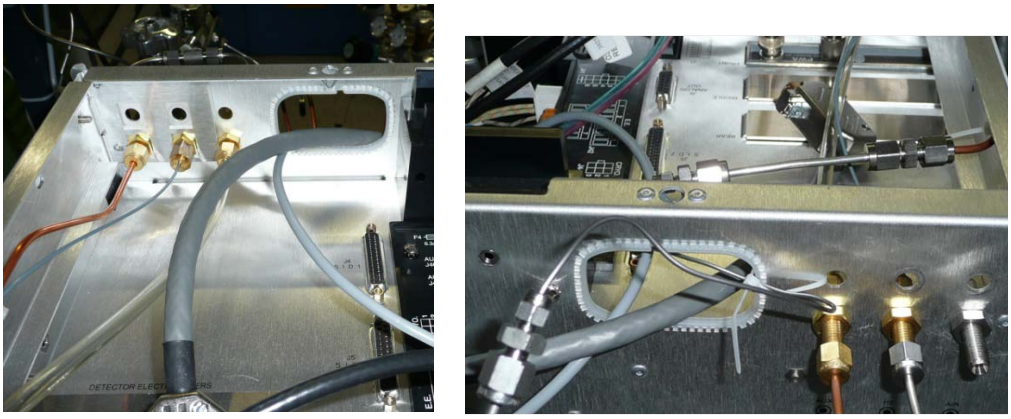


Fig. 9: Look into the housing of the gas chromatograph in the laboratory of the WCC-N_2O. Left picture: Gas lines (1/8") through the rear wall, the very left one is the carrier gas line. Right picture: Newly installed 1/16" tube, conducted through the opening in the rear wall (seen from outside). The thinner tube was expected to interrupt possible resonance vibrations.

3.1.3.3 Pressure Regulator Tests

Although only pressure regulators were used for the standards in the laboratory that had been tested in the past and were carefully flushed, a few of them had caused concern about minor artefacts.

For improved quality control, identification numbers had been assigned to the regulators in 2008. These were stored in a file together with information on the performance ('good', 'further tests needed', 'suspicious'). Laboratory protocols of analysis runs were supplemented with the number of the regulator used on the cylinder involved. For the audits dedicated regulators were assigned to the five cylinders employed during the comparisons.

In 2010, tests of regulators previously flagged as suspicious did not confirm any contamination. All pressure regulators yield good results. Nonetheless, all newly acquired regulators were carefully tested before being used in the operational work. As a possible cause of the 2008 findings, insufficient pressure equilibration prior to GC injection is now assumed. This might also have contributed to the unfavourable result obtained for the "CCQM-K68 N_2O International Comparison". The instrumental improvement to avoid future pitfalls of this kind has been described above under Instrumental Setup and Gas Flows (3.1.1.1).

In June 2010 the pressure regulator employed for the "CCQM-K68 N_2O International Comparison" was tested in detail again. In conclusion, it seems possible that the N_2O mole fractions measured for the CCQM-K68 cylinder were biased by about 0.3 ppb due to insufficient pressure equilibration of the sample loop.

3.1.3.4 Handling of Travelling Standards

From the pool of travelling standards two sets of cylinders were selected, each one covering the mole fraction range requested for audits or external comparisons. During the project period 2009 - 2011, a number of comparisons of travelling standards with the laboratory standards were conducted in the laboratory of the WCC-N_2O, notably as pre- and post-audit analyses.

Statistics over the mole fractions calculated from the GC data show that the expanded standard uncertainty (2 σ) related to a single analysis sequence is typically less than 0.1 ppb. The expanded standard uncertainty of the mean value over a series of sequences ranges mainly between 0.08 and 0.2 ppb.

3.1.3.5 Tests of CO_2 Removal from the Samples

As Fig. 5 shows, a small CO_2 signal appears before the N_2O peak, without overlap. Nonetheless, to fully exclude any risk of interference for the quantification of N_2O, CO_2 was removed testwise by inserting an Ascarite® cartridge in the sample line. The test has confirmed that the presence of CO_2 at ambient levels does not affect the quantification of the N_2O content in the sample.

3.2 Intercomparisons

3.2.1 CCQM-K68 N_2O International Comparison

This international experiment was coordinated by the Division of Metrology for Quality of Life, Korea Research Institute of Standards and Science (KRISS) (http://www.kriss.re.kr/eng/services/01_2.html). The round-robin involved primarily a number of National Metrology Institutes (NMI), but also the GAW CCL and the WCC-N_2O. Details of the analysis of the travelling standard involved had been described in the WCC-N_2O Report 2007-2008.

The results of the CCQM-K68 N_2O International Comparison were first presented by Lee et al. on a poster shown at the 15th Experts Meeting in Jena in September 2009 (http://www.bgc.mpg.de/service/iso_gas_lab/IAEA-WMO2009/Posters/Lee_KrissGAS_v3.pdf). Thereafter, they were sent round by KRISS as 'CCQM-K68 Draft A Report Ver. 1.31' in November 2009 from which the following table and figure have been taken.

VSL	ME5589	330.93	0.19	330	5	-0.93	5.00
NOAA	ME5572	319.52	0.19	319.39	1.06	-0.13	1.08
IMK-IFU	ME5529	319.88	0.19	320.64	0.16	0.74	0.25

Fig. 1 shows the relative deviation and its uncertainty (k=2) of each NMI. The figure indicates that the reported results agree well with the KCRVs within 0.5 % relative. The only laboratoriy at a position greater than the associated expanded uncertainty is IMK-IFU, where the laboratory IMK-IFU has reported a relatively small value for the measurement uncertainty.

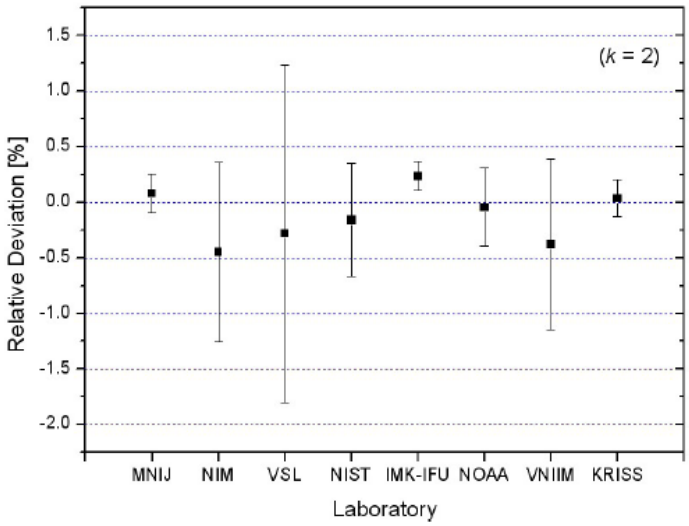


Figure 1 Relative Deviation for CCQM-K68

Panel 1: Table and Figure reproduced from the preliminary report 'CCQM-K68 Draft A Report Ver. 1.31', November 2009.

In response to the questioned small uncertainty noted in the above cited figure caption, in March 2010 the WCC-N_2O again submitted the analysis results, this time together with an updated estimate of the associated uncertainty. The new calculation was performed on the basis of specific information about the uncertainty of the GAW N_2O scale provided by the Central Calibration Laboratory (NOAA ESRL GMD).

1) Table of results with the Expanded Uncertainty only related to the gas chromatographic analyses:

Component	Result (nmol/mol)	Expanded Uncertainty	Coverage factor[1]
N_2O	320.64	0.05	2

2) Estimate of the overall uncertainty (March 2010):

The overall uncertainty of analysis (u_{meas}) is determined using the following equations:
$u_{meas} = 2 *(\sqrt{(u^2_{sample})}) + u_{standard(propagation)} + u_{standard(calibration)} = 0.1 + 0.18 +1.06 = 1.34$ ppb. This corresponds to 0.42 % at 320.64 ppb.
u_{sample} is the expanded uncertainty of the analysis result, as given in the Table above.
$u_{standard(propagation)}$ is the uncertainty of the propagation of the calibration scale as estimated by NOAA (Brad Hall, personal communication).
$u_{standard(calibration)}$ is the expanded uncertainty of the NOAA calibration scale (NOAA-calibrated laboratory standards at the WCC-N_2O) as determined by NOAA (Brad Hall, personal communication).

Panel 2: Information submitted to KRISS by the WCC-N_2O in March 2010.

The relatively great difference of 0.74 ppb between the mole fraction reported by the WCC-N_2O and the KRISS reference value was quite surprising, in particular in view of the good agreement achieved for other intercomparisons. Subsequent checks of the analytical procedure of the WCC-N_2O finally led to the assumption that about half of the deviation might be due to an insufficient pressure equilibration of the sample loop (cf. 3.1.1.1).

For completeness it is noted that the final report can be assessed on the web: Jinbok Lee *et al.,* 2011 *Metrologia* **48** 08004 doi:10.1088/0026-1394/48/1A/08004, source (http://iopscience.iop.org/0026-1394/48/1A/08004) or via http://www.bipm.org/utils/common/pdf/final_reports/QM/K68/CCQM-K68.pdf.

As noted by the organizers, the final report has been peer-reviewed and approved for publication by the CCQM, according to the provisions of the CIPM Mutual Recognition Arrangement (MRA). Since this key comparison is part of the programme of the Gas Analysis Working Group (GAWG) of the CCQM, results in the final report were only shown for members, but not for the WCC-N_2O as an external participant. The BIPM key comparison database is accessible via kcdb.bipm.org/.

3.2.2 WMO 2009 Intercomparison

3.2.2.1 Concept

Already in July 2008 the planning of a large-scale GAW intercomparison was initialized by NOAA ESRL GMD. This experiment was meant to continue the tradition of previous round-robins, which, however, were initially focused merely on CO_2. The new experiment, termed WMO 2009 was designed for a large number of trace gases, with N_2O being one of them. Therefore the participation of the WCC-N_2O was mandatory.

3.2.2.2 Handling by the WCC-N_2O

In agreement with the time schedule of the experiment, at the beginning of November 2009 three boxes containing an aluminium cylinder and a dedicated pressure regulator arrived at the WCC-N_2O. Unfortunately, the N_2O instrumentation in the laboratory was not running properly at that time because of technical problems. When it became evident that the cause of the poor analytical performance was not easily detectable, it was decided to forward the cylinders - in the meantime - to the next participant, which was the Global Station Zugspitze/Schneefernerhaus (ZSF), and to analyse the gas samples at the WCC-N_2O after their return in January 2010. This happened as intended. A special word of thanks goes to L. Ries (ZSF), who supported the WCC-N_2O by taking over the cylinders at short note.

After the three cylinders had been successfully analyzed for N_2O and CO by the WCC-N_2O, the boxes were shipped to the next participant in Budapest at the beginning of February.

Fig. 10: Aluminium boxes employed for the WMO 2009 round-robin experiment when prepared for the shipping to the next participant. Each box contains a 30-L high-pressure cylinder and pressure regulator.

3.2.2.3 Results

Several series of analyses were carried out at the end of January 2010. The results are shown in form of histograms below (Fig. 11). For comparison, the plot also shows a histogram obtained from a performance test conducted in September 2010.

It was only during the "16th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2011)" when results of the round-robin experiment were shown in an oral presentation. Some confusion was caused by the use of either the NOAA-2006 or NOAA-2006A scale. However, the WCC-N_2O was directly informed about its results in comparison to the values obtained by the CCL as determined before shipment and after return of the cylinders at the end of the round-robin (thus six numbers in total), with all mole fractions expressed in the NOAA-2006 scale in agreement with the originally submitted results.

Since the outcome of the entire round-robin has not yet been communicated officially in writing, no final mole fraction values are shown here. However, the results of the WCC-N_2O can be summarized as follows. The maximum difference (WCC-N_2O minus CCL) amounts to 0.18 ppb for the 6 values, with a minimum of only 0.01 ppb. On average the absolute deviation was 0.07 ppb. The WCC-N_2O thus fulfils the DQOs as set out for N_2O by the GAW Programme.

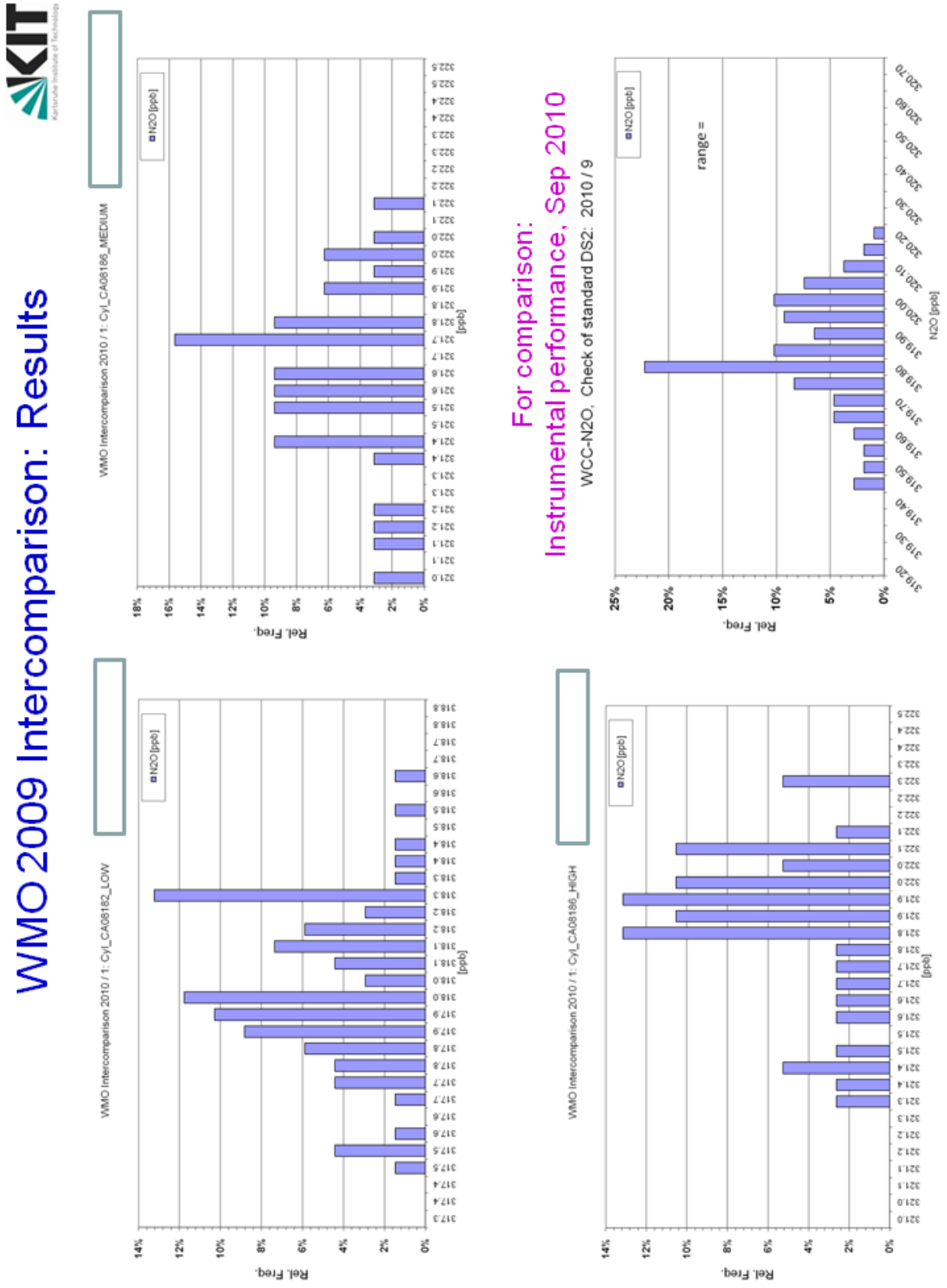


Fig. 11: Histograms summarizing the analysis results obtained for the three WMO gas mixtures. For comparison, a histogram from a performance test of September 2010 is shown.

3.2.3 Comparisons of WCC-Empa Travelling Standards

In June 2011, six travelling standards of the WCC-Empa were analysed for N_2O in the laboratory of the WCC-N_2O. This comparison formed part of an intensified collaboration between these two GAW central facilities, which will enable the WCC-Empa to conduct N_2O comparisons as part of their audits in future.

The comparison experiment employed six WCC-Empa high-pressure cylinders. Two of them had already previously been measured by the WCC-N_2O, while the other four cylinders were analysed for the first time in the WCC-N_2O laboratory. Prior to the comparison experiment, all six gas mixtures had been carefully quantified for N_2O by WCC-Empa, thereby employing a laser-based Aerodyne spectrometer and CCL-calibrated laboratory standards.

The outcome of the comparison is summarized in Table 6, where the mole fraction assigned by WCC-Empa and the analysis results of the WCC-N_2O are listed. The differences (WCC-Empa minus WCC-N_2O) indicate very good agreement to better than 0.1 ppb for four of the six cylinders. At the upper end a deviation of –0.17 ppb was obtained, while the deviation of 0.30 ppb at 317 ppb looks like an outlier. In summary, good overall agreement of mole fractions between the two laboratories was found, and there is currently no need for any corrections. However, cylinder No. 30491 should be compared again in the near future.

Table 6: Results of a N_2O comparison between WCC-Empa and WCC-N_2O conducted in June 2011.

Cylinder No.	N_2O [ppb], NOAA-2006		
	WCC-Empa	WCC-N_2O	Difference Empa - WCC-N_2O
3367	310.34	310.40	-0.06
3382	311.58	311.64	-0.06
30491	317.52	317.22	0.30
2270	322.94	322.86	0.08
3348	323.90	323.97	-0.07
2493	354.43	354.60	-0.17

3.2.4 Comparison WCC-N_2O / CCL

In 2011 another bilateral comparison of five travelling standards with the CCL was conducted. After an appropriate date had been agreed upon, the cylinders were shipped to the CCL in August 2011. Analyses by the CCL took place at the beginning of September. From the CCL in Boulder the travelling standards were shipped directly to the NIWA laboratory in Wellington (New Zealand), where a N_2O audit was scheduled for October/November 2011.

The results of the comparison WCC-N_2O / CCL are shown in Table 7 and Table 8. The mole fractions determined by the CCL were communicated in the NOAA-2006A scale. Since the

previously assigned mole fractions of the WCC-N_2O were based on the NOAA-2006 scale, the values had to be updated. This was done according to the available information on the WCC-N_2O laboratory standards as of October 2011 and May 2012. Since one value for a laboratory standard (CA08456) was differently reported on the CCL web page between May and July 2012, the most recent numbers available for the LS were used for the calculation of updated mole fractions of the travelling standards involved in the comparison. Note that the problems regarding the scale adjustment have been explained above in section 3.1.2.1.

While the absolute differences (WCC – CCL) are ≤ 0.15 ppb for four of the five standards in Table 7, one value is at 0.27 ppb (for DS19). Interestingly, when using the most recent parameters for the scale update (Table 8), the outlier shifted to DS22, with a difference of 0.37 ppb. For DS13 the difference increased from 0.10 ppb to 0.21 ppb, while the differences for the other three standards fall within an interval of 0.15 ppb. As already pointed out above, some details still need to be discussed with the CCL in the light of the scale changes.

Table 7: Comparison WCC-N_2O / CCL in September 2011. Results based on values available in October 2011. Column 2 shows the mole fractions originally assigned in the NOAA-2006 scale. In column 3 the numbers are converted to the NOAA-2006A scale based on a relationship determined from the respective mole fractions of the WCC-N_2O laboratory standards as of October 2011. CCL numbers as reported in September 2011.

Short name	N_2O [ppb] NOAA-2006	N_2O [ppb], NOAA-2006**A**		
	WCC-N_2O (Oct 2011)	WCC-N_2O (Oct 2011)	CCL (Sep 2011)	Difference WCC - CCL
DS18	305.55	305.48	305.39	0.09
DS19	313.04	312.97	312.70	0.27
DS15	318.96	318.89	318.74	0.15
DS13	332.91	332.84	332.74	0.10
DS22	347.28	347.21	347.06	0.15

Table 8: Comparison WCC-N_2O / CCL in September 2011. Results based on values available in May 2012. Column 2 shows the mole fractions originally assigned in the NOAA-2006 scale. In column 3 the numbers are converted to the NOAA-2006A scale based on a relationship determined from the respective mole fractions of the WCC-N_2O laboratory standards as of July 2012, i.e. the most recent numbers made available by the CCL.

Short name	N_2O [ppb] NOAA-2006	N_2O [ppb], NOAA-2006**A**		
	WCC-N_2O (May 2012)	WCC-N_2O (July 2012)	CCL (May 2012)	Difference WCC - CCL
DS18	305.55	305.37	305.42	-0.05
DS19	313.04	312.88	312.73	0.15
DS15	318.96	318.83	318.77	0.06
DS13	332.91	332.86	332.65	0.21
DS22	347.28	347.34	346.97	0.37

3.2.5 Comparison WCC-N_2O / Zugspitze (ZSF)

A previous comparison between the GAW station Zugspitze (ZSF) and the WCC-N_2O had been conducted as part of the full system and performance audit of 2005. This had shown an average difference (ZSF – WCC) of 0.49 ppb, with negligible mole fraction dependence (range 0.44 - 0.55 ppb), if one outlier (0.92 ppb at 333.57 ppb) is disregarded.

In December 2011 a new comparison experiment was launched. For this purpose, the five travelling standards employed for the audit at NIWA in New Zealand were directly forwarded to the Zugspitze station (ZSF) after their return. Note that these standards had been analysed in the CCL in September 2011. Analyses at ZSF took place in February 2012. The mole fractions reported by the CCL (NOAA-2006A scale) were used here as the assigned values of the WCC-N_2O. The ZSF results were submitted in the NOAA-2006A scale since the most recent mole fractions of the laboratory standards (as taken from the CCL web site) were used.

The mole fractions determined by the analyses at ZSF were submitted in two series. The first submission is based on the values of all laboratory standards involved, while for the second submission a single laboratory standard was disregarded for the determination of the detector response curve because its assigned mole fraction did not fit well. The results of the comparison are summarized in Table 9 and Fig. 12. The deviations between the station and the WCC-N_2O are unexpectedly great and do not show a systematic dependence on mole fractions.

In conclusion, the results determined before this report was finalized are difficult to interpret. Both the magnitude of the differences between reported and assigned mole fractions (here using the CCL values) and the lack of a mole fraction dependence in the range of 311 to 349 ppb are irritating. Communication with regard to checks of analytical problems and possible errors in the data processing were still ongoing while this report was being completed. How-

ever, irrespective of the outcome of these efforts, a repetition of the comparison experiment should be conducted in the near future.

Table 9: Results of the comparison with the GAW station Zugspitze (ZSF). All mole fractions are expressed in the NOAA-2006A scale.

Short name	N_2O [ppb], NOAA-2006A scale				
	WCC-N_2O	ZSF (1st calc.)	Difference ZSF(1) - WCC	ZSF (rev.calc.)	Difference ZSF(1) - WCC
DS18	305.42	304.85	-0.57	304.81	-0.61
DS19	312.73	311.75	-0.98	311.53	-1.21
DS15	318.77	318.02	-0.75	317.63	-1.14
DS13	332.65	332.42	-0.23	332.08	-0.57
DS22	346.97	347.86	0.89	347.82	0.85

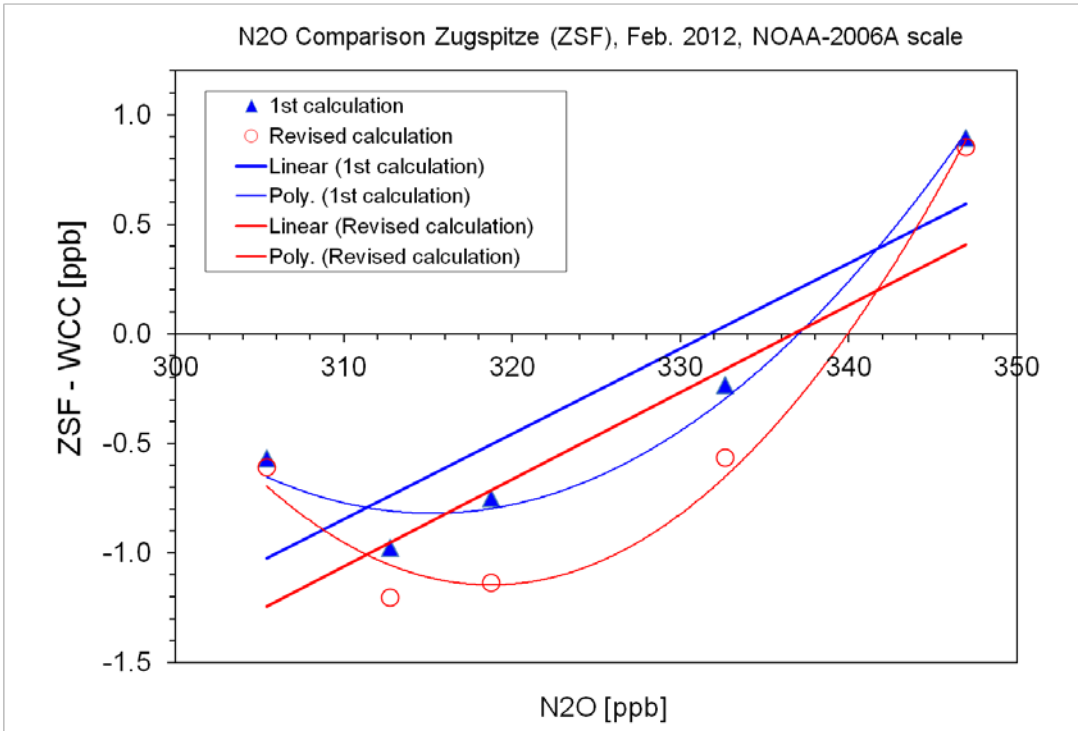


Fig. 12: Results of the comparison experiment. The differences are shown for both the originally submitted results and the revised results. For the latter, one of the ZSF laboratory standards had been disregarded for the determination of the detector response curve.

3.2.6 Remarks on Intercomparison Activities of the WCC-N_2O

As described above, the WCC-N_2O has been involved in a complex WMO intercomparison experiment organized by NOAA ESRL GMD, which started in 2008. Given this global round-robin, it was questionable if GAW stations would be in favour of another round-robin in parallel. It is noted that the participation in such a large-scale experiment requires a con-

siderable effort from each participant, not only in terms of labour and laboratory capacity, but also in terms of the shipping of the travelling standards involved. Therefore it did not seem advisable to organize a separate large-scale N_2O round-robin experiment involving mainly global GAW stations, as was originally foreseen. Consequently, the WCC-N_2O has modified its task list accordingly.

Moreover, there are specific arguments against a big WCC-N2O-organised round-robin at the present time. Intercomparisons involving only one or two stations or laboratories yield results within a relatively short time frame. Therefore, they can better meet the needs of the participants for short-term information about the outcome and thus enable earlier planning of possible follow-up activities.

3.3 Audits

3.3.1 Selection Criteria

Currently, the main criteria for the selection of stations to be audited by the WCC-N_2O are:
(i) N_2O measurements were only started recently,
(ii) a station is not directly part of well-established global networks (such as NOAA/ESRL or AGAGE),
(iii) major changes, in particular upgrade of N_2O instrumentation, were made recently or since the last audit.

3.3.2 WMO/GAW Documents for Audits

The audits conducted during 2009 – 2011 were performed according to the respective GAW documents. These are:

- SOP for Audits (a guideline for the auditor's tasks)
- Audit Questionnaire (a tool for collecting relevant information).
- Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance (WMO/GAW Report No. 185)

Moreover, all these activities are performed with reference to the tasks described in the GAW Strategic Plans (GAW Reports No. 142, 156 und 172).

3.3.3 Summary of N_2O Scale and Range of Mole Fractions

Since its inception, the WCC-N_2O has been using the NOAA N_2O scale, which is the accepted scale for WMO/GAW. A direct link to the Central Calibration Laboratory is established through a series of eight laboratory standards calibrated by the CCL at NOAA and kept at the WCC-N_2O. A recalibration by the CCL in 2009 ensured the direct link to the recent version of the GAW scale. In the case of updated values due to minor changes of the scale, the latest mole fraction numbers for each standard can be taken from the CCL web site.

The laboratory standards cover the range from 254 to 358 ppb. The currently used travelling standards range from 285 to 347 ppb. Within GAW, the recommended range for QA/QC

measures is 290 – 350 ppb. The deviations from the ordered mole fractions reflect the capabilities of the gas manufacturer to hit the specified values.

3.3.4 Audit GAW Station Monte Cimone (CMN)

On August 31 and September 1, 2010 a N_2O audit was conducted for the station Monte Cimone (CMN) in northern Italy (located to the southwest of Bologna). The station was selected because N_2O measurements had only started there in 2008. At the time of the audit, the station was still classified as GAW Regional Station. However, the station had gained an excellent reputation over some time already because of its comprehensive measuring programme and the valuable scientific results achieved. In view of this, the authorities responsible for the station within the Meteorological Service had made initiatives for a classification as GAW Global Station in 2010 already. The upgrade was confirmed by WMO/GAW in early 2011.

3.3.4.1 Description of the Station

The station is located near the summit of the Monte Cimone, in the northern Apennine (Fig. 13), a with free view in all directions, which implies the absence of local pollution sources. The dominant wind directions are SSW and NE.

Coordinates: 44,17 °N, 10,68 °E, 2165 m a.s.l. Time zone UTC +1.

The entire installation (Fig. 14) is part of the Italian Air Force that is also responsible for the Italian Meteorological Service. The GAW measurements are conducted in the "Laboratorio Ottavio Vittorio" (existing since 1983) of the ISAC-CNR (Institute of Atmospheric Sciences and Climate, Bologna). The laboratory building is shown in Fig. 15. Details are described at the station's web site http://www.isac.cnr.it/cimone/. Further information is given in GAWSIS under http://gaw.empa.ch/gawsis/reports.asp?StationID=-1988709498.

Fig. 13: Geographical location of the station Monte Cimone in northern Italy.

Fig. 14: Summit of the Monte Cimone. The building on top of the mountain and the neighbouring installations are operated as a weather station of the Italian Meteorological Service. The GAW measurements are conducted in a laboratory building situated below the summit.

Fig. 15: Laboratory building for the GAW measurements of the station Monte Cimone.

3.3.4.2 Realisation of the Audit

The measurements of N_2O and several halocarbons fall within the responsibility of the University of Urbino. These measurement programmes are conducted in association with the global network AGAGE (http://agage.eas.gatech.edu/). In this way they are supported by the expertise available within AGAGE, including software tools.

As agreed upon, the five travelling standards of the WCC-N_2O – packed in aluminium boxes – were sent out at the end of July 2010 and were being analysed already on the day of the audit. The analyses were continued for some time thereafter by the responsible scientist, who could not be permanently at the station. In consequence, the boxes with the cylinders only returned to the WCC-N_2O in October 2010.

The system audit itself was conducted on 31 August with nearly all station staff being present. On the following day the outcome and further details were discussed.

Fig. 16: Gas chromatographic system for the analysis of N_2O at the station Monte Cimone, with the five travelling standards of the WCC-N_2O in the foreground.

3.3.4.3 Results

According to the audit procedure, the results of an audit are presented in a dedicated Audit Report. This has not yet been completely finished for Monte Cimone. In the following paragraphs the main results are summarized.

At the time of the audit comparison, the N_2O measurements at Monte Cimone were only based on a 1-level calibration of the detector (ECD) with a working standard. According to the typical response curve of an ECD, such a procedure can yield acceptable results only if

the N_2O content of the sample is very close (less than ± 1 ppb) to the mole fraction of the standard.

Two working standard were available at the station, with mole fractions of 324.4 and 324.55, which had been calibrated by the MPI for Biogeochemistry in Jena with reference to the NOAA-2006 scale. It was thus evident that it would not be possible to determine all five travelling standards correctly, but that systematic deviations would appear, reflecting the detector response curve. The results are visualised in Fig. 17 in terms of differences between station CMN and WCC as a function of mole fraction. The regression line shows an offset of 0.48 ppb at the mole fraction of the working standard (compared to the red regression line, which, for test purposes, was tuned to zero offset). The observed bias is rather surprising given the link to the GAW scale via the calibration of the working standard at the MPI-BGC. So far no explanation for the results has been found. As conclusion of the audit there is a recommendation to acquire at least five laboratory standards that are directly calibrated by the CCL (NOAA in Boulder, USA). It is noted that the station staff was aware of the importance of a direct link to the GAW scale. It was planned to acquire a set of laboratory standards rather soon after the audit.

When the peak areas or peak heights, respectively, as measured for the travelling standards are normalised to a reference gas, such as a working standard, the relationship to the assigned values of the travelling standards can be established. This defines the detector response curve for the N_2O interval under consideration. As Fig. 18 shows, the response curve is practically linear between 305 and 340 ppb. However, when extrapolating to zero (Fig. 19), the linear and second order fits display pronounced differences. The details of such behaviour are dependent on the individual ECD. It is noted that the curvature of the second order fit is rather strong compared to other ECDs encountered during audits.

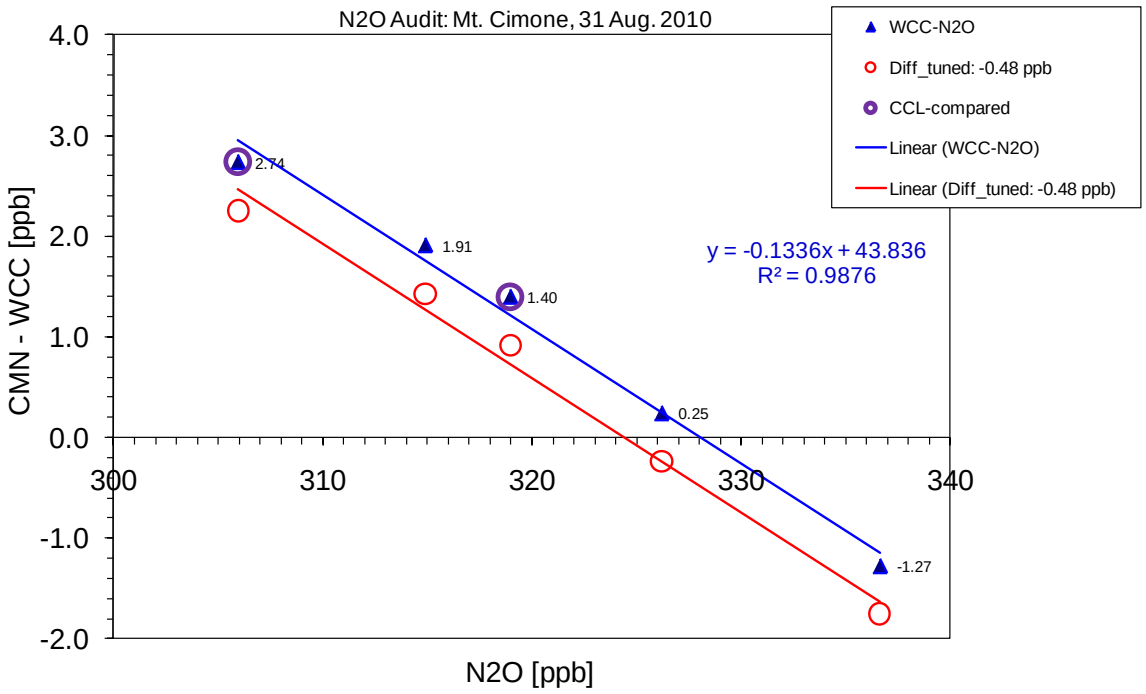


Fig. 17: Results of the comparisons as part of the N_2O audit. The plot shows the differences between reported values and the mole fractions assigned to the travelling standards by the WCC-N_2O. The violet circles denote two travelling standards that had been measured in the Central Calibration Laboratory (CCL) in 2007. When the original regression line is lowered by an offset of 0.48 ppb, zero difference is obtained at the mole fraction of the working standard.

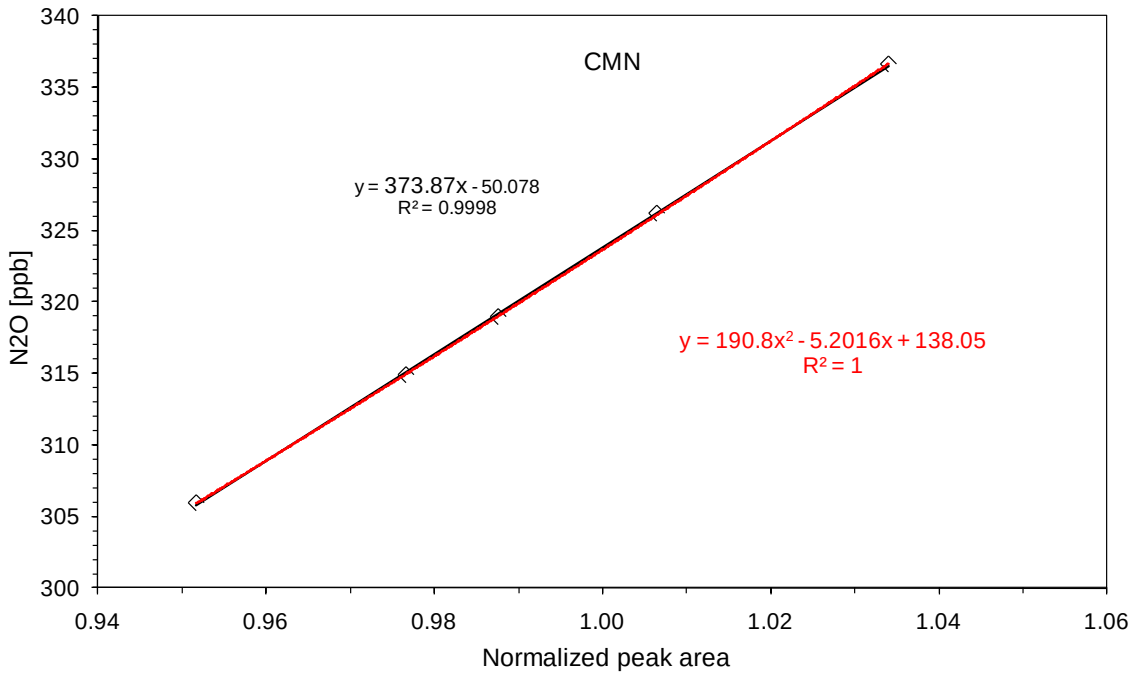


Fig. 18: Nominal values of the WCC-N_2O travelling standards as a function of normalised peak areas (average of several repeated analyses at the station). The relationship characterises the detector response curve. Within the interval considered here, the linear and second order fit coincide.

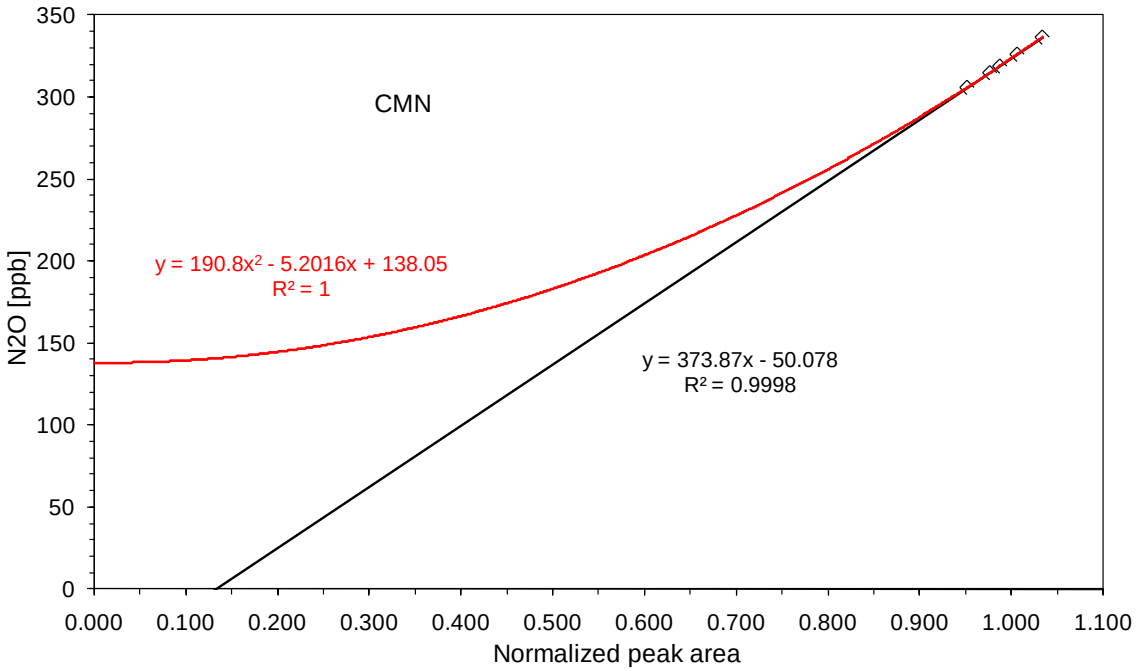


Fig. 19: Same as Fig. 18, but with extrapolation to zero.

3.3.5 Audit GAW Station Schauinsland (SSL)

A system and performance audit for N_2O was conducted at the GAW station Schauinsland (SSL) on 18 - 19 November 2010. The station is part of the monitoring network of the German Federal Environment Agency (Umweltbundesamt (UBA)). Within GAW it is classified as a Regional Station, but is of great importance to the GAW Programme, notably because of its long CO_2 record. A first N_2O audit in November 2002 had shown that the station did not fully comply with the N_2O Data Quality Objectives (DQO) of GAW, which were being developed at that time. In particular, the link to the GAW N_2O scale was missing. In the meantime a complete set of CCL-calibrated laboratory standards had been commissioned. Moreover, the analytical system had been further developed, notably by the addition of instrumentation for the simultaneous measurements of CO and H_2. Taken together, these aspects suggested conducting a new audit in order to control the quality of the N_2O data.

3.3.5.1 Description of the Station

Since the station Schauinsland is part of the monitoring network of the Federal Environment Agency (UBA) (http://www.umweltbundesamt.de/luft-e/luftmessnetze/ubamessnetz.htm), no detailed site description is necessary in the context of this project report. Nonetheless, some details are given below:

Coordinates: 47° 55' N, 7° 55' E, altitude 1205 m a.s.l.. Time zone UTC + 1.

The station is located on a mountain top in the southern part of the Black Forest, about 10 km south-east of the city of Freiburg (Fig. 20). Further information can be found in GAWSIS under http://gaw.empa.ch/gawsis/reports.asp?StationID=-1988709498.

Fig. 20: The Monitoring Network of the Federal Environment Agency (Umweltbundesamt – UBA) (Source: http://www.umweltbundesamt.de/luft-e/luftmessnetze/ubamessnetz.htm).

Fig. 21: View on the laboratory building of the station Schauinsland (Source: http://www.umweltbundesamt.de/luft/luftmessnetze/stationen/schau/index.htm).

3.3.5.2 Realisation of the Audit

Measurements of N_2O are performed continuously at the station in the context of greenhouse gas monitoring. The station collaborates closely with the Institut für Umweltphysik of the University of Heidelberg, which implies support in the case of analytical problems.

As agreed upon with the station manager, three aluminium boxes with five WCC-N_2O travelling standards and an additional cylinder containing a gas mixture without CO_2 were sent to Schauinsland several days prior to the audit. Unfortunately, due to unsatisfactory handling of the freight by a local courier, the delivery to the station was delayed for no obvious reasons. In consequence, the travelling standards had not yet arrived at the date of the audit and thus the work on the performance audit (comparisons) could not be conducted in parallel to the system audit.

The system audit, which comprised an inspection of the station's infrastructure, began immediately after the arrival of the auditor on 18 November 2010. It was continued on the following day and included detailed discussions of matters pertaining to the monitoring activities at the site. Comparisons of the travelling standards began a few days later. Finally the cylinders arrived back in the WCC-N_2O laboratory at the beginning of January 2011. The five travelling standards employed for the audit at Schauinsland were the same that had previously served for the comparisons at Monte Cimone. This furthermore implied a comparison between the two stations and thus added value to the two individual comparison experiments. Table 10 lists the travelling standards with the mole fractions assigned by the WCC-N_2O.

Table 10: Travelling standards used for the audit at the station Schauinsland with their assigned mole fractions, related to the NOAA-2006 scale.

Short name	N_2O [ppb]
DS14	305.95
DS8	314.90
DS15	318.96
DS12	326.19
DS21	336.62

3.3.5.3 Results

According to the audit procedure, the results of an audit are presented in a dedicated Audit Report. This has not yet been completely finished for Schauinsland. In the following the main results are summarized. As can be seen below, this audit can be viewed as a textbook example of the value of this kind of quality assurance and quality control (QA/QC) activities within GAW.

The gas-chromatographic system operated at Schauinsland (Fig. 22) is a complex unit developed at the University of Heidelberg. The core is a gas chromatograph of the type HP6890 equipped with ECD, FID, and reduction gas detector, which permit the simultaneous measurements of N_2O, SF_6, CO_2, CH_4, CO and H_2. For the quantification of N_2O, the separately determined response curve of the ECD is considered. Furthermore, the slight interference between a CO_2 signal with the N_2O peak is taken into account by applying an empirically determined correction function.

The results of the comparisons as reported by the station are visualized in Fig. 23 and Fig. 24. One puzzling feature of Fig. 23 is the sign of the differences ([Station] – [WCC]). While four of the five standards yield negative values, the cylinder DS8 (314.9 ppb) yielded a positive deviation. The reason for this could not be clarified, even after intense investigations of the respective analytical details. In consequence, the travelling standard DS8 was flagged as an unexplained outlier and was excluded from further evaluations of the comparison.

More importantly, the great differences of about –1 ppb constituted a major problem for the data quality. Such a result could not be explained given the direct link to the CCL through laboratory standards kept at the station. It was only in early 2011 when the reason was found and revised comparison results were submitted (Fig. 24). By careful revision of all steps involved in the data processing, the station manager finally identified an erroneous value of a working standard. The error had remained undetected for a long time, since all internal checks and comparisons – although affected by the error – remained internally consistent among each other.

This experience has clearly documented that data errors can occur which remain undetected in spite of careful internal QA/QC measures and comparisons with the station's laboratory standards. This finding underlines the necessity of external audits.

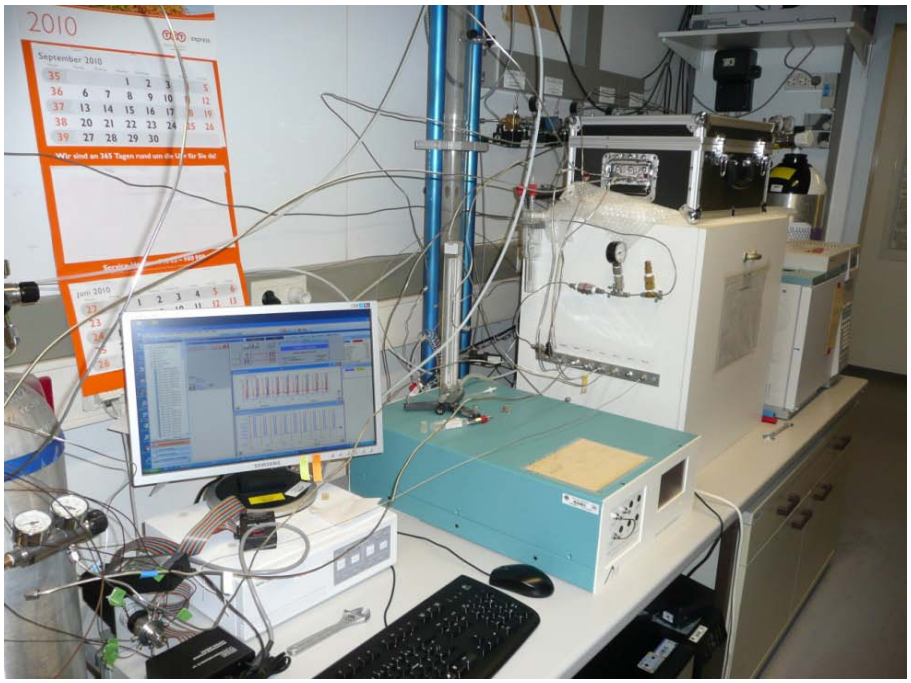


Fig. 22: Analytical system, based on a gas chromatograph of the type HP6890 (right part of the photo), which serves for the measurements of N_2O and other species.

As documented by Fig. 24, finally a very good result for the audit comparison was achieved. The maximum absolute difference only amounts to 0.19 ppb. The other three values are even below 0.1 ppb. This means that the ambitious GAW DQOs for N_2O (WMO/GAW Report No. 185) have been fulfilled.

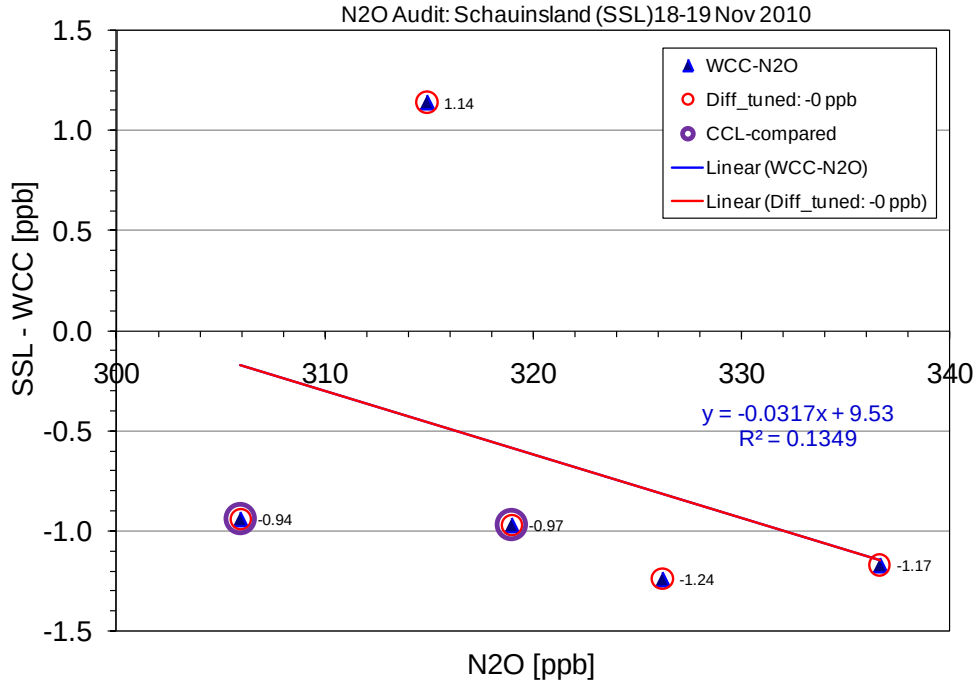


Fig. 23: Originally submitted results of the comparisons as part of the N2O audit. The plot shows the differences between reported values and the mole fractions assigned to the travelling standards by the WCC-N2O (cf. Fig. 24). For details see text.

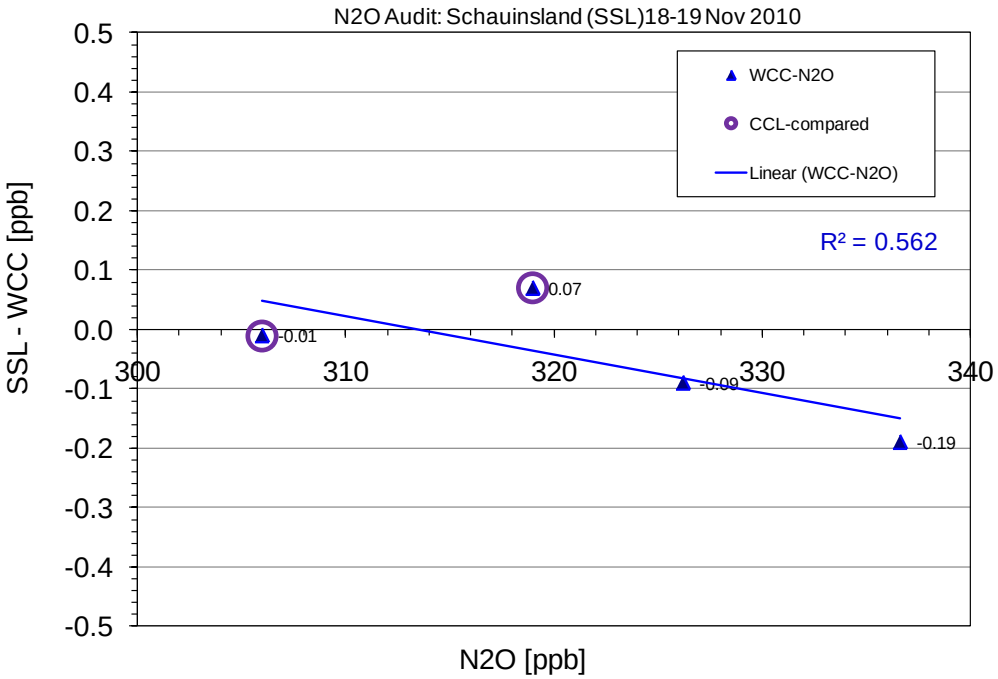


Fig. 24: Revised results of the audit comparison experiment after a data processing error had been detected. For details see text.

3.3.6 Audit GAW Station Cape Point (CPT)

A system and performance audit was conducted at the GAW global station Cape Point in February 2011. The audit was motivated by an update of the N_2O instrumentation in 2008, according to the above-named criterion (iii).

3.3.6.1 Description of the Station

The southern hemispheric GAW Global Station Cape Point (CPT, 34^0 S; 18^0 E) is located on top of a cliff (230 m a.s.l.) at the southernmost point of the Cape Peninsula, about 60 km south of Cape Town. The time zone is UTC + 2. Details of the location were described in a first N_2O audit report (WCC-N_2O Report 2003/2). In addition, information about the station and its measuring programme is provided by GAWSIS (http://gaw.empa.ch/gawsis/reports.asp).

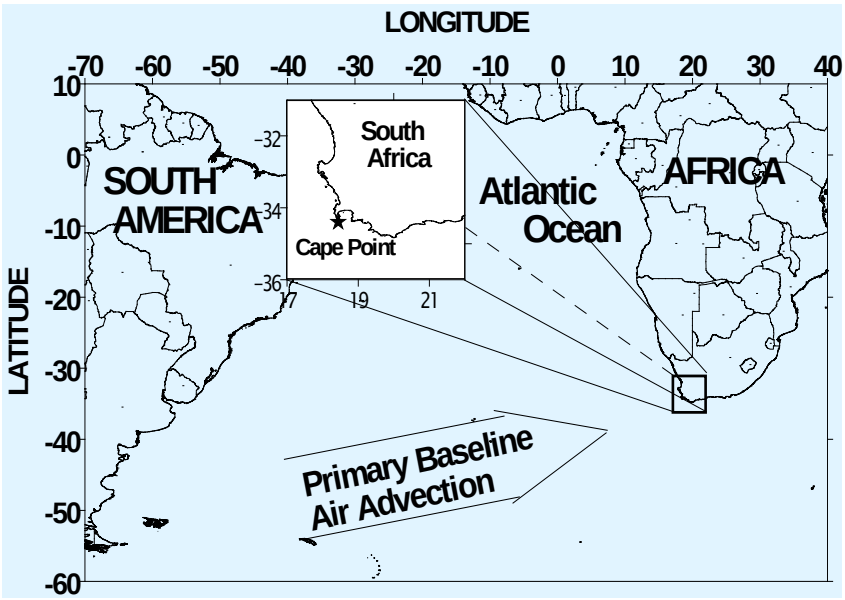


Fig. 25: Schematic of location and main air advection. Source: South African Weather Service (SAWS)

Unfortunately, the new analytical system for N_2O – based on an Agilent 6890 N gas chromatograph with micro-ECD – had not been working satisfactorily since its installation in February 2008. Keywords in this context are poor repeatability and reproducibility. A great number of different test were conducted by the CPT staff, however, without identifying the cause of the problems. Several technical discussions took place with the WCC-N_2O and colleagues at other GAW stations or laboratories. Finally, in November 2010, following another joint discussion of the problems, the WCC-N_2O suggested to reduce the system to its essentials and bypassing GC components, such as gas sampling valve (GSV) and stream selection valve (SSV), by external components. These technical changes were then implemented before the audit.

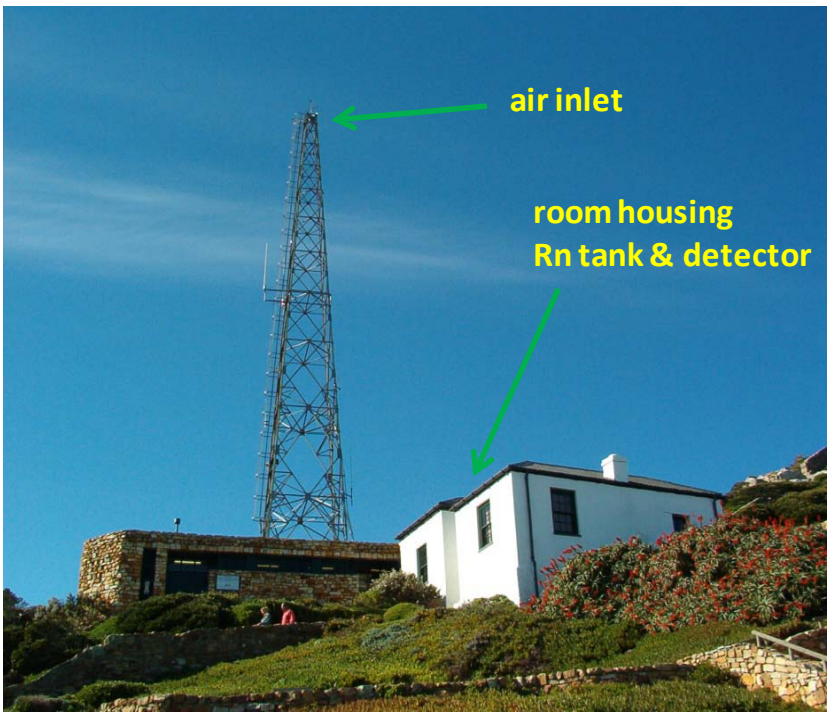


Fig. 26: Station buildings and 30 m high mast for sample air intake. Source: South African Weather Service (SAWS).

3.3.6.2 Realisation of the Audit

Measurements of N_2O are performed continuously at the station Cape Point within the context of greenhouse gas monitoring. As agreed upon with the station manager, three boxes with five travelling standards and pressure regulators were shipped to CPT prior to the audit. When the audit took place, starting on 8 February 2011, the travelling standards were already operational in the station laboratory.

The system audit comprised an inspection of the infrastructure of the station and began shortly after the arrival of the auditor at the site. During the subsequent days the focus was primarily on the analytical problems associated with the N_2O system. Analytical results were immediately discussed as they became available in the offices at Stellenbosch via remote access to the station PCs.

The analyses of the travelling standards were continued after the departure of the auditor. The travelling standards were finally reanalysed in the WCC-N_2O laboratory in June 2011.

Table 11: Travelling standards used for the audit at the station Cape Point with their assigned mole fractions, related to the NOAA-2006 scale.

Short name	N_2O [ppb]
DS18	305.55
DS19	313.04
DS15	318.96
DS13	332.91
DS22	347.28

3.3.6.3 Results

According to the audit procedure, the results of an audit are presented in a dedicated Audit Report. This has not yet been completely finished for Cape Point. In the following the main results are summarized.

The Cape Point results of the audit comparison involving five travelling standards of the WCC-N_2O are reported in Table 12. While the standard deviations of four cylinders are quite acceptable, the statistics for DS19 yielded a rather high value. In Table 13 the outcome of the comparison is listed as difference (CPT - WCC) [ppb]. These results are visualized in Fig. 27. The two circles denote travelling standards that had been compared with the CCL in 2007, which implies improved confidence in the assigned mole fractions. With the exception of one outlier at 347 ppb, the differences between CPT and WCC-N_2O are in the range of -19 to +0.16 ppb. This can be regarded as a satisfactory result, although the GAW target of 0.1 ppb has not yet been achieved.

Based on the favourable outcome of the audit comparison, the analytical procedure for ambient samples at Cape Point was improved during the months after the audit. Finally, ambient data of satisfactory quality were obtained for the last months of the year 2011.

Table 12: Results for the five travelling standards of the audit comparison as reported by the CPT station. The mole fractions are related to the NOAA-2006 scale.

Short name	N_2O [ppb], NOAA-2006		
	CPT (avg)	CPT (std)	CPT (rel std [%])
DS18	305.36	0.23	0.07%
DS19	312.93	0.51	0.16%
DS15	318.84	0.05	0.01%
DS13	333.07	0.24	0.07%
DS22	347.63	0.21	0.06%

Table 13: Results of the audit comparison as differences between the values reported by CPT (Table 12) and the mole fractions assigned by the WCC-N_2O, NOAA-2006 scale (Table 11).

Short name	N_2O [ppb], NOAA-2006 scale		
	WCC-N_2O	CPT	Difference CPT - WCC
DS18	305.55	305.36	-0.19
DS19	313.04	312.93	-0.11
DS15	318.96	318.84	-0.12
DS13	332.91	333.07	0.16
DS22	347.28	347.63	0.35

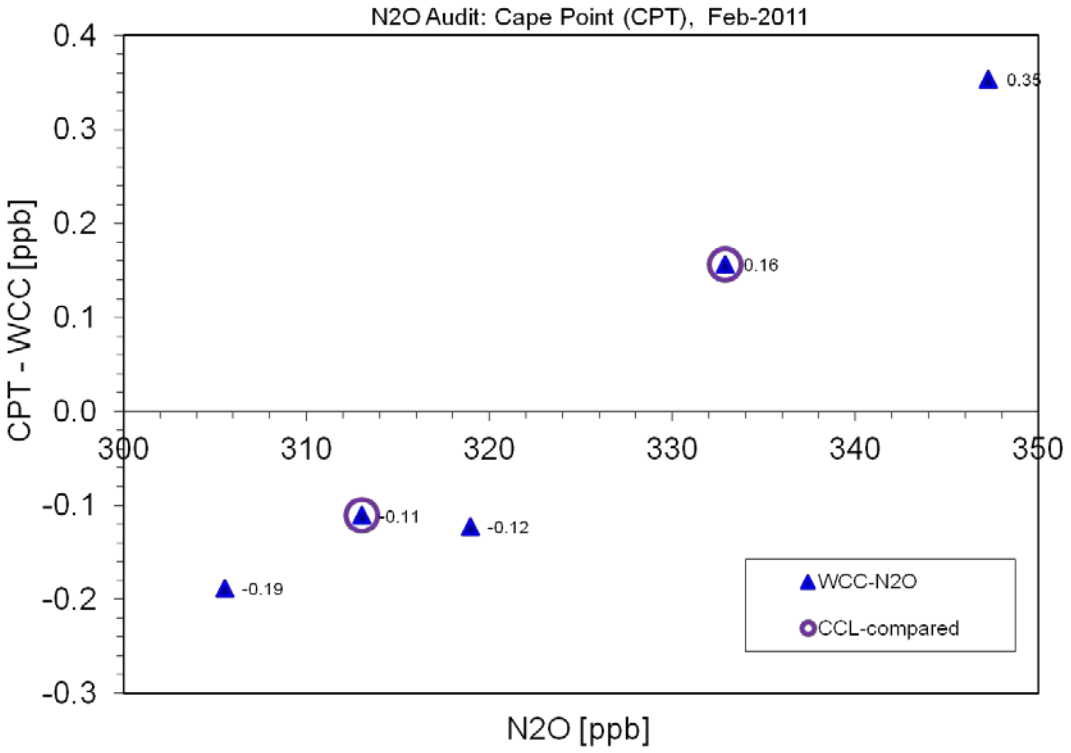


Fig. 27: Result of comparisons with 5 travelling standards of the WCC-N_2O as part of the N_2O audit of the station Cape Point. The two circles denote standards that had been compared with the CCL in 2007.

When the peak areas or peak heights, respectively, as measured for the travelling standards are normalised to a reference gas, such as a working standard, the relationship to the assigned values of the travelling standards can be established. This defines the detector response curve for the N_2O interval under consideration. As Fig. 28 shows, in this case the response curve is practically linear between 305 and 347 ppb. The second order fit coincides with the linear regression line. The details of such behaviour are dependent on the individual ECD. Interestingly, when extrapolating to zero, the quasi-linear characteristic is retained (Fig. 29). This is in contrast to a curvature at low values, which has been observed with the ECDs previously examined during audits.

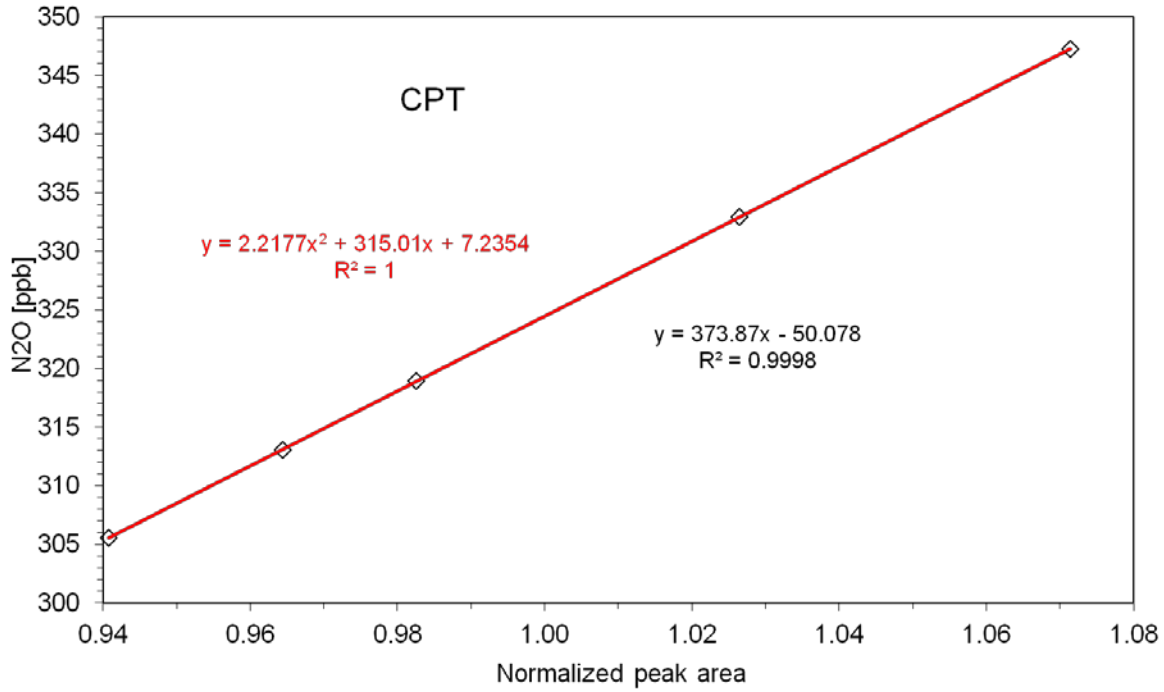


Fig. 28: Nominal values of the WCC-N_2O travelling standards as a function of normalised peak areas (average of several repeated analyses at the station). The relationship characterises the detector response curve. Within the interval considered here the linear and second order fit coincide.

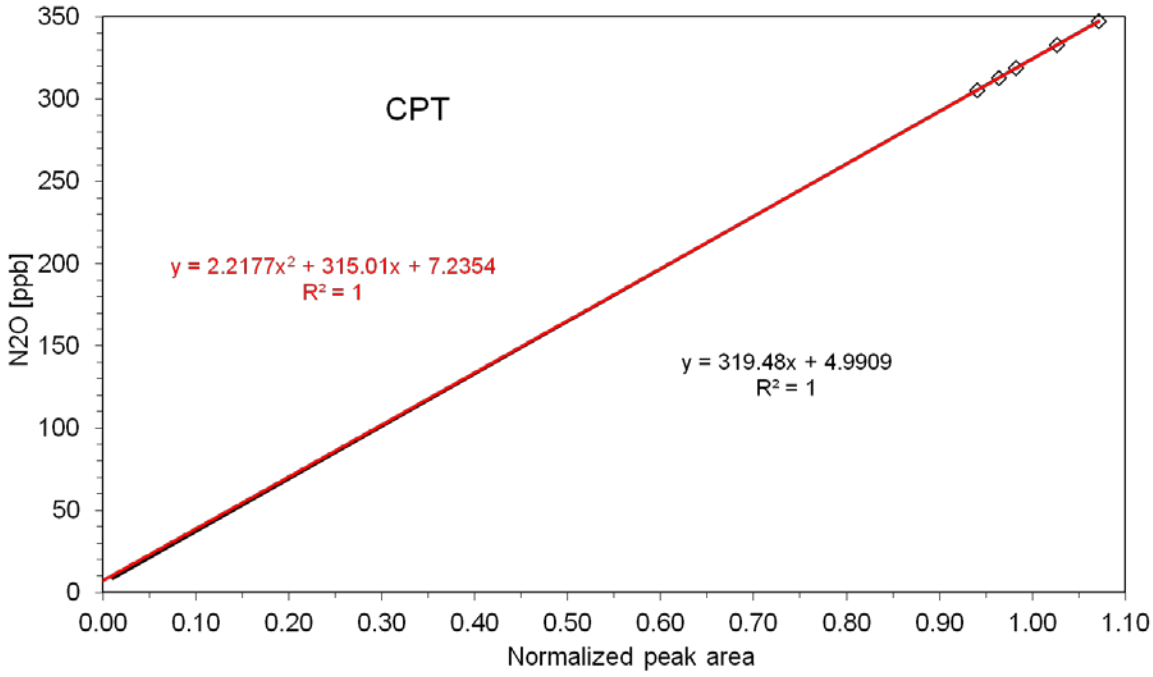


Fig. 29: Same as Fig. 28, but with extrapolation to zero.

3.3.7 Audit Station Baring Head (BHD) / NIWA Laboratory

A system and performance audit of the New Zealand station Baring Head was conducted in October 2011. Given the importance of the Baring Head monitoring activities, it was decided to conduct an audit there, which could be favourably combined with the mandatory participation in the 2011 Greenhouse Gas Measurement Technique meeting (cf. 3.10.10). Moreover, the station fulfils the above criterion (ii) for the selection of stations for audits.

The web site http://www.niwa.co.nz/our-science/atmosphere/baring is the starting page for detailed information about Baring Head. From there the following information was adopted. "The Baring Head Clean Air Monitoring Station, which has been in operation for more than 30 years, makes significant contributions toward the global understanding of greenhouse gases, other trace gases and related species in air that is representative of the mid latitude southern hemisphere. The internationally recognised site contributes to global scientific studies into climate change and our impact on the earth's atmosphere."

3.3.7.1 Description of the Station / Laboratory

In GAWSIS (http://gaw.empa.ch/gawsis/reports.asp) a brief station description is given, from which the following text has been adopted: "Baring Head Clean Air Monitoring Station is located on a remote coastal cliff top on the south coast of the North Island of New Zealand, overlooking the Southern Ocean (Fig. 32). The station, which was established in 1970, is 85 m above mean sea level, and approximately 240 m from the ocean (Fig. 30, Fig. 31). Southerly wind episodes at the site represent oceanic air to the south of New Zealand."

Baring Head (BHD) is classified as Regional Station in WMO RA V - South West Pacific-

Coordinates: 41.41 S, 174.87 E, 85 m a.s.l. Time zone: UTC + 12

The station is operated by NIWA, the New Zealand National Institute of Water and Atmospheric Research (www.niwa.co.nz). While in-situ measurements of CO_2 and O_3 are conducted at the site, N_2O monitoring is made using grab samples that are analysed in the NIWA laboratory in Wellington. The system audit thus consisted of two parts, one conducted on site at Baring Head, the other performed thereafter in the analytical laboratory of NIWA in Wellington.

3.3.7.2 Realisation of the Audit

For the performance audit (comparison experiment) five travelling standards were used that had previously been analysed at the CCL. From there they were shipped directly to New Zealand. They arrived at the NIWA laboratory before the scheduled audit visit. Employing travelling standards that had undergone such a recent comparison at the CCL helped minimizing the uncertainty associated with the assigned mole fractions.

The on-site system audit at the remote station was conducted on 24 October 2011, prior to the GGMT-2011 meeting. The system and performance audit of the NIWA laboratory for the N_2O analyses took place after the meeting and its follow-up activities on 1 November 2011.

During that day the analytical set-up was inspected, relevant information collected and details of the N_2O measurements discussed.

Fig. 32: Geographical location of the station Baring Head (BHD).
Map: http://www.weltkarte.com/

Fig. 30: View on Baring Head, located directly on the cliff. Source: NIWA web site http://www.niwa.co.nz/our-science/atmosphere/baring.

Fig. 31: NIWA's Baring Head monitoring station (Dave Allen). Source: NIWA web site http://www.niwa.co.nz/our-science/atmosphere/baring.

3.3.7.3 Results

According to the audit procedure, the results of an audit are presented in a dedicated Audit Report. This has not yet been completely finished for Baring Head. In the following the main results are summarized.

As described in 2.4 and 3.1.2.1, the CCL has updated its NOAA-2006 scale to slightly modified values under the name NOAA-2006A scale. Since the NIWA laboratory had already updated its standards to the most recent mole fractions, the audit comparison results presented here are all related to the NOAA-2006A scale. The travelling standards employed for the

audit had been analyzed at the CCL in September 2011 with the results being expressed in the NOAA-2006A scale. Since these mole fraction numbers were considered to be the best estimate for the travelling standards, they were directly used for the audit comparison. It is noted that the CCL applied small corrections to the originally reported numbers (Table 14).

The results for the travelling standards calculated by NIWA were related to a detector response curve determined during the respective analysis series and based on eight CCL-calibrated laboratory standards. The resulting statistics are shown in Table 15. Finally, Table 16 displays the outcome of the comparison in terms of the difference (NIWA - WCC) [ppb]. The most striking feature are the relative great differences with an average of 0.65 ppb. This result is not easy to explain, since the NIWA laboratory standards had been calibrated by the CCL. Detailed investigations of the cause of the bias still need to be done. In Fig. 33 it can be seen that the bias is not a function of the N_2O level in the range of 300 to 350 ppb. When the bias is subtracted, the graph shows deviations that all fall within a narrow interval of –10 to +0.12 ppb.

Table 14: Travelling standards used for the audit of the station Baring Head (BHD) / NIWA Laboratory with the mole fractions determined by the CCL prior to the use in New Zealand. The scale is NOAA-2006A. The table shows the values reported by the CCL in September 2011 and revised numbers as of May 2012. The latter are used for the audit comparison and are termed WCC-N_2O mole fractions in the following.

Short name	N_2O [ppb], NOAA-2006A	
	CCL Sep 2011	CCL May 2012
DS18	305.39	305.42
DS19	312.70	312.73
DS15	318.74	318.77
DS13	332.74	332.65
DS22	347.06	346.97

Table 15: Results for the five travelling standards of the audit comparison as reported by NIWA. Mole fractions are related to the NOAA-2006A scale. The numbers are averages of two series of 15 sample analyses each. The standard deviations (std) represent numbers averaged over the series 1 and 2.

Short name	N_2O [ppb], NOAA-2006A		
	NIWA (avg)	NIWA (std)	NIWA (n)
DS18	305.97	0.19	15
DS19	313.39	0.18	15
DS15	319.54	0.14	15
DS13	333.26	0.34	15
DS22	347.63	0.16	15

Table 16: Results of the audit comparison as differences between the values reported by NIWA (Table 15) and the assigned mole fractions (Table 14).

Short name	N_2O [ppb], NOAA-2006A		
	WCC-N_2O (= CCL)	NIWA	Difference NIWA - WCC
DS18	305.42	305.97	0.55
DS19	312.73	313.39	0.66
DS15	318.77	319.54	0.77
DS13	332.65	333.26	0.61
DS22	346.97	347.63	0.66

According to the analytical procedure, which involved all eight laboratory standards, the detector response curve was determined as part of a series for the audit comparison. A representative data set is shown in Fig. 34. Because of the very good agreement between linear and 2nd order fit, a quasi-linear relationship (mole fraction vs. normalised height) can be assumed for the interval covered by the laboratory standards. An extrapolation to zero (Fig. 35) reveals an offset for both fits, which, however, is rather moderate compared to the characteristics of similar ECDs in other instruments (cf. Fig. 19, for example).

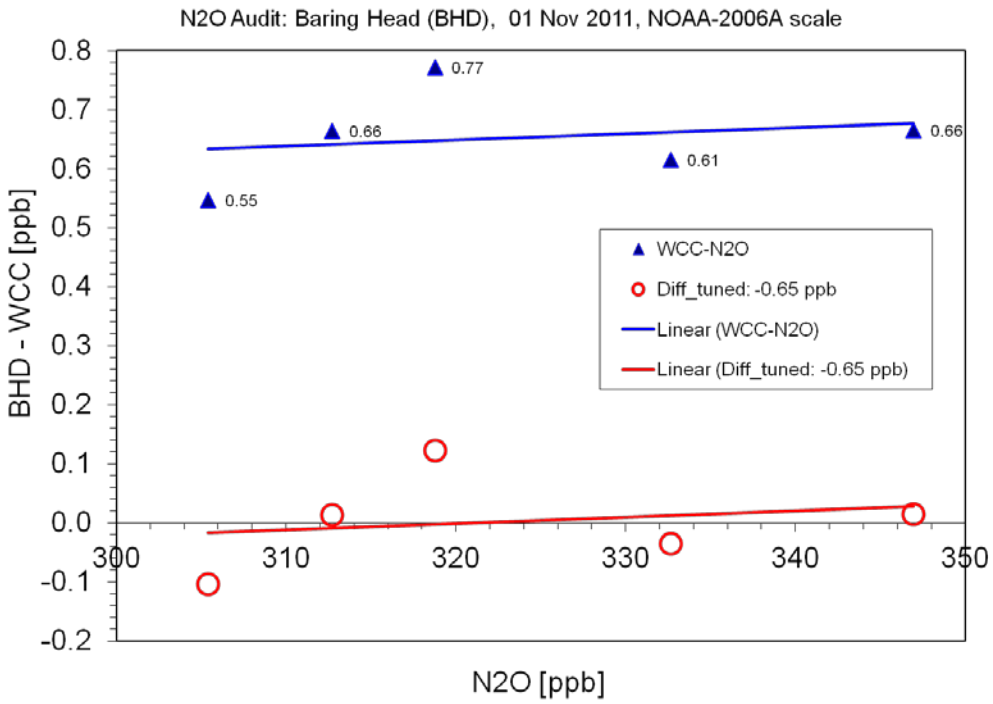


Fig. 33: Visualisation of the comparison results. The NIWA values show a systematic offset with an average of 0.65 ppb. When this is subtracted, the deviations fall into the narrow range of –0.10 to +0.12 ppb.

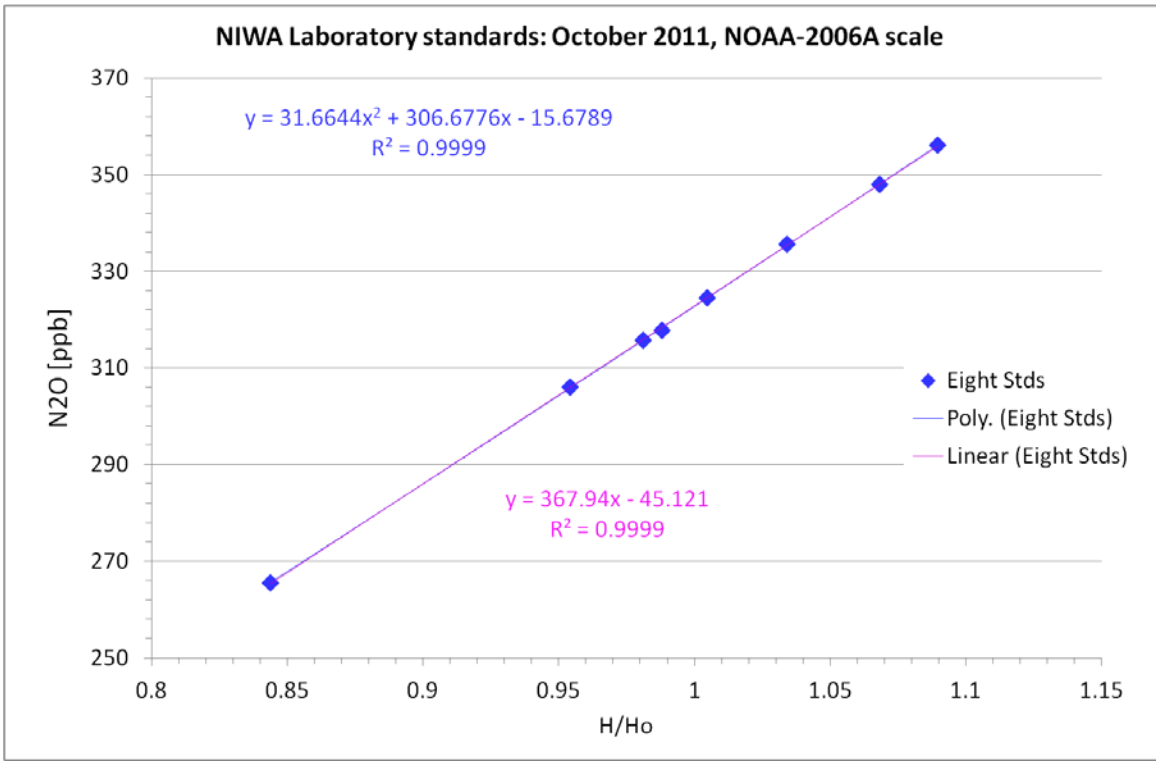


Fig. 34: Nominal values (NOAA-2006A scale) of the NIWA laboratory standards as a function of normalised peak height. The relationship characterises the detector response curve. Within the interval considered here the linear and second order fit coincide.

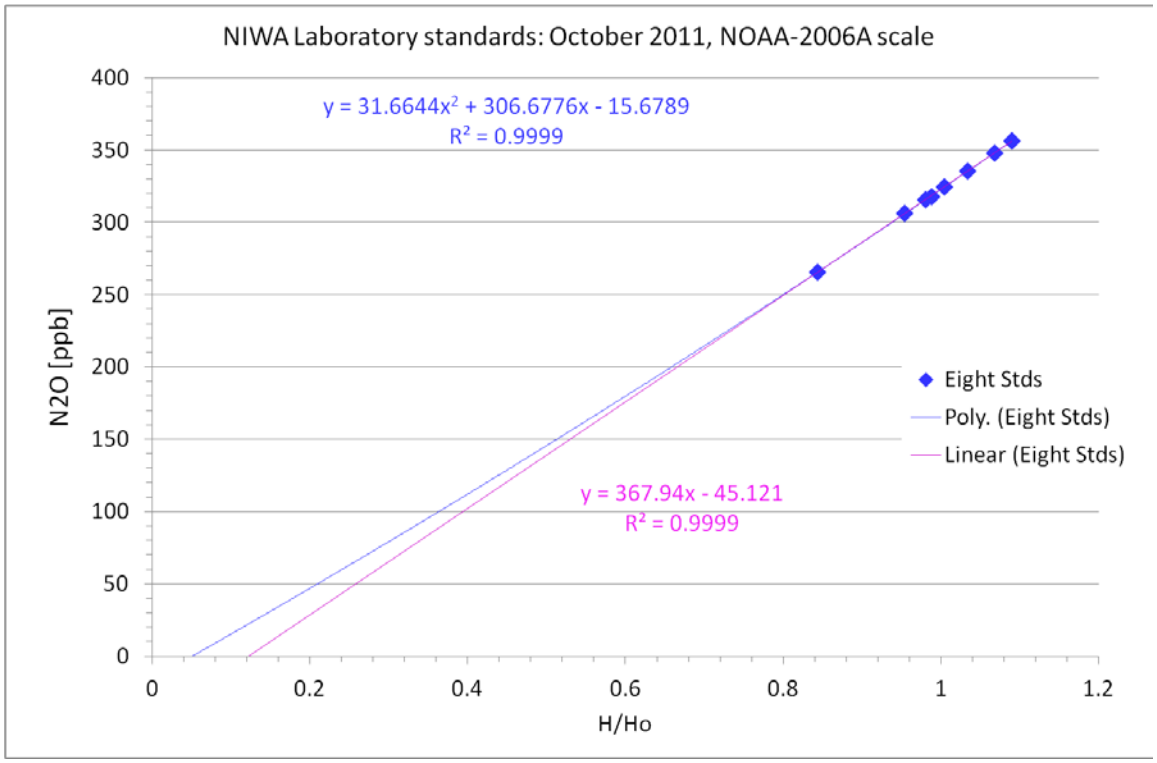


Fig. 35: Same as Fig. 34, but with extrapolation to zero.

3.3.8 Audit of the CARIBIC Project

The project named CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrumented Container) is based on measurements onboard a cargo container (http://www.caribic-atmospheric.com/). CARIBIC forms part of the German contributions to GAW, as described in detail in WMO/GAW Report No. 167. N_2O ranges among the species that are in the scientific focus of the project. However, no in-situ measurements of N_2O are performed. Instead flask samples are collected during the flights and are analysed in the laboratory of the Max-Planck Institute for Chemistry in Mainz (MPI Mainz) after return of the container. Since these data are aimed at contributing towards the global picture of N_2O, compatibility within the GAW network has to be assured. In line with this, it was agreed upon with the responsible scientists of the MPI Mainz that an audit including a comparison with five travelling standards would be desirable.

The system audit already took place on 1 December 2008. The travelling standards were sent out well in advance and were returned in January 2009. Due to some problematic details of the 2008 comparison results, it was decided to repeat the experiment. The repetition was conducted in December 2011. Again five WCC-N_2O travelling standards were employed. In the following the results of both experiments are presented.

3.3.8.1 Description of the Project

The project entitled **C**ivil **A**ircraft for the **R**egular **I**nvestigation of the atmosphere **B**ased on an **I**nstrument **C**ontainer (CARIBIC) aims at measuring a large number of atmospheric components during long-distance flights of passenger aircraft.

Fig. 36: Logo of the CARIBIC project (Source: http://www.mpic.de/CARIBIC.144.0.html)

The scope of the project and its motivation are presented at the CARIBIC web site http://www.caribic-atmospheric.com/index_2.htm. A brief description is also found under http://www.mpic.de/CARIBIC.144.0.html.

In practice, a container equipped with automatically operating scientific equipment is frequently flown on board a passenger aircraft (Fig. 37). Besides in-situ instruments, the container also has a system for collecting air samples. After return, these are analyzed in the laboratory for more than 40 gases, amongst them nitrous oxide (N_2O). The coloured map of Fig. 38 shows the flight routes of the CARIBIC2 part of the project.

Fig. 37: Project CARIBIC: Overview on aircraft and equipment (Source: CARIBIC web site)

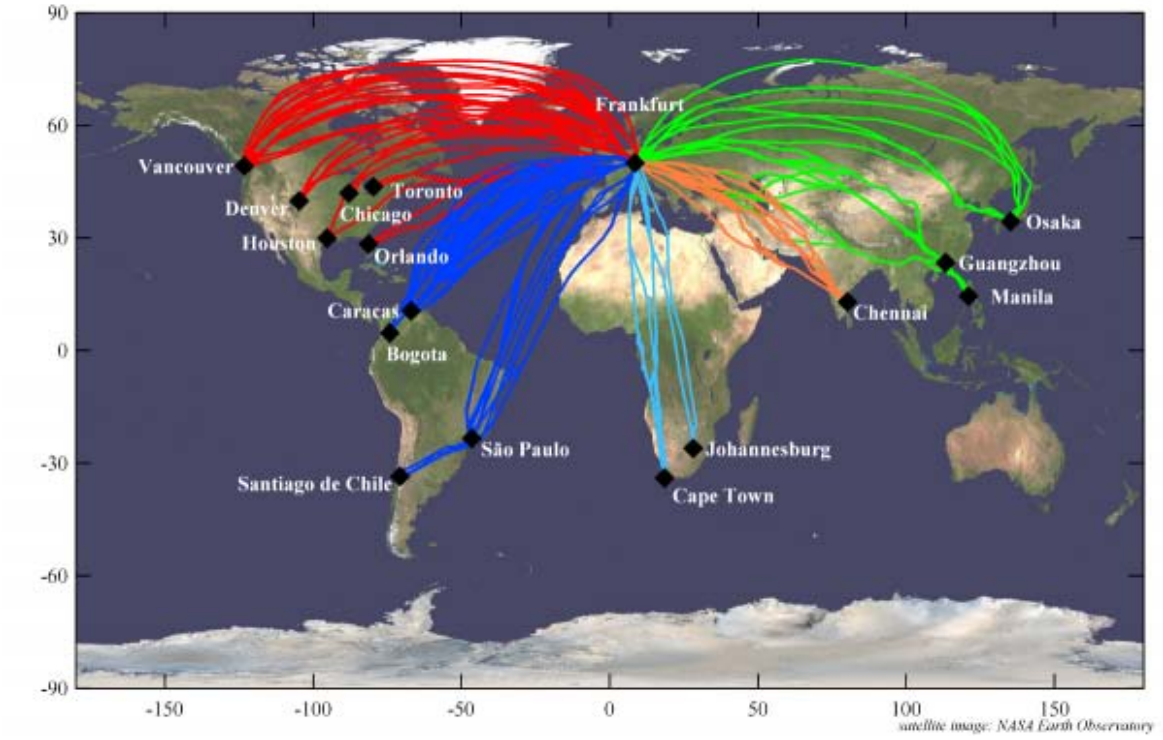


Fig. 38: CARIBIC2 flight routes (Source: http://wiki.caribic-atmospheric.com/index.php?title=Hauptseite).

3.3.8.2 Results 2008 Comparison

The comparison experiment involved the working standard of the MPI laboratory and five of the WCC-N_2O travelling standards, which are listed in Table 17. All data processing was performed by the responsible scientist of the MPI Mainz. N_2O mole fractions were determined for the individual analysis runs and submitted to the WCC-N_2O, with all N_2O mole fractions being reported based on the NOAA-2006 scale.

Table 17: Gas mixtures in 10-L cylinders serving as Travelling Standards of the WCC-N_2O. Cylinders employed for the audit of the MPI laboratory in 2008 and for the recent comparison of 2011 are listed in columns 3 and 4, respectively. For DS16 and DS21 the mole fractions assigned by the WCC-N_2O indicate a slight drift in the cylinders. Cylinder DS14 was among the five travelling standards compared with the CCL in 2007.

Cylinder		N_2O [ppb] as assigned by the WCC-N_2O (NOAA-2006 scale)		CCL results (comparison 2007) [ppb]	Diff.: WCC – CCL [ppb]
Number	Short name	in 2008	in 2011	NOAA-2006 scale	
4585D	DS8	314.94	314.97		
4618D	DS12	326.30			
4616D	DS14		305.95	305.89	0.06
4590D	DS16	331.51	330.98		
481362	DS17	284.94			
481333	DS20		316.97		
481356	DS21	337.08	336.67		

The individual analyses of the 5 travelling standards were evaluated using a single working standard, i.e. 1-level calibration, and the detector response curve was separately determined by means of the laboratory standards. The results are listed in Table 18. For DS8 revised mole fractions were reported in early 2012, while a new comparison experiment was going on. The revised numbers originate from reprocessing of the peak integration for the DS8 samples and are also listed in the tables (Table 18 and Table 19).

The N_2O standard deviations and relative standard deviations, respectively, obtained for the audit comparisons vary over a wide range. The minimum at 0.12 ppb (0.04 %) is in agreement with GAW Target Data Quality Objectives. However, all values greater than 0.5 ppb (0.16 %) do not meet GAW requirements and should be flagged if included in a database. Astonishingly, the comparisons results show standard deviations as high as 1.29 ppb (0.38 %). It is noted that these values are much higher than would be expected from modern N_2O GC instrumentation.

In Table 19 the average mole fractions reported for the travelling standards are compared with those assigned by the WCC-N_2O. Column 4 of Table 19 shows the average mole fractions as calculated from the MPI analyses. Based on these values, the differences between MPI and WCC-N_2O are given in the 5th column. In the two additional columns those mole fractions are displayed that are associated with a minimum difference to the WCC-N_2O. The last column contains the respective differences.

Table 18: Individual results of the analysis sequences for the comparison as reported by the MPI laboratory. For DS8 also revised mole fractions are shown (column 7).

Cylinder No.	Short name	N_2O [ppb]	Mean error [ppb]	Standard dev. [ppb]	Rel. std. dev. [%]	N_2O revised [ppb]	Mean error [ppb]
4585D	DS8	316.27	0.09	0.12	0.04%	315.97	0.09
"	"	316.14	0.53	0.73	0.23%	315.84	0.33
"	"	315.74	0.68	0.96	0.30%	315.17	0.67
4618D	DS12	325.82	0.86	1.21	0.37%		
"	"	326.22	0.25	0.35	0.11%		
4590D	DS16	331.30	0.18	0.25	0.08%		
"	"	331.42	0.24	0.29	0.09%		
481362	DS17	286.75	0.50	0.70	0.24%		
"	"	284.55	0.27	0.36	0.13%		
481356	DS21	335.76	0.85	1.19	0.36%		
"	"	335.10	0.91	1.29	0.38%		

Table 19: Comparison of the average N_2O mole fractions calculated from the MPI results with the mole fractions assigned by the WCC-N_2O as of 2008. The last two columns show the comparison results for the minimum difference out of the series measured by the MPI laboratory. For DS8 the average values obtained with the revised results are listed in a separate row (DS8 rev). All mole fractions are expressed in the NOAA-2006 scale.

Cylinder No.	Short name	WCC-N_2O	N_2O (MPI) average	Diff. MPI – WCC	N_2O (MPI) for min. difference	Min. diff. MPI - WCC
		[ppb]				
4585D	DS8	314.94	316.05	1.11	315.74	0.80
4585D	DS8 rev	314.94	315.66	0.72	315.17	0.23
4618D	DS12	326.30	326.02	-0.28	326.22	-0.08
4590D	DS16	331.51	331.36	-0.15	331.42	-0.09

481362	DS17	284.94	285.65	0.71	284.55	-0.39
481356	DS21	337.08	335.43	-1.65	335.76	-1.32

In Table 19 the differences "MPI - WCC" [ppb] range between -1.65 and +1.11 with no systematic mole fraction dependence and with the smallest difference value amounting to -0.15 ppb. The selection of the minimum differences out of the analysis series narrows the range of differences: -1.32 to +0.80 ppb, and the smallest absolute difference of -0.08 and -0.09 ppb for 326.30 and 331.51 ppb, respectively. When the revised results for DS8 (obtained from reintegration of the N_2O peak) are considered, the differences decrease from 1.11 to 0.72 ppb for the average value, and from 0.80 to 0.23 ppb for the minimum difference of the series.

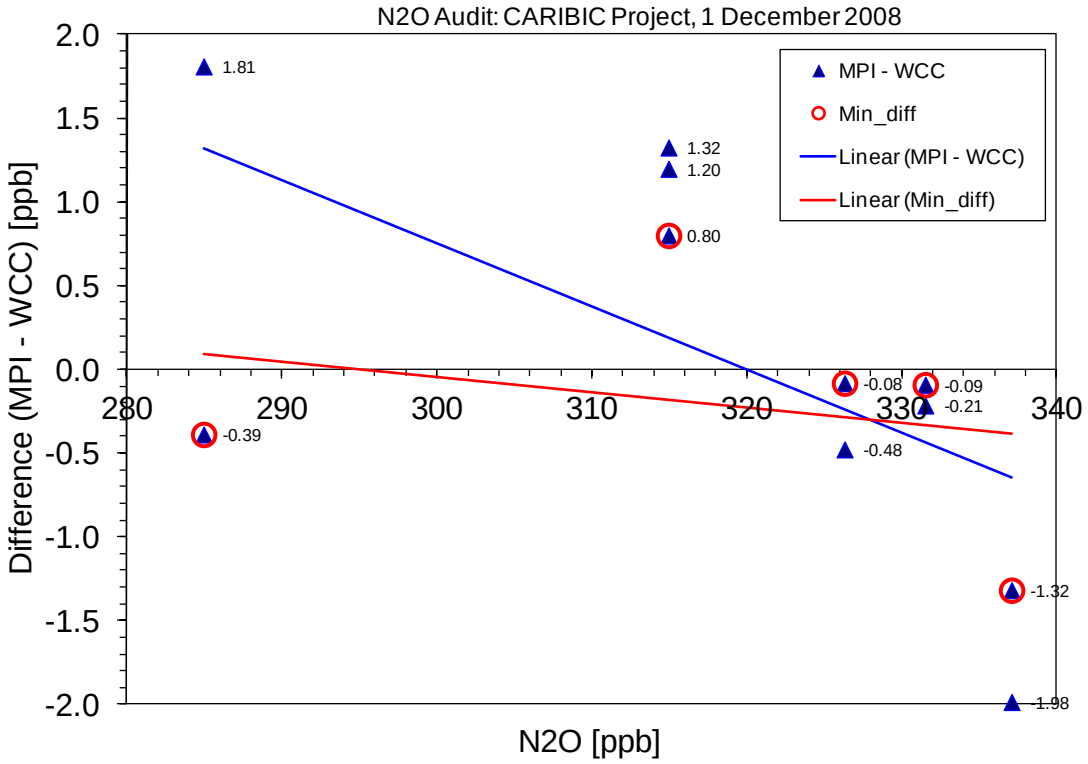


Fig. 39: Graphical representation of the results of the comparison experiment as part of the audit in 2008. Blue triangles: N_2O differences [ppb] between the MPI results originally reported and the values assigned by the WCC-N_2O. Red circles: Minimum difference within the individual sequences of analysis. The lines represent a linear regression fit.

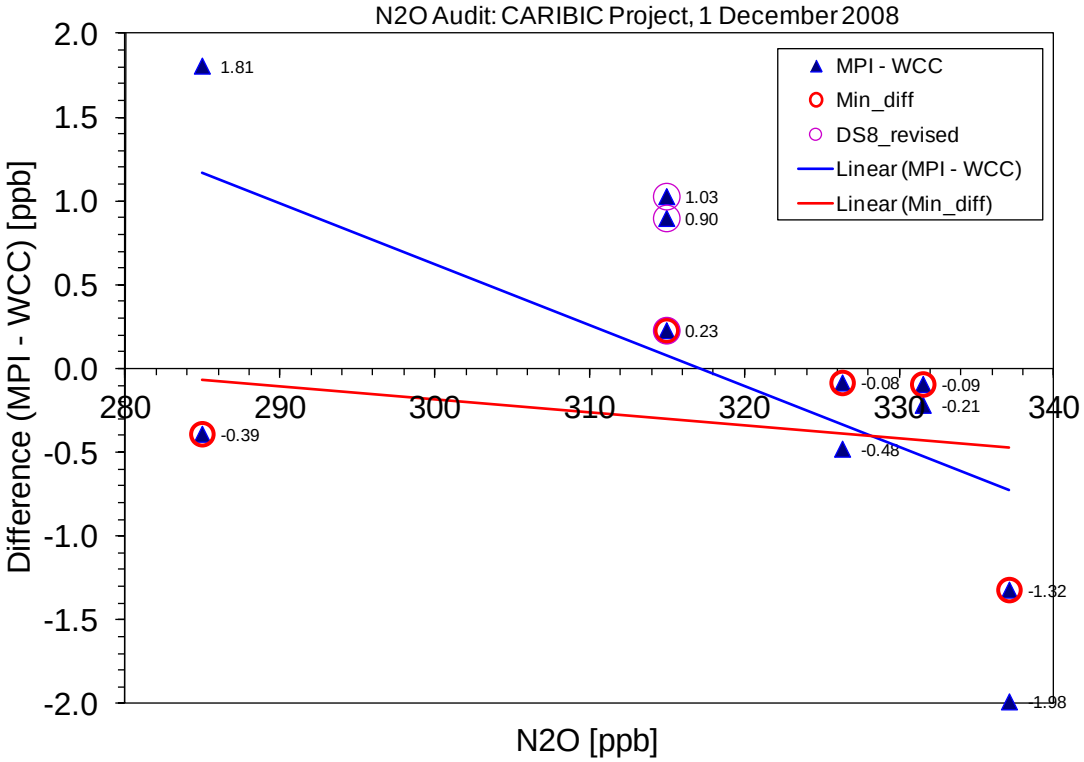


Fig. 40: Similar to Fig. 39, but based on the revised values for DS8. For explanations see text as well as caption of Fig. 39.

Unfortunately, the outcome of the audit comparison experiment shows that the N_2O analyses of the CARIBIC laboratory at the MPI Mainz do not fulfil the Data Quality Objectives set out by the GAW Programme. Most of the differences between reported mole fractions and the values assigned by the WCC-N_2O are unacceptably large. The individual series of analysis are characterised by poor reproducibility of the GC system. As the statistics of the individual series indicate, some of them yielded poor repeatability, as evidenced by the standard deviations (Table 18).

3.3.8.3 Comparison of N_2O Standards in 2011

Because of deficiencies that had become evident from the comparison experiment as part of the performance audit in December 2008, it was agreed to repeat the experiment. This took place from December 2011 until January 2012. The general experimental procedure was similar to 2008. Three of the five travelling standards involved were the same as used in the first comparison. The entire set was composed to cover the most relevant range of N_2O mole fractions.

The results of the analyses as reported are shown in Table 20. The statistical results indicate that the uncertainties associated with each series are rather large again. The N_2O data are partly characterised by poor repeatability within the individual series and poor reproducibility among the series for the individual cylinders. The average over the relative standard

deviations listed in the last column of Table 20 amounts to 0.43 % (n = 18), with values ranging from 0.02 % to 1.63 %.

The results of the comparisons are summarised in Table 21. The column of the differences indicates sufficient agreement for DS8, DS20 and DS21. In contrast, deviations from the WCC-N_2O mole fractions are too large for DS14 and DS16. Since more analysis series were measured during the recent comparison than for the 2008 experiment, it is now possible to identify outliers. As seen from Table 21, the removal of a single outlier greatly improves the results for DS8, DS16, and DS21. In this way an overall result of the comparison emerges that shows very good agreement to better than 0.1 ppb associated with 4 of the 5 gas mixtures. The only exception is DS14, for which no single outlier can be identified (Table 20).

Table 20: Individual results of the analysis sequences for the 2011 comparison as reported by the MPI laboratory.

Cylinder No.	Short name	N_2O [ppb]	Mean error [ppb]	Standard dev. [ppb]	Rel. std. dev. [%]
4585D	DS8	315.76	1.47	2.07	0.66
"	"	314.82	0.57	0.78	0.25
"	"	315.06	1.18	1.67	0.53
"	"	315.08		0.17	0.05
4616D	DS14	305.95		0.20	0.07
"	"	305.15	1.38	1.95	0.64
"	"	304.89	1.19	1.68	0.55
4590D	DS16	332.13	3.86	5.43	1.63
"	"	330.97		0.30	0.09
"	"	331.03	0.70	0.99	0.30
481333	DS20	317.09	0.43	0.58	0.18
"	"	317.05	1.55	2.18	0.69
"	"	316.86	1.51	2.14	0.68
"	"	316.90		0.07	0.02
481356	DS21	337.93	1.81	2.55	0.75
"	"	336.98	0.59	0.83	0.25
"	"	336.60	0.63	0.87	0.26
"	"	336.20		0.16	0.05

Table 21: Similar to Table 19, comparison of the average N_2O mole fractions calculated from the MPI 2011 results with the mole fractions assigned by the WCC-N_2O as of 2011. "N_2O (MPI) std dev" denotes the standard deviation calculated from statistics over 4 or 3 individual series. The last two columns show the comparison results when discarding 1 outlier out of the respective series measured by the MPI laboratory. All N_2O mole fractions are expressed in the NOAA-2006 scale.

Cylinder No.	Short name	WCC-N_2O	N_2O (MPI) average	N_2O (MPI) std dev	Diff. MPI – WCC	N_2O (MPI), 1 outlier discarded	Diff., 1 outlier discarded
		[ppb]					
4585	DS8	314.97	315.18	0.40	0.21	314.99	0.02
4616D	DS14	305.95	305.33	0.55	-0.62		
4590D	DS16	330.98	331.58	0.78	0.60	331.03	0.05
481333	DS20	316.97	316.98	0.11	0.01		
481356	DS21	336.67	336.93	0.74	0.26	336.59	-0.08

The results described above are visualised in two figures below (Fig. 41, Fig. 42). For the minimum difference excellent agreement with the WCC-N_2O mole fractions is apparent.

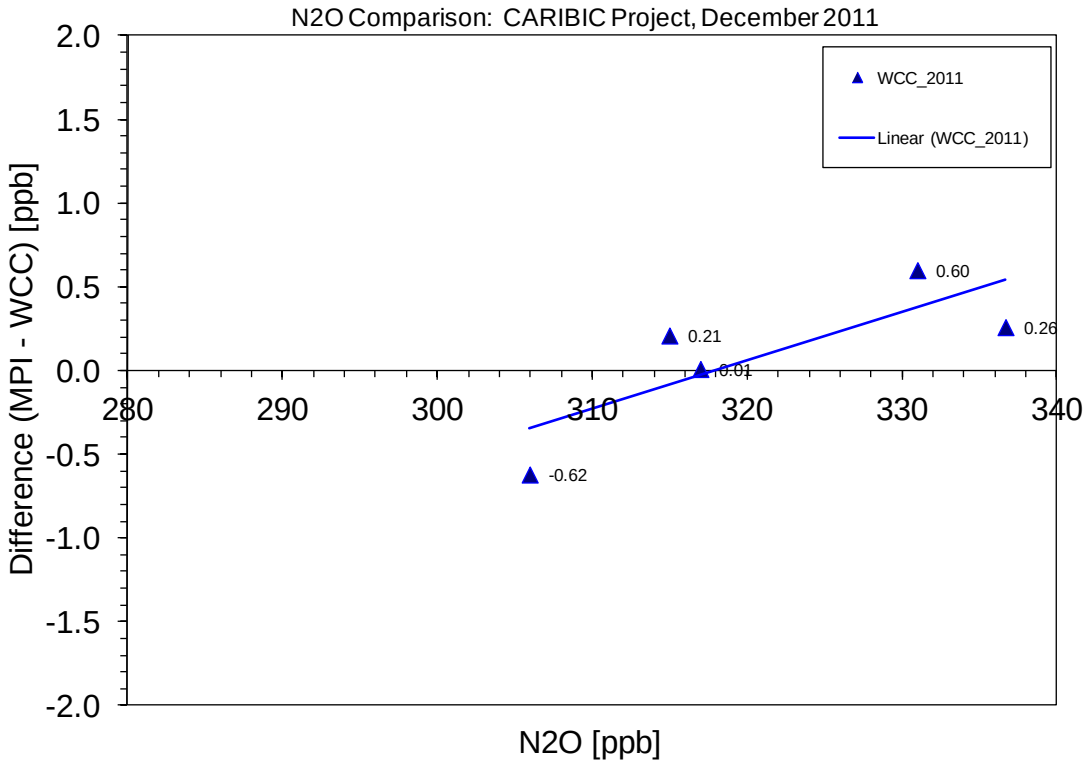


Fig. 41: Results of the comparison experiment conducted during December 2011/January 2012. Average N_2O differences between the MPI mole fractions and the values assigned by the WCC-N_2O as of 2011. The straight line represents a linear regression.

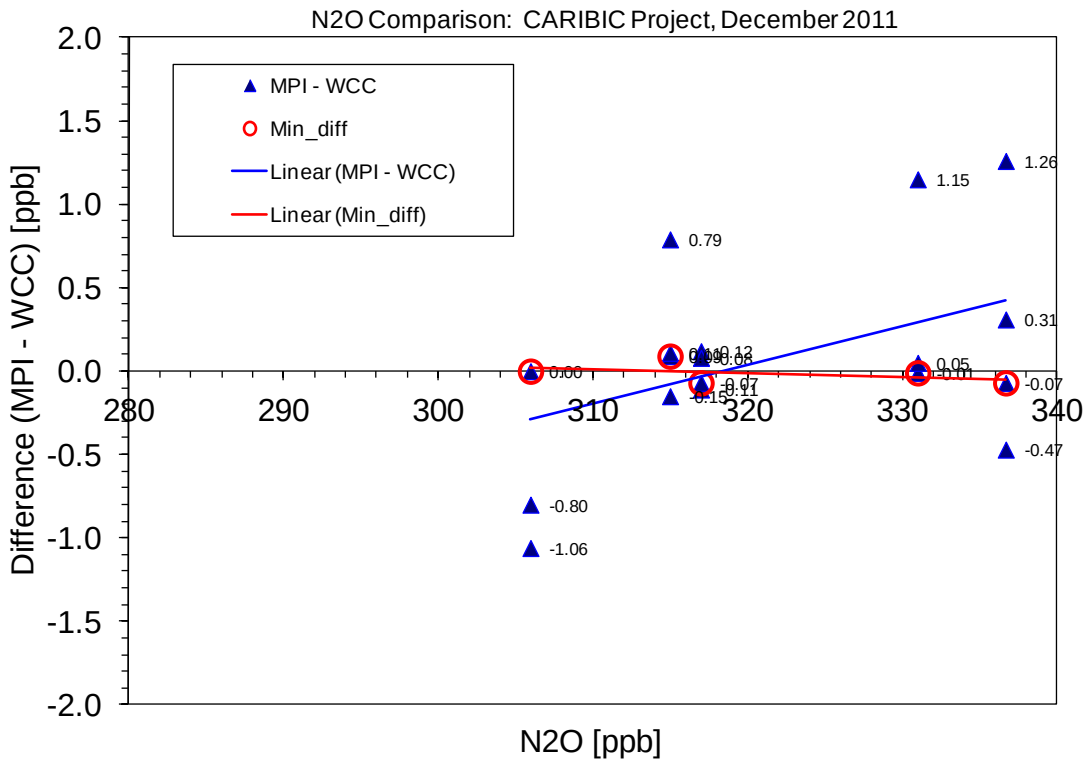


Fig. 42: Individual differences between the MPI mole fractions and the values assigned by the WCC-N_2O. Red circles: Minimum difference within the sequences of analysis. The lines represent a linear regression fit.

Due to the increased number of analysis series compared to the 2008 comparison experiment, it is now possible to remove an outlier showing up for a single analysis series out the four or three. This can yield a considerable improvement of the overall result. In summary, the agreement between MPI-Mainz and the WCC-N_2O obtained for the mole fractions of five travelling standards is much better in 2011/2012 than it was in 2008. However, the need for major improvements still remains for both repeatability as well as reproducibility of the N_2O analyses in the MPI laboratory.

3.3.8.4 Modified Data Processing for Comparison of N_2O Standards in 2011

The insufficient repeatability has been discussed with the responsible scientists at the MPI-Mainz during the months following the submission of the results. While the focus was on experimental conditions first, the WCC-N_2O finally took the initiative and recalculated the N_2O mole fraction results for one of the analysis series. This was based on concepts that closely resembled calculation schemes routinely used by the WCC-N_2O. With this procedure a drift of the detector sensitivity, evidenced by systematically decreasing peak areas, was accounted for. As a result, the repeatability was significantly improved. In the example under consideration, a relative standard deviation (representing the repeatability) as low as 0.04 % was achieved. Efforts for similar improvements of the data processing procedures were still ongoing while this report was being finalized.

3.4 N_2O Comparisons as Part of WCC-Empa Audits

3.4.1 General Concept

Collaboration between the WCC-N_2O and WCC-Empa was initiated with the aim of increasing the number of stations where N_2O comparisons are conducted. Therefore 10 WCC-Empa cylinders (travelling standards) without previously assigned N_2O values were already quantified by the WCC-N_2O in 2008, covering a N_2O mole fraction range of 295 - 355 ppb (see WCC-N_2O Report 2007-2008). One or more of these travelling standards were employed during WCC-Empa audits. In 2011, a reanalysis of some of these standards or a first analysis of newly prepared WCC-Empa travelling standards, respectively, was conducted for 6 WCC-Empa cylinders (cf. 3.2.3). It is noted that the reanalysis was originally scheduled for 2010 already. However, due to technical reasons on the side of the WCC-Empa, this was delayed.

A desirable increase in the number of N_2O comparisons was also an issue during the 16th CO_2 Experts Meeting (GGMT-2011) in October 2011 and will be addressed in the meeting recommendations within the respective WMO/GAW report.

3.4.2 WCC-Empa Audits with N_2O Comparisons

3.4.2.1 Station Barrow (BRW)

Based on one travelling standard a N_2O comparison was conducted by the WCC-Empa at the GAW Global Station Barrow (Alaska, USA). The result was presented in the WCC-Empa audit report entitled "SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE AND NITROUS OXIDE AT THE GLOBAL GAW STATION BARROW, USA, MARCH 2008". The manager of the WCC-N_2O is listed as a co-author.

The N_2O content of the travelling standard had been quantified to 315.73 ± 0.30 ppb (NOAA-2006 scale) by the WCC-N_2O. The comparisons at the site yielded a value of 315.74 ± 0.30 ppb (1σ), based on 11 injections, which is a surprisingly good agreement.

3.4.2.2 Station Mt. Waliguan (WLG)

Informal information about a WCC-Empa audit at the Chinese Global Station Mt. Waliguan was forwarded during the 15th CO_2 Experts Meeting in September 2009. Obviously the N_2O comparison results were contradictory and could not be explained so far. Therefore, either a repetition of the N_2O comparison or a full N_2O audit should be envisaged.

3.4.2.3 Station Izaña (IZO)

Based on five travelling standards with quantified N_2O content, WCC-Empa conducted comparisons as part of their audit of the GAW Global Station Izaña in March 2009. This was only a few months after the system and performance audit performed by the WCC-N_2O in November 2008. The outcome of the experiment for five different N_2O levels was presented

in the WCC-Empa REPORT 09/1: SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE AND NITROUS OXIDE AT THE GLOBAL GAW STATION IZANA, SPAIN, MARCH 2009 (http://gaw.empa.ch/gawsis/reports.asp). The manager of the WCC-N_2O was included in the list of co-authors.

The deviations between IZO and WCC-N_2O values ranged between -0.23 and +0.22 ppb for the interval 317.03 to 323.39 ppb (i.e. close to ambient levels). These results confirmed the outcome of the previously conducted full N_2O audit.

3.4.2.4 Station Mace Head (MHD)

The results obtained from N_2O comparisons at the GAW Global Station Mace Head in the course of an audit are presented in the WCC-Empa REPORT 09/3: SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE AND NITROUS OXIDE AT THE GLOBAL GAW STATION MACE HEAD, IRELAND, DECEMBER 2009 (http://gaw.empa.ch/gawsis/reports.asp). Again the manager of the WCC-N_2O is among the co-authors.

The experiment comprised four WCC-Empa travelling standards with N_2O mole fractions between 294.44 and 346.41 ppb (values assigned by the WCC-N_2O). For the three lower N_2O levels the deviations of MHD were between -0.17 and +0.29 ppb. This is still in agreement with the data quality objectives. For the standard at 346.41 ppb the deviation was 1.20 ppb. This can be explained by the fact that this mole fraction was outside the calibrated range of the Mace Head GC system. In order to fulfil GAW requirements in the future, the mole fraction range covered by the standards at the site should be extended. It is noted that GAW requests a range of 290 to 350 ppb.

3.5 Control of Success

3.5.1 General Remarks

The issue of control of success is an ongoing challenge for the WCC-N_2O as well as for other WCCs. So far the progress made at a site - after recommendations based on the outcome of an N_2O audit have been made known to the station's staff – is only checked on the basis of informal communication. This has been recognised as not being entirely satisfactory, and the development of appropriate measures is called for.

Up to now, no formal procedures for controlling the successful implementation of audit recommendations exist for GAW. The issue of control of success still remains a topic of future discussions within GAW, particularly involving the SAGs and QA/SACs. As an initial step, a list of priorities of actions to be taken by a station after the audit has been added to the template for audit reports.

3.5.2 Communication with Stations and Reported Success

In the following, some of the major audit recommendations and the status of their implementation are discussed. It is noted that specific actions and improvements cannot in all

cases be directly attributed to the audit recommendations. Some of the achievements may have been on the task lists of the stations anyhow. However, this is of minor importance. What counts is the overall progress at a GAW site.

3.5.2.1 Schauinsland (SSL)

Since the audit in November 2002, there were several contacts at irregular intervals with the station manager, either by phone or e-mail or by direct conversation during a meeting. The recommendation of the audit concerned the acquisition of additional laboratory standards in order to cover a wider range of mole fractions than was possible at that time, and the establishment of a direct link to one of the current major international calibration scales, preferably the NOAA scale. This was achieved. The success was documented by the audit of 2010.

3.5.2.2 Cape Point (CPT)

Contacts have mainly been maintained by frequent e-mail communication and by personal conversation on several occasions. Based on the audit conducted in February 2003 it had been suggested to envisage an upgrade of the N_2O instrumentation in the future. After a new GC had been commissioned in 2008, problems with its analytical performance persisted until 2011. A close link to the GAW N_2O scale has been established through a suite of CCL-calibrated laboratory standards. The success was documented by the audit of 2011.

3.5.2.3 Zugspitze (ZSF)

Contacts have taken place frequently at irregular intervals by phone calls and direct personal communication with members of the Schneefernerhaus GAW staff. Following up from the audit of December 2005, there were no immediate actions requested. The recommended in-house comparisons of the station's standards have been conducted in recent years. Through recalibration of laboratory standards and commissioning of additions standards, a close link to the CCL has been achieved.

Concerning the recommended improvements of the N_2O separation in the chromatogram, i.e. full separation of the CO_2 signal from the N_2O peak as well better separation between N_2O and SF_6, no efforts have been made so far. As communicated by the station manager, this is due to different reasons, notably lack of personal resources, given the comprehensive measurement programme at the site.

3.6 Work on WMO/GAW Documents

As in previous years, the WCC-N_2O was again involved in the preparation of WMO/GAW documents.

3.6.1 GAW Terminology and Definitions

The "WMO/GAW Glossary of QA/QC-Related Terminology" (Editors: J. Klausen, H.-E. Scheel and M. Steinbacher, http://gaw.empa.ch/glossary/glossary.html) is intended as a tool

for facilitating the use of GAW-recommended terminology, which is widely based on ISO definitions.

In 2010 it was recognized that the first version of the glossary (0.4 2007-04-26) was outdated because of more recent definitions in the latest versions of ISO documents. Therefore efforts for updating the glossary were initialized. During the editing process, criticism and input from the GAW secretariat was received. This was mainly related to the purpose of better meeting the requirements of GAW participants. The current version is available on the web and was named "version 1.0 2010-09-14". Moreover, ideas for further improvement have already been collected within the WCC-N_2O and will be discussed with the other editors in the near future.

3.6.2 Measurement Guidelines for CH_4 and N_2O

The work on Measurement Guidelines for CH_4 and N_2O and the involvement of the manager of the WCC-N_2O had already been described in previous WCC-N_2O reports. Finally, in the summer of 2009 a long process of editing came to its end after several last-minute suggestions by O. Tarasova, as a new member of the GAW secretariat, had been implemented. In August 2009 both the printed and the electronic version were available as WMO/GAW Report No. 185. The PDF file can be downloaded from
http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html.

3.6.3 Contributions to other WMO/GAW Documents

3.6.3.1 Review of Minutes of SAG GG Meetings

A draft of the agenda for the biennial meetings of the Scientific Advisory Group for Greenhouse Gases (SAG GG) is usually sent around by the chairman of the SAG prior to the meeting, requesting feedback and suggestions. After the meetings a draft of the minutes is circulated among the participants, thus aiming at corrections and clarifications. In the case of two meetings, 2009 in Jena (Germany) and 2011 in Wellington (New Zealand), the WCC-N_2O has actively contributed.

3.6.3.2 Expert Group Recommendations

As had been the case for previous meetings of this kind, the scientists present at the "15th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques", 7-10 September 2009 in Jena, Germany recommended a number of procedures and actions to achieve the adopted WMO goals for the Global Atmosphere Watch (GAW) network compatibility among different laboratories and various components. These issues are usually summarized in the 'Recommendations' as part of the Meeting Proceedings released as WMO/GAW Reports. During March to May 2010, editing of the Recommendations took place with active involvement of the manager of the WCC-N_2O. He contributed in particular to paragraphs of the Introduction as well as to Table 2, which presents a selection of frequently used terms related to the recommended ISO terminology.

Similarly, a draft of the Recommendations compiled after the "16t^{h} WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2011)", which took place in Wellington (New Zealand) from 25 - 28 October, 2011, was critically reviewed. As a result, several details were addressed in the response to the editorial committee.

3.6.3.3 Cooperative Agreement

During 2011 efforts were made to move forward with a Cooperative Agreement between the Karlsruhe Institute of Technology (KIT) and the World Meteorological Organization / Global Atmosphere Watch Programme (WMO/GAW) with regard to the recognition of the World Calibration Centre (WCC) for nitrous oxide (N_2O) to the WMO/GAW Programme. The agreement was finally signed for WMO/GAW in Geneva on 29 November 2011 and for KIT in Karlsruhe on 12 December 2011.

3.7 Contributions to GAWTEC

3.7.1 Lectures

From the beginning of the GAW Technical Education Centre it was foreseen that the WCC-N_2O should contribute to GAWTEC courses. Since N_2O measurements are being done at only a few stations worldwide (and most of them with long-term experience), also during the period 2009 -2011 there has been no demand for specific training on N_2O. On the other hand, an urgent need to improve the general skills of data visualisation was identified already shortly after the inception of GAWTEC. Moreover, ISO terminology, which should be used in fulfilment of GAW requirements, has gained increasing relevance over the years.

Therefore, a lecture on visualisation - entitled "Graphical Presentation of Measurement Data" - had been outlined already in 2002. Based on the experience gained during the courses, the content of the presentation was progressively extended over the years. In its last part the lecture contains a tutorial based on an Excel spreadsheet where some advanced skills for routine work are presented. Part of the issues of the lecture can be deepened by two practical exercises to be done by the participants. It is noted that the files provided for the practical training are designed for the English version of Excel, since English is the official language within GAW in general.

Issues related to the use of ISO terminology have been addressed by GAW documents, notably the Strategic Plan (WMO/GAW Reports No. 142 and 156). However, practical steps for the implementation within GAW were lacking. With regard to the involvement of the manager of the WCC-N_2O in these matters, the terminology issue was also placed on the agenda of the GAWTEC courses. A lecture entitled "GAW Terminology and ISO Definitions" was prepared. Its purpose is to familiarise the participants with current developments within GAW and to give them a flavour of the use of ISO terms for their practical work. Since the WMO/GAW Glossary of QA/QC-Related Terminology is available on the web (http://gaw.empa.ch/glossary/glossary.html), the lecture could directly refer to this document.

Both types of lectures were generally well received by the participants. This was especially evident by the feedback received from the questionnaire on the lectures and their usefulness. The lectures and exercises (as PowerPoint and Excel files) were included in the CD-ROM of the GAWTEC courses handed out to the participants or – increasingly popular – distributed via USB memory stick during the course. It is noted that the selection of the trainees did not fall within the responsibility of the WCC-N_2O, but was made by the GAWTEC management in close contact with the GAW secretariat.

In 2009 the WCC-N_2O has contributed to two courses, i.e. No. 16 (March) and No. 17 (August), with the above described lectures.

In 2010 the WCC-N_2O was in charge of the respective contributions for two courses. These were the courses No. 18 (April) and No. 19 (October). Since the GAWTEC course 19 was focussed on greenhouse gases, in addition a lecture on N_2O measurements was given. It comprised an overview on different aspects of this greenhouse gas, according to the following outline:

1) N_2O in the Atmosphere
2) Why is N_2O measured?
3) Where are background levels measured?
4) How is N_2O measured ?
5) N_2O within GAW: Standard Scale, Data Quality Objectives (DQO), Quality Assurance and Quality Control (QA/QC)

Unfortunately, in 2011 the dates of the GAWTEC courses were in conflict with times of absence of the WCC-N_2O manager due to business trips. Therefore, updates of the two standard lectures were jointly prepared with the GAWTEC manager, K. Woudsma, and the lectures finally presented by her.

3.7.2 Experience from Recent Practical Exercises

The lectures on graphical representations with practical exercises have revealed widespread deficiencies amongst the trainees with regard to their skills of data visualisation. Until a few years ago, the exercises, which are based on two Excel files, were performed on GAWTEC PCs equipped with software in English. In recent years, however, most of the trainees brought along their own laptop PCs with country-specific installations (Russian, Chinese, Polish, etc.). Unfortunately, work with the files provided for the exercises has turned out to be difficult if important functions and Excel commands are not known by the trainees and/or not found on their PCs. In such cases the supervisor cannot be of assistance, which questions the success of such exercises. So far, no solution has been found yet. Therefore, the matter calls for further discussion among the GAWTEC management and lecturers.

3.8 Contacts and Cooperation

3.8.1 Central Calibration Laboratory (CCL)

The contacts and collaboration have already been described in preceding sections.

3.8.2 World Data Centre for Greenhouse Gases

Contacts with the WDCGG took place with respect to:

- use of N_2O data archived by the data centre,
- personal communication with the new (2011) director of the WDCGG on the occasion of GGMT-2011 in October 2011,
- communication with the director of the WDCGG during the meetings of the SAG GG in 2009 and 2011.

3.8.3 Scientific Advisory Group for Greenhouse Gases (SAG GG)

Since the manager of the WCC-N_2O is also a member of the SAG GG, there were several e-mail contacts with the chairman of this group or through circulars involving all members. Response was also provided to requests of the GAW secretariat. It is noted that the number of contacts from the GAW secretariat to the SAG GG increased during the last years. Response was usually given by the individual members with "CC to all".

The active cooperation by the manager of the WCC-N_2O was explicitly appreciated by the chairman of the SAG on several occasions. Details of special topics pertaining to the SAG are described elsewhere in this report.

3.8.4 WMO/GAW Secretariat

In a number of cases the manager of the WCC-N_2O was contacted directly by the GAW secretariat. Response was given depending on own expertise and resources of information.

3.9 Consulting

In fulfilment of the task of the WCC-N_2O to provide technical assistance to stations, exchange of know-how again took place during the period 2009 - 2011. In particular the 15th and 16th Experts Meeting in Jena (2009) and Wellington (2011), respectively, provided a good platform for the discussion of QA/QC and related matters. Below several noteworthy details are supplied.

3.9.1 Global Station Cape Point

After a new N_2O gas chromatograph had been installed at Cape Point in early 2008, contacts on analytical details, notably fine-tuning of the N_2O analysis, were maintained throughout the years 2009 to 2011. The WCC-N_2O was able to render a number of suggestions for improving the initially poor data quality of the new instrument.

Since a Cape Point staff member had participated in the GAWTEC course No.19, there was the opportunity for specific know-how transfer in the laboratory of the WCC-N_2O, which actually took place during three days. Based on this and in view of the forthcoming audit at Cape Point in February 2011, expectations grew for making substantial progress with the N_2O data quality.

In response to recommendations of the manager of the WCC-N_2O, the N_2O system at Cape Point was reduced to its essentials, thereby employing separately installed spare units, such as a Gas Sampling Valve. These measures contributed toward improving the data quality for comparisons among standards, as documented by the results of the audit in February 2011.

3.9.2 KRISS (Korea)

In the year 2011, the two organizations KMA (Korea Meteorological Administration) and KRISS (Korea Research Institute of Standards and Science) have launched a joint initiative with the aim of establishing a WCC for SF_6 within GAW.

On the basis of existing contacts to KRISS, the WCC-N_2O has forwarded information on its experience with the operation of this type of GAW Central Facility. In particular, a member of KRISS took part as a guest in the N_2O audit conducted in the NIWA laboratory in Wellington (New Zealand) in November 2011. This provided a good opportunity to get familiar with such a QA/QC activity. In addition to contacts via e-mail, a delegation of three persons (two from KMA, one from KRISS) visited the WCC-N_2O in April 2012. The staff of this WCC provided detailed information, in particular on the practical aspects of running a WCC, such as budget, foreseeable workload and size of staff.

3.9.3 Others

Advice pertaining to the N_2O analysis was rendered to the station Zugspitze at Schneefernerhaus. Moreover, a general exchange of know-how took place on several occasions. Over the years there were direct personal as well as telephonic contacts with the Zugspitze station staff.

Moreover, contacts by telephone and e-mail took place with the station Schauinsland.

Consultations with the Monte Cimone station were related to post-audit contacts.

At the end of December 2010 an inquiry from India was received, thereby requesting information on various aspects of the establishment of a GAW station for greenhouse gas monitoring. Detailed answers were provided in January 2011, however, no response was received on this matter.

3.10 Participation in Meetings and Workshops

In the following, the meetings and workshops are listed chronologically.

3.10.1 GAW Workshop 2009

From 5 -7 May 2009 a workshop entitled "GAW 2009 Workshop" was held in the WMO Headquarters in Geneva. It belongs to a series of meetings that take place every four years. For details see: http://www.wmo.int/pages/prog/arep/gaw/GAW_2009_Workshop.html. The workshop provided a good platform for the general exchange of ideas, for an overview on the current status of GAW and for the discussion of present and future focal areas. A dedicated

presentation of the WCC-N_2O, as had been made four years before, did not seem to be appropriate. However, the manager of the WCC-N_2O has actively participated in two working groups. Details on the first one can be found at the conference web site. Group: Quality Aspects of Observations, Data and Information Flow, http://www.wmo.int/pages/prog/arep/gaw/documents/WMONetwork_GAW2009.pdf. The group report to the plenary session in given under http://www.wmo.int/pages/prog/arep/gaw/-GAW_2009_Workshop_materials.html.

3.10.2 German GAW Meeting at UBA Langen

The 2nd workshop of the German WCCs was held in the UBA offices in Langen (Germany) on June 6, 2009. For the WCC-N_2O its manager gave a talk in German under the title "Arbeit des WCC N_2O: Rückschau und Ausblick". By way of a PDF file, the PowerPoint presentation was made available to all participants.

3.10.3 15th WMO/IAEA Meetings of Experts

The 15th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques formed part of a series of bi-yearly meetings of this kind and was held in Jena (Germany) from 7-10 September 2009. It was organized by the local Max-Planck Institute for Biogeochemistry ((MPI-BGC) (http://www.bgc.mpg.de/service/iso_gas_lab/IAEA-WMO2009/index.shtml)

The state of the work of the WCC-N_2O was presented in a talk entitled "Report of the WCC-N_2O". It can be downloaded from: http://www.bgc.mpg.de/service/iso_gas_lab/IAEA-WMO2009/programm.shtml.

3.10.4 Meeting of the Scientific Advisory Group for Greenhouse Gases 2009

Traditionally the bi-yearly meeting of the SAG GG members is scheduled for the day after the WMO/IAEA Meeting of Experts. The 2009 meeting was again organised by the chairman of the SAG GG and was held on 11 September in a seminar room of the MPI-BGC in Jena. Since the manager of the WCC-N_2O is a member of the SAS GG, his participation is mandatory. Prior to the meeting, the items for the agenda were suggested by the chairman and modified or supplemented by individual members. The outcome of the SAG GG meetings is summarized in its minutes, which are usually distributed by e-mail to the members only. Due to some misunderstanding, the 2009 minutes were added to the GAW web site and can be found there under
http://www.wmo.int/pages/prog/arep/gaw/ghg/documents/Minutes_ghg_sag_20090911.pdf.

Of the items discussed during the meeting, the following are worth being mentioned in the context of this project report:

- *Item 2: WMO plans to sign a Mutual Recognition Agreement (MRA) with the International Committee of Weights and Measures (CIPM). … This action will help make atmospheric measurements used to verify GHG emissions legally defensible. In*

general, the MRA assures equivalency among standards among its signatories through "key comparisons".

- *Item 7. Status of measurement guidelines for CH_4 and N_2O. WMO report 185, now available on WMO/GAW webpage! The group thanked Eckhart for a job well done for his efforts in preparing the report and seeing it through to fruition.*

The procedure addressed under Item 2 shall ensure that the GAW calibration scales are accepted as being compatible with the scales maintained by NMIs under the umbrella of CIPM.

3.10.5 German GAW Meeting 2010 (GAW-Statustreffen)

On March 16 and 17, 2010, a German GAW meeting (Statustreffen) took place in Munich with focus on the German activities within the GAW Programme. An oral presentation ("Aktivitäten des WCC-N_2O") of the manager of the WCC-N_2O outlined the work of this GAW facility. The PowerPoint slides were submitted as a PDF file to the organizer, W. Fricke (DWD, Meteorologisches Observatorium Hohenpeißenberg) and placed in the internet under http://www.dwd.de/bvbw/appmanager/bvbw/dwdwwwDesktop?_nfpb=true&_pageLabel=_dwdwww_klima_umwelt_ozon&T22801286021158040147152gsbDocumentPath=Navigation%2FForschung%2Fchemie__der__atmos%2FMOHP%2Faktuelles__de__node.html%3F__nnn%3Dtrue.

3.10.6 GAW Meeting Leipzig 2010

On October 5 - 6, 2010, the 3rd workshop of German WCCs was held in Leipzig (Germany) and was hosted by the IfT Leipzig. The contribution of the WCC-N_2O consisted of two talks, dealing with the work of the WCC-N_2O as well as the work of the SAG GG and news from the GAW Programme. Both presentations were made available to the participants as PDF files.

3.10.7 2nd International Workshop on Atmosphere Watch in Asia

From October 21 to 22, 2010 a GAW workshop entitled "2nd International Workshop on Atmosphere Watch in Asia – Greenhouse Gases Monitoring Activities" took place in Jeju (Republic of Korea). It was jointly organized by the Korea Meteorological Administration (KMA) and the Korea Research Institute of Standards and Science (KRISS). The manager of the WCC-N_2O was invited to give a talk on quality assurance activities for the measurements of greenhouse gases within the GAW Programme. Accordingly, a presentation was made under the title "The Role of CCLs and WCCs in the GAW Programme for the Observation of Greenhouse Gases".

Moreover, a representative of the GAW secretariat had also been invited to the workshop. Unfortunately, nobody from the secretariat could find time to honour the invitation. Therefore the manager of the WCC-N_2O - actually the only European participant - was asked by L. Jalkanen (WMO/GAW) to give an overview talk on behalf of GAW. A complete suite of PowerPoint slides ("WMO/GAW observation system and greenhouse gases") was made available in advance. This talk was scheduled as the first presentation of the workshop.

Authors as listed by the GAW secretariat were: H.E. Scheel, O. Tarasova, L. Jalkanen and L. Barrie.

Both presentations were submitted to the organizers as PDF files and were shown under the address http://www.climate.go.kr/index.html on the web for several weeks, together with the other presentations as well as posters. Unfortunately, the files have since been removed.

3.10.8 Workshop of the Department of Environmental Affairs (South Africa)

While the manager of the WCC-N_2O stayed in South Africa on the occasion of a Cape Point audit in February 2011, the South African Department of Environmental Affairs (DEA) had scheduled a workshop entitled "Establishment and Implementation of the National Reference Laboratory". It took place in Pretoria on February 17, 2011. The workshop was aimed at defining a concept for a national reference laboratory to be established in South Africa. This future laboratory will prescribe uniform scales to be used in all monitoring activities, ranging from regional to industry-related. In this context the global perspective of GAW was of interest too. Therefore, the manager of the WCC-N_2O was invited to participate and give a talk entitled "Monitoring in the GAW Network". This actually took place as requested, and the presentation was well received. A PDF file of the PowerPoint presentation was submitted to the organizers after the workshop.

3.10.9 GAW Workshop Garmisch-Partenkirchen

On June 8 - 9, 2011 the "4th workshop of the German WCCs and QA/SAC in GAW" was held in Garmisch-Partenkirchen, where it was hosted by the two WCCs within KIT IMK-IFU, namely the WCC-N_2O and the WCC-VOC. The WCC-N_2O contributed with two oral presentations under the titles "Arbeit des WCC-N_2O" (Work of the WCC-N_2O) and "Zur Arbeit der Scientific Advisory Group for Greenhouse Gases (SAG GG) und Neues aus GAW" ("Work of the Scientific Advisory Group for Greenhouse Gases (SAG GG) and recent news from GAW"). After the workshop, both PowerPoint presentations were submitted to QA/SAC Germany as PDF files, which were distributed to all participants thereafter.

3.10.10 GGMT-2011

The "16th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2011)" took place in Wellington (New Zealand) from 25 - 28 October, 2011. This type of meeting is a regular, bi-yearly conference (e.g. held in Jena in 2009) that brings together about hundred participants involved in various ways in global greenhouse gas monitoring and research. The meeting was organised by members of NIWA (National Institute of Water and Atmospheric Research of New Zealand). The participation of the manager of the WCC-N_2O as a GAW central facility is mandatory. A poster presentation was made under the title "Overview on 10 years of WCC-N_2O". The poster permitted an overview on the different activities of the WCC-N_2O as well as the progress achieved since the inception of this facility.

3.10.11 Meeting of the Scientific Advisory Group for Greenhouse Gases 2011

Following GGMT-2011, the bi-yearly meeting of the Scientific Advisory Group for Greenhouse Gases (SAG GG) took place in the NIWA buildings on 29 October 2011. As a member of the SAG GG, the manger of the WCC-N_2O had to participate. Several items were discussed, following the agenda that had been circulated before the meeting. However, there were no specific points that are noteworthy in the context of this report.

Finally, the manager of the WCC-N_2O has expressed his willingness to stay on as a SAG member for another two years, i.e. until the time of the next SAG GG meeting in 2013.

3.11 Project Control

3.11.1 Year 2009

According to the contract between UBA (QA/SAC-Germany) and the Forschungszentrum Karlsruhe (FZK, now KIT), funding of two months for one person was foreseen for the year 2009. Expressed in project calculations of the FZK and the KIT, respectively, this is equivalent to 34.34 days. In practice the work of the WCC-N_2O covered about 42.6 days, as explained in detail below.

The WCC-N_2O has been operated by a single scientist of the IMK-IFU. The total working time devoted to the project in 2009 can be separated into (1) directly recorded working hours and (2) estimated expenditure of time.

(1) 20.8 days could be directly assigned. This refers to working hours spent for GAWTEC courses, travelling and work in the laboratory. The latter activities were mainly concentrated in the months November and December.

(2) In addition, other activities during 21.8 days were estimated. This refers mainly to work on reports and GAW documents, communication with the SAG GG and others GAW facilities as well as technical support and advice.

3.11.2 Year 2010

According to the contract for the WCC-N_2O project, in 2010 activities of one person during 3.5 months were funded. This is equivalent to 60.1 days, based on the project calculations of the Karlsruhe Institute of Technology. In reality, the work done for the WCC-N_2O by the IMK-IFU amounted to at least 64.7 days, as detailed below.

The staff of the WCC-N_2O was the same as in 2009. Again the total time devoted to the project can be split up into two categories of activities.

(1) 32.7 days could be directly assigned to similar types of work as for 2009.

(2) An estimation of other activities yielded a sum of 32 days. This refers mainly to work on reports and GAW documents, communication with the SAG GG and other GAW facilities, preparation of audits, participation in workshops as well as technical support and advice.

3.11.3 Year 2011

According to the contract for the WCC-N_2O project, in 2011, the activities of one person were funded for a period of 3.0 months. This is equivalent to 51.5 days, based on the project calculations of the Karlsruhe Institute of Technology. In reality, the work done for the WCC-N_2O by the IMK-IFU amounted to at least 58.6 days, as detailed below.

The staff of the WCC-N_2O was the same as during the two preceding years. Again the total time devoted to the project can be split up into two categories of activities.

(1) 14.1 days could be directly assigned, primarily to laboratory work.

(2) An estimation of other activities yielded a sum of 44.5 days. This refers mainly to work on reports and GAW documents, communication with the SAG GG and other GAW facilities, preparation and conduction of audits, participation in workshops as well as technical support and advice.

4 Overview on Ten Years of WCC-N_2O

Since the end of the 3-year project period under consideration here (2009 - 2011) coincides with a major change in the management of the WCC-N_2O, it seems appropriate to present an overview on findings and conclusions from the ten years of operation of the WCC-N_2O since its inception.

4.1 Summary of Audit Findings

- Crucial point in the gas chromatogram: Sufficient separation of the N_2O peak from preceding CO_2 signal and the subsequent small SF_6 peak.
- No relationship between standard deviation of analysis runs (repeatability) and quality (closeness of agreement) of comparison results.
- Careful determination of the response curve is of importance if one wants to quantify gas mixtures over the entire range between 290 and 350 ppb.
- 1-point calibration of the detector signal (use of 1 working standard only) is insufficient, since it does not yield correct results, except for very special cases (working standard close to ambient N_2O level) .
- For comparisons, agreement within ± 0.2 ppb at ambient levels seems to be achievable at present.

- Post-audit contacts with the stations are a continuous task (control of success)

- The audits have revealed significant differences in the performance of gas chromatographic systems, even if equipped with similar instrumentation.

4.2 Conclusions

From the system and performance audits conducted by the WCC-N_2O, considerable progress over the years can be noted. This refers to several aspects of high-quality N_2O monitoring according to GAW requirements:
(i) change of the calibration scale from SIO to NOAA (GAW scale),
(ii) extension of the range covered by the standards available at a station or in the responsible laboratory.

Major factors that have contributed to the achievements at the individual stations, notably regarding the overall goal of the requested network compatibility of N_2O measurements, are:

- Recommendations compiled at GAW meetings (see WMO/GAW Reports), which address, for example, DQOs, scientific requirements and terminology issues.

- GAW Measurement Guidelines including DQOs (WMO/GAW Report No. 185).

- Acquisition of a set of CCL-calibrated standards and recalibrations. Several stations improved or recently established their link to the GAW N_2O scale.

Unfortunately, in most cases there are no obvious parameters of the GC system promising major future improvements. In summary, gas-chromatic instrumentation remains a system that cannot be easily controlled in all its facets.

The fulfilment of the N_2O DQOs still remains a challenge. Expectations for the future are with laser-based instruments.

5 Outlook

Planned or foreseeable activities of the WCC-N_2O from the end of 2011 onwards include:

(1) In response to the end of the 2009 - 2011 contract with QA/SAC-Germany (UBA) and the retirement of the manager of the WCC-N_2O on 29 February 2012, the operation of the WCC-N_2O needs to be transferred to the new manager, Rainer Steinbrecher (IMK-IFU).

(2) For all new WCC-N_2O analyses: Transition from the NOAA-2006 scale to the most recent NOAA-2006A scale.

(3) Check of the assigned mole fractions (reanalysis) of all travelling standards and back-up standards of the WCC-N_2O.

(4) Lectures for the GAWTEC course in June 2012.

(5) N_2O comparison experiments should be conducted with the CCL and with WCC-Empa.

(6) Planning of future audits and comparisons.
Candidates:

- Mace Head (Ireland) because of insufficient characterization of ECD response curve (according to audit by WCC-Empa). – Comparison or audit to be conducted once the station has extended the mole fraction range of its standards.
- Korea Global Atmosphere Watch Center (KGAWC), although not a global GAW site, of great importance for the N_2O data quality in that region. – Audit.
- Mt. Waliguan (China) because of major analytical problems as reported by WCC-Empa. – Audit including technical advice.
- Cape Verde because N_2O measurements started only recently. – Audit.

(7) Participation in the next GGMT-2013 meeting that is scheduled for June 2013, i.e. some months earlier in the year than it is usually the case.

6 Publications and Presentations of the WCC-N_2O

Publications and presentations from the period 2009 - 2011 are listed below in chronological order. Presentations at internal meetings of the German WCCs – QA/SAC-Germany are not included.

"Report of the WCC-N_2O" (H.E. Scheel), Talk, 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, other Greenhouse Gases and Related Tracer Measurement Techniques, Jena, 7 - 10 September 2009

"Aktivitäten des WCC-N_2O" [Activities of the WCC-N_2O] (H.E. Scheel), Talk in German, GAW-Statustreffen, DWD-Niederlassung München, 16./17.3.2010

"WMO/GAW observation system and greenhouse gases" (H.E. Scheel, O. Tarasova, L. Jalkanen and L. Barrie), Invited talk on behalf of WMO/GAW, The 2nd International Workshop on Atmosphere Watch in Asia “Greenhouse Gases Monitoring Activities”, Jeju, Rep. of Korea, October 21-22, 2010

"The Role of CCLs and WCCs in the GAW Programme for the observation of greenhouse gases" (H.E. Scheel), Invited talk, The 2nd International Workshop on Atmosphere Watch in Asia “Greenhouse Gases Monitoring Activities”, Jeju, Rep. of Korea, October 21-22, 2010

"Monitoring in the GAW Network" (H.E. Scheel), Invited talk, DEA Workshop "Establishment and Implementation of the National Reference Laboratory", Pretoria, South Africa, 17 February 2011

Scheel, H.E., Report of the WCC-N_2O, in: World Meteorological Organization, Global Atmosphere Watch, Report No. 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, April 2011, 187-190.

"Overview on Ten Years of WCC-N_2O" (H.E. Scheel), Poster, "16th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2011)", Wellington, New Zealand, October 2011

Scheel, H.E., Overview on Ten Years of WCC-N_2O, Extended abstract of poster presented at the "16th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2011)", Wellington, New Zealand, October 2011, 2012, submitted for publication in the respective WMO/GAW Report.

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Acknowledgements

The WCC-N_2O gratefully acknowledges valuable contacts and collaboration with QA/SAC Germany, the WMO/GAW Secretariat, GAW Central Calibration Laboratory for N_2O, Scientific Advisory Group for Greenhouse Gases, GAWTEC, WCC-Empa as well as with the staff members of the audited stations.

8 Annex

8.1 Abbreviations and Acronyms frequently used in GAW Documents

BIPM	Bureau International des Poids et Mesures (International Bureau of Weights and Measures)
CCL	Central Calibration Laboratory
CCQM	Consultative Committee for Amount of Substance (related to NMIs)
CIPM	Committee of Weights and Measures
CMDL	Climate Monitoring and Diagnostics Laboratory, Boulder, CO, U.S.A.
CSIRO	Commonwealth Scientific & Industrial Research Organisation
DBMS	Data Base Management Strategy
DQO	Data Quality Objectives
ECD	Electron Capture Detector
EMPA	EidgenössischeMaterialPrüfungsAnstalt
ESRL	Earth System Research Laboratory (part of NOAA)
FID	Flame Ionisation Detector
GAW	Global Atmosphere Watch (WMO Programme)
GAWG	Gas Analysis Working Group (NMIs)
GAWTEC	GAW Training and Education Centre
GG (or GHG)	Greenhouse Gas(es)
GGMT–<year>	WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (**G**reenhouse **G**as **M**easurement **T**echniques)
GMD	Global Monitoring Division (part of NOAA/ESRL)
GSP	GAW Strategic Plan
ICP	InterComParison experiment
ISO	International Organization for Standardization
LS	Laboratory standard
MG	Measurement Guidelines
NIST	National Institute of Standards and Technology
NMI	National Metrology Institute
MRA	Mutual Recognition Agreement
NOAA	National Oceanic and Atmospheric Administration (USA)
QA	Quality Assurance
QC	Quality Control
QA/SAC	Quality Assurance/Science Activity Centre
SAG	Scientific Advisory Group
SAG GG	Scientific Advisory Group for Greenhouse Gases

SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedure
SRM	Standard Reference Material
TS	Travelling standard
WCC	World Calibration Centre
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization

8.2 GAW Glossary

With the aim of familiarizing with the web-based GAW Glossary (http://gaw.empa.ch/glossary/glossary.html), its first page is reproduced here.

WMO/GAW Glossary of QA/QC-Related Terminology

Version 1.0 2010-09-14

Version 0.4 2007-04-26 (for comparison only - no longer recommended)

Editors: J. Klausen, H.-E. Scheel and M. Steinbacher

Table of Contents

Introduction

The evaluation and characterisation of data obtained from measurements made within WMO/GAW Programme involve a number of statistical parameters and specific terms to characterise data quality. At present, several of these terms (e.g. precision) are frequently used with different meaning by different people. Efforts for standardization have been made in the past, involving contributions from a number of international organizations, and are coordinated under the umbrella of →ISO.

With the aim of ensuring the comparability and compatibility of measurements, the GAW Strategic Plan [6] recommends adoption and use of internationally accepted methods and vocabulary to deal with measurement uncertainty as outlined in various ISO/BIPM publications [1-5]. Since each term should have the same meaning for all of its users, efforts are called for to familiarize all individuals involved in the WMO/GAW Programme and the associated scientific community with the relevant terminology. GAW members are strongly encouraged to use these terms in their own publications and to suggest their use when reviewing manuscripts of others.

Since the first edition (ver 0.4) of this glossary, the VIM [2] has been greatly expanded. The current 3rd edition of the VIM [1], entitled "International vocabulary of metrology — Basic and general concepts and associated terms (VIM)", is freely available through the Joint Committee for Guides in Metrology. It includes now a number of terms that were - to the knowledge of the editors - not previously defined in ISO/BIPM publications and that can now be referenced directly to this one authoritative source. As a result, the number of terms defined in the latest edition of the VIM is over-whelming at first encounter, and the editors have tried to select those that are deemed most relevant for

WMO/GAW. Moreover, in some cases notes/and or examples given in the VIM [1] have been removed, while additional notes and/or examples have been added with respect to the specific requirements of the WMO/GAW Programme. If you find that terms are missing from this glossary, please contact one of the editors.

The 3rd edition of the VIM, while freely available on the internet, is copy-righted material. The editors of this WMO/GAW glossary are therefore grateful to BIPM and the JCGM for a generous handling of copyright matters and are pleased to insert the following acknowledgment: "Extracts from the International Vocabulary of Metrology – Basic and General Concepts and Associated Terms (VIM), 3rd edition, JCGM 200:2008 (→www.bipm.org/en/publications/guides/vim.html) are published with permission of the Director of the International Bureau of Weights and Measures (BIPM), in his function as Chairman of the JCGM."

8.3 List of WMO/GAW Global Stations with current N_2O Monitoring

Station	Latitude	Longitude	Altitude	Time zone	G / R[1)]	Institution / Programme	In situ	Flasks	Country
Barrow	71.323	-156.609	11	UTC-9	G	NOAA ESRL GMD	X	X	USA
Mauna Loa	19.539	-155.578	3397	UTC-10	G	NOAA ESRL GMD	X	X	USA
Samoa	-14.232	-170.563	77	UTC-11	G	NOAA ESRL GMD	X	X	USA
South Pole	-89.997	102.000	2837	UTC+12	G	NOAA ESRL GMD	X	X	Antarctica
Mace Head	53.326	-9.899	5	UTC	G	University of Galloway / AGAGE	X		Ireland
Trinidad Head	41.054	-124.151	107	UTC-8	G	AGAGE, NOAA ESRL GMD	X	X	USA
Samoa	-14.000	-171.000	77	UTC-11	G	AGAGE	X		Amer. Samoa
Cape Grim	-40.682	144.688	94	UTC+10	G	CSIRO / AGAGE	X	X	Australia
Alert	82.450	-62.517	210	UTC-4	G	Met. Service of Canada	X	X	Canada
Pallas	67.974	24.116	560	UTC+2	G	Finnish Meteorological Inst.	X	X	Finland
Zugspitze	47.417	10.983	2650	UTC+1	G	Umweltbundesamt	X		Germany
Jungfraujoch	46.548	7.987	3580	UTC+1	G	EMPA	X		Switzerland
Izaña	28.310	-16.500	2373	UTC+0	G	National Met. Inst.	X		Spain
Cape Verde	16.85	-24.87	10	UTC+0	G	National Met. Inst	X		Spain
Cape Point	-34.353	18.490	230	UTC+2	G	SAWS	X		South Africa

[1)] G= global / R = regional GAW station; [2)] 1 sample per day.

Main source of information: GAWSIS (http://www.empa.ch/gaw/gawsis/)

8.4 List of WMO/GAW Regional Stations with current N_2O Monitoring of Global Relevance

Station	Latitude	Longitude	Altitude	Time zone	G / R[1)]	Institution / Programme	In situ	Flasks	Country
Schauinsland	47.90	7.92		UTC+1	R	Umweltbundesamt	X		Germany
Baring Head	41.41	174.87	85	UTC+12	R	NIWA		X	New Zealand