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GAW Report No. 186

14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques

(Helsinki, Finland, 10-13 September 2007)
WORKSHOP PROCEEDINGS

All oral presentations and national reports given during the workshop are on the enclosed CD and are also available online for download at http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html
WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

14th WMO/IAEA Meeting of Experts on
Carbon Dioxide, Other Greenhouse Gases
and Related Tracers Measurement Techniques

(Helsinki, Finland, 10-13 September 2007)

Edited by Tuomas Laurila
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AGAGE</td>
<td>Advanced Global Atmospheric Gases Experiment</td>
</tr>
<tr>
<td>AVD</td>
<td>Absolute Volumetric Determination</td>
</tr>
<tr>
<td>BIPM</td>
<td>International Bureau of Weights and Measures</td>
</tr>
<tr>
<td>CARBOEUROPE</td>
<td>Programme regrouping ecosystem and atmospheric research on the carbon balance of Europe (EU funded project)</td>
</tr>
<tr>
<td>CARIBIC</td>
<td>Civil Aircraft for Regular Investigation of the atmosphere Based on an Instrument Container</td>
</tr>
<tr>
<td>CARIBOU</td>
<td>An automated NDIR CO2 analyzer used by LSCE</td>
</tr>
<tr>
<td>cat/GC-FID</td>
<td>CO analysis technique with catalytic reduction of CO to CH4, followed GC-FID</td>
</tr>
<tr>
<td>CCGG</td>
<td>Carbon Cycle Greenhouse Gases group of the NOAA/ESRL</td>
</tr>
<tr>
<td>CCL</td>
<td>Central Calibration Laboratory</td>
</tr>
<tr>
<td>CDIC</td>
<td>Carbon Dioxide Information Analysis Centre</td>
</tr>
<tr>
<td>CEA-CNRS</td>
<td>Commissariat a l’Energie Atomique - Centre National de la Recherche Scientifique (French Nuclear Energy Agency – National Centre for Scientific Research)</td>
</tr>
<tr>
<td>CLASSIC</td>
<td>Circulation of Laboratory Air Standards for Stable Isotope inter Comparisons</td>
</tr>
<tr>
<td>CMA</td>
<td>China Meteorological Administration</td>
</tr>
<tr>
<td>CMDL</td>
<td>Climate Monitoring and Diagnostics Laboratory, Boulder, CO, U.S.A. (now NOAA ESRL GMD)</td>
</tr>
<tr>
<td>CSIRO</td>
<td>Commonwealth Scientific &amp; Industrial Research Organisation</td>
</tr>
<tr>
<td>CU</td>
<td>University of Colorado, Boulder</td>
</tr>
<tr>
<td>DBMS</td>
<td>Data Base Management Strategy</td>
</tr>
<tr>
<td>ECD</td>
<td>Electron Capture Detector</td>
</tr>
<tr>
<td>ECMWF</td>
<td>European Centre for Medium-range Weather Forecasting</td>
</tr>
<tr>
<td>EMPA</td>
<td>Eidgenössische MaterialPrüfungsAnstalt</td>
</tr>
<tr>
<td>ESRL</td>
<td>Earth System Research Laboratory (NOAA, Boulder, CO U.S.A.)</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionisation Detector</td>
</tr>
<tr>
<td>GAW</td>
<td>Global Atmosphere Watch (WMO Programme)</td>
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<tr>
<td>GAWTEC</td>
<td>GAW Training and Education Centre</td>
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<tr>
<td>GCP</td>
<td>Global Carbon Project</td>
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<tr>
<td>GG or GHG</td>
<td>Greenhouse Gases</td>
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<tr>
<td>GLOBALVIEW</td>
<td>Co-operative Atmospheric Data Integration Project</td>
</tr>
<tr>
<td>GMD</td>
<td>Global Monitoring Division (NOAA ESRL, Boulder, CO, U.S.A.)</td>
</tr>
<tr>
<td>GOOS</td>
<td>Global Ocean Observing System</td>
</tr>
<tr>
<td>GTOS</td>
<td>Global Terrestrial Observing System</td>
</tr>
<tr>
<td>HITRAN–04</td>
<td>High-resolution TRANsmission molecular absorption database - 2004 version</td>
</tr>
<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
</tr>
<tr>
<td>ICOS</td>
<td>Integrated Carbon Observation System (EU-funded project)</td>
</tr>
<tr>
<td>ICP</td>
<td>InterComParison (experiment)</td>
</tr>
<tr>
<td>IGACO</td>
<td>Integrated Global Atmospheric Chemistry Observation (system), a WMO programme</td>
</tr>
<tr>
<td>IGBP</td>
<td>International Geosphere-Biosphere Programme</td>
</tr>
<tr>
<td>IGO</td>
<td>Integrated Global Carbon Observation</td>
</tr>
<tr>
<td>IHALICE</td>
<td>International HALocarbon in Air Comparison Experiment</td>
</tr>
<tr>
<td>IHDP</td>
<td>International Human Dimensions Programme</td>
</tr>
<tr>
<td>INSTAAR</td>
<td>Institute for Arctic and Alpine Research, University of Colorado</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>JMA</td>
<td>Japan Meteorological Agency</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>KMA</td>
<td>Korean Meteorological Administration</td>
</tr>
<tr>
<td>KRISS</td>
<td>Korea Research Institute of Standards and Science</td>
</tr>
<tr>
<td>LN₂</td>
<td>Liquid Nitrogen (coolant)</td>
</tr>
<tr>
<td>LOFLO</td>
<td>A low volume NDIR CO₂ analyzer</td>
</tr>
<tr>
<td>LSCE</td>
<td>Laboratoire des Sciences du Climat et de l’Environnement (Laboratory for Climate and Environmental Science) (France)</td>
</tr>
<tr>
<td>MOPITT-TERRA</td>
<td>Measurements Of Pollution In The Troposphere</td>
</tr>
<tr>
<td>MOZAIC</td>
<td>Measurement of ozone, water vapour, carbon monoxide and nitrogen oxides aboard Airbus in-service aircraft</td>
</tr>
<tr>
<td>MPI-BGC</td>
<td>Max-Planck Institut für Biogeochemie, Jena, Germany</td>
</tr>
<tr>
<td>MSC</td>
<td>Meteorological Service of Canada</td>
</tr>
<tr>
<td>NACP</td>
<td>The North American Carbon Programme</td>
</tr>
<tr>
<td>NCAR C-DAS</td>
<td>National Centre for Atmospheric Research Carbon Data-Model Assimilation</td>
</tr>
<tr>
<td>NIAIST</td>
<td>National Institute of Advanced Industrial Science and Technology (formerly National Institute for Resources and Environment -- NIRE) (Japan)</td>
</tr>
<tr>
<td>NIES</td>
<td>National Institute for Environmental Studies, Tsukuba, Japan</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NIWA</td>
<td>National Institute of Water and Atmospheric Research (New Zealand)</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration (USA)</td>
</tr>
<tr>
<td>OCO</td>
<td>Observing System Simulation Experiment</td>
</tr>
<tr>
<td>OSSE</td>
<td>Orbit Carbon Observatory</td>
</tr>
<tr>
<td>PAN</td>
<td>PeroxyAcetylNitrate</td>
</tr>
<tr>
<td>per mil (per meg)</td>
<td>part per thousand (million) deviation from a reference value. Per mil is used in reporting stable isotope (e.g. δ13C) and per meg for O2/N2 results. Typically used with δ-notation: $\delta = \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right) \times 10^3$ per mil (or 106 for per meg)</td>
</tr>
<tr>
<td>PI</td>
<td>Principal Investigator</td>
</tr>
<tr>
<td>ppm (ppb, or ppt)</td>
<td>parts per million (106) (billion -- 109, or trillion -- 1012). When used in reporting mixing ratios (mole fractions), defined as moles of trace gas per mole of dry air, where, e.g.: 1 ppm CO₂ = (10-6 mole CO₂)/(mole of dry air)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>QA/SAC</td>
<td>Quality Assurance/Science Activity Centre</td>
</tr>
<tr>
<td>RAMCES</td>
<td>LSCE atmospheric greenhouse gas network</td>
</tr>
<tr>
<td>RGD</td>
<td>Reduction Gas Detector</td>
</tr>
<tr>
<td>Rms</td>
<td>root mean square (error)</td>
</tr>
<tr>
<td>SAG</td>
<td>Scientific Advisory Group</td>
</tr>
<tr>
<td>Sccm</td>
<td>Standard cubic centimeters per minute (volumetric flowrate normalized to standard temperature and pressure)</td>
</tr>
<tr>
<td>SCIAMACHY</td>
<td>SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY</td>
</tr>
<tr>
<td>SIO</td>
<td>Scripps Institution of Oceanography</td>
</tr>
<tr>
<td>SOPs</td>
<td>standard operating procedures</td>
</tr>
<tr>
<td>SRM</td>
<td>Standard Reference Material</td>
</tr>
<tr>
<td>TACOS</td>
<td>Terrestrial and Atmospheric Carbon Observing System -Infrastructure (EU funded project)</td>
</tr>
<tr>
<td>TCO</td>
<td>Terrestrial Carbon Observations</td>
</tr>
<tr>
<td>TDLAS</td>
<td>Tunable Diode Laser Absorption Spectroscopy</td>
</tr>
<tr>
<td>UEA</td>
<td>University of East Anglia</td>
</tr>
<tr>
<td>UNFCCC</td>
<td>United Nations Framework Convention on Climate Change</td>
</tr>
<tr>
<td>VOCs</td>
<td>volatile organic compounds</td>
</tr>
<tr>
<td>VPDB</td>
<td>Vienna Pee Dee Belemnite (Isotope Standard)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>VSMOW</td>
<td>Vienna Standard Mean Ocean Water (Isotope Standard)</td>
</tr>
<tr>
<td>VUV</td>
<td>Vacuum UltraViolet. Used with reference to a fluorescence technique used to measure carbon monoxide</td>
</tr>
<tr>
<td>WCC</td>
<td>World Calibration Centre</td>
</tr>
<tr>
<td>WCRP</td>
<td>World Climate Research Programme</td>
</tr>
<tr>
<td>WDCGG</td>
<td>World Data Centre for Greenhouse Gases</td>
</tr>
<tr>
<td>WMO</td>
<td>World Meteorological Organization</td>
</tr>
</tbody>
</table>
THE WMO GLOBAL ATMOSPHERE WATCH (GAW) PROGRAMME

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1. INTRODUCTION

The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) was established in 1989. It is focused upon the role of atmospheric chemistry in global change (Strategic Plan, 2008). Consisting of a partnership of managers, scientists and technical expertise from 80 countries, GAW is coordinated by the WMO Secretariat in Geneva and the Working Group on Environmental Pollution and Atmospheric Chemistry (WG-EPAC) of the WMO Commission for Atmospheric Science (CAS). The international greenhouse gas measurement community that met at this 14th meeting co-sponsored by WMO and IAEA are involved in nationally funded measurement programmes that constitute the global long term greenhouse monitoring network supported by GAW. The first meeting of this group, held in 1975 at Scripps Institute of Oceanography, was co-sponsored by WMO (Figure 1). It was a milestone in leadership of global greenhouse gas monitoring by US-NOAA. Comparison of this small group with the large group in the photo of this meeting shows how much our community has grown.

Figure 1. The 1st WMO sponsored CO₂ experts meeting at Scripps, La Jolla, California, 1975. Back left to right: Dave Lowe (New Zealand), Ernie Hughes (NIST), Bob Bacastow (Scripps), Don Pack (1st dir. of NOAA/GMCC), Walter Bischof (Sweden), Arnold Bainbridge (Scripps), C.S. Wong (Canada), Ken Pettit (AES, Canada), Walter Komhyr (NOAA). Front left to right Graeme Pearman (CSIRO, Australia), Michel Benarie (IRCHA, France), Lester Machta (NOAA), Charles (Dave) Keeling(Scripps) and G. Kronebach of WMO Secretariat, Geneva (photo supplied courtesy of P. Tans).

The WMO/GAW office and leaders of its Scientific Advisory Groups (SAGs) have been actively involved in supporting the United Nations Framework Convention on Climate Change (UNFCCC) through contributions to the Strategic Implementation Plan of the Second Report on the Adequacy of the Global Observing Systems for Climate by the Global Climate Observing Strategy (GCOS). This plan is officially accepted by the Parties to the Convention. Essential Climate Variables (ECVs) that need to be systematically measured globally in order to address major issues are officially recognized. Greenhouse gases, ozone and aerosols are amongst those ECVs
and GAW is designated as the lead international programme in furthering the observational requirements. In October 2005, the steering committee of the Global Climate Observing System (GCOS) which is co-sponsored by WMO approved the GCOS-GAW Agreement establishing the “WMO-GAW Global Atmospheric CO2 & CH4 Monitoring Network” as a comprehensive network of GCOS.

The focus, goals and structure of GAW are outlined in detail in the Strategic Implementation Plan 2008-2015 (GAW Report 172). Recognizing the need to bring scientific data and information to bear in the formulation of national and international policy, the GAW mission is to:

a. Reduce environmental risks to society and meet the requirements of environmental conventions.
b. Strengthen capabilities to predict climate, weather and air quality.
c. Contribute to scientific assessments in support of environmental policy.

Through

i. Maintaining and applying global, long-term observations of the chemical composition and selected physical characteristics of the atmosphere.
ii. Emphasising quality assurance and quality control.
iii. Delivering integrated products and services of relevance to users.

This mission is conducted through the ongoing activities of the group of experts representing carbon cycle research and measurements that were assembled at this 14th meeting and the GAW Scientific Advisory Group for Greenhouse Gases chaired by Dr Ed Dlugokencky that met after this expert meeting.

2. GAW MONITORING

GAW focuses on six measurement groups: greenhouse gases, UV radiation, ozone, aerosols, major reactive gases (CO, VOCs, NOx and SO2), and precipitation chemistry. The GAW Station Information System (GAWSIS) was developed and is maintained by the Swiss GAW programme. It is the host of all GAW metadata on observatory managers, location and measurement activities. According to GAWSIS there are 24 Global, 640 Regional and 73 Contributing stations operating or submitted data to a GAW World Data Centre. GAW Scientific Advisory Groups (SAGs) for each of the six measurement groups establish measurement standards and requirements while calibration and quality assurance facilities ensure valid observations. Five GAW World Data Centres collect, document and archive data and quality assurance information and make them freely available to the scientific community for analysis and assessments. Note the linkages of GAW to Contributing partner networks and to aircraft and satellite observations that contribute to Integrated Global Atmospheric Chemistry Observations (IGACO).

In the past decade, the emphasis of the GAW community on standardization, calibration, quality assurance, data archiving/analysis and building the air chemistry monitoring networks has resulted in major advances. Figure 2 shows the components diagram of the “WMO-GAW Global Atmospheric CO2 & CH4 Monitoring Network”.

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There are GAW Global, Regional and Contributing stations that support the monitoring of GAW target variables in each of the six groups. Global and Regional stations are operated by a WMO Member and are defined by Technical Regulations adopted by the WMO Executive Council in 1992 (EC XLIV; 1992) as well as the GAW Strategic Plan:2008-2015 (Strategic Plan, 2007). Contributing stations are those that conform to GAW measurement guidelines, quality assurance standards and submit data to GAW data centres. They are mostly in partner networks that fill major gaps in the global monitoring network. The difference between a Global and a Regional GAW station lies in the facilities available for long term measurements, the number of GAW target variables measured, the scientific activity at the site and the commitment of the host country. The location of the 24 GAW Global stations is shown in Figure 3a.

Figure. 3a. Global stations in the WMO GAW network Dec. 2007.

Figure 3b. All stations in the GAW surface carbon dioxide network Dec. 2007 (courtesy of the GAW World Data Centre for Greenhouse Gases).
The GAW global network for surface based carbon dioxide observations is shown in Figure 3b. To monitor global distributions and trends of a particular variable with sufficient resolution to provide quantitative estimates of regional sources and sinks of greenhouse gases requires not only Global but also Regional and Contributing surface-based stations but also aircraft and satellite observations. All stations submitting data to the GAW World Data Centre for Greenhouse Gases provides essential information on how their observations are linked to the WMO world reference scale maintained at NOAA/ESRL in Boulder, USA. In future, many more stations will hopefully be added to fill gaps in Asia, Africa and South America. Also, aircraft and satellite observations will be added as the integrated global atmospheric carbon observation system outlined in the IGACO (2004) report is implemented through the WMO-GAW programme in partnership with national and regional research partners.

Figure 4. The hierarchy of international activities related to promoting, organizing and conducting systematic atmospheric observations of carbon dioxide and other greenhouse gases. The foundation for this system are networks and facilities operated by leading countries in the field in cooperation with many other countries. The leaders include US/NOAA, Australia, Canada, China, France, Finland, Germany, Japan and Switzerland. The WMO-GAW programme is the international meeting point for national efforts.

Where do the many carbon research and systematic observation/analysis programmes fit amongst the many projects, programmes, strategies and systems involved in support global carbon observations? This is an often-asked question by many carbon cycle experts, managers and policy makers interested in the global carbon cycle and its impact on global change. One way of viewing the hierarchy of programmes and their connection to each other and to major users of the outcome of systematic observations research is shown in Figure 4. Activities are founded in national efforts coordinated through GAW with linkage to the UNFCCC through GCOS. In turn, it links to the satellite community through CEOS and the informal Integrated Global Observing Strategy (IGOS) consortium that initiated development of the IGACO and IGCO strategies. IGOS ended in 2008. The Global Earth Observation System of Systems now assists GAW in linking to key societal benefit areas of global atmospheric carbon monitoring.

Every year in November just before the annual convention of the Parties to the United Nations Framework Convention on Climate Change (UNFCCC), the WMO-GAW community with the support of the Secretariat in Geneva issues the WMO Greenhouse Gas Bulletin summarizing the state of atmospheric composition from observations up to December of the previous year. It highlights the global network and in each annual issue a particular observational or analysis product that is useful in understanding greenhouse gas related issues. These can be seen at the GAW website (www.wmo.int/gaw)
References
2003 GAW Current activities of the Global Atmosphere Watch Programme (as presented at Cg-XIV, May 2003), Report 152.
EXPERT GROUP RECOMMENDATIONS

The scientists present at the 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, 10-13 September 2007 in Helsinki, Finland, recommend the following procedures and actions, to achieve the adopted WMO goals for the Global Atmosphere Watch (GAW) network comparability among different laboratories and various components as summarised in Table 1. Definitions of terms concerning precision, accuracy etc. are given in Table 2.

### Table 1. Recommended inter-laboratory (network) comparability of components discussed

<table>
<thead>
<tr>
<th>Component</th>
<th>Inter-Laboratory comparability</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>± 0.1 ppm (± 0.05 ppm in the southern hemisphere)</td>
</tr>
<tr>
<td>δ¹³C-CO₂</td>
<td>± 0.01 ‰</td>
</tr>
<tr>
<td>δ¹⁸O-CO₂</td>
<td>± 0.05 ‰</td>
</tr>
<tr>
<td>Δ¹⁴C-CO₂</td>
<td>± 1 ‰</td>
</tr>
<tr>
<td>O₂/N₂</td>
<td>± 1 per meg</td>
</tr>
<tr>
<td>CH₄</td>
<td>± 2 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>± 2 ppb</td>
</tr>
<tr>
<td>N₂O</td>
<td>± 0.1 ppb</td>
</tr>
<tr>
<td>H₂</td>
<td>± 2 ppb</td>
</tr>
<tr>
<td>SF₆</td>
<td>± 0.02 ppt</td>
</tr>
</tbody>
</table>

### Table 2. Definitions of terms related to data quality

(Step: 1. [http://www.empa.ch/gaw/glossary.html](http://www.empa.ch/gaw/glossary.html) for a more comprehensive glossary)

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>Accuracy (of a test method)</td>
<td>The closeness of agreement between a test result and the accepted reference value.⁵</td>
<td>1</td>
</tr>
<tr>
<td>Comparability</td>
<td>Mean difference between two (or more) sets of measurements, which should be within given limits.⁶</td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>The difference between the expectation of the test results and an accepted reference value.¹</td>
<td>2</td>
</tr>
<tr>
<td>Precision</td>
<td>Degree of internal agreement among independent measurements made under specific conditions ²</td>
<td>2</td>
</tr>
<tr>
<td>Repetability (of results of measurements)</td>
<td>Closeness of the agreement between the results of successive measurements of the same measure and carried out under the same conditions of measurement.²⁶</td>
<td>2</td>
</tr>
<tr>
<td>Reproducibility (of results of measurements)</td>
<td>Closeness of the agreement between results of measurements of the same measure and carried out under changed conditions of measurement.²⁶</td>
<td>2</td>
</tr>
<tr>
<td>Uncertainty (Standard uncertainty)</td>
<td>A parameter associated with the result of a measurement that characterises the dispersion of values that could reasonably be attributed to the measurement.²⁶ (Uncertainty of the result of a measurement expressed as a standard deviation)</td>
<td>2</td>
</tr>
<tr>
<td>Coverage factor</td>
<td>Numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty.³ Note: A coverage factor of k=2 typically yields expanded uncertainties that correspond to a 95% confidence interval.</td>
<td>3</td>
</tr>
</tbody>
</table>
Recommendations

(a) Note that accuracy and precision are qualitative concepts and should be avoided in quantitative expressions.

(b) 1. For example, difference in a comparison of measurements of a species in a discrete sample with the hourly average for the same hour in which the discrete sample was collected. 2. In the case of significantly different variances of the two sample sets, the difference of the mean may not be meaningful. The Wilcoxon-Mann-Whitney test can be used to test for statistical significance.

(c) Precision must not be confused with accuracy or trueness. It is a measure for the dispersion of values.

(d) Repeatability and reproducibility may be expressed quantitatively in terms of the dispersion characteristics of the results. In practice quantitative expressions of repeatability or reproducibility often refer to a dispersion of ± 1 standard deviations.

(e) The concept of "uncertainty" is explained in detail in ISO Publications 1995.

(f) In practice the term "error (measurement error)" seems to be often used when actually "uncertainty" is meant. An error is viewed as having two components, a random and a systematic component. As further stated in ISO Publications (1995), "error" is an idealised concept and errors cannot be known exactly. "Error" and "uncertainty" are not synonyms, but represent completely different concepts.

Ref. 1, 2, 3: ISO Publications 1993a & b; 1995.

R1. CALIBRATION OF GAW MEASUREMENTS - WMO CENTRAL CALIBRATION LABORATORIES

R1.1 Background
Round-robin comparisons of laboratory standards and comparisons of field measurements and samples over the last decades have regularly shown differences in trace gas measurements larger than the target comparability for merging data from different field sites (see Table 1). These systematic differences contribute to uncertainties in the location and magnitude of surface fluxes derived from atmospheric composition measurements. The WMO Central Calibration Laboratories (CCL) for important greenhouse and trace gases therefore remain one of the fundamental components of the WMO GAW network (WMO GAW Strategic Plan, 2007) to achieve and maintain inter-comparability of global observations. WMO-GAW CCLs currently exist for the following trace gases: carbon dioxide (CO2, at NOAA/ESRL), methane (CH4, at NOAA/ESRL), nitrous oxide (N2O, at NOAA/ESRL) and carbon monoxide (CO, at NOAA/ESRL). At the 14th WMO Experts Meeting in Helsinki, Finland, the Max-Planck Institute for Biogeochemistry (MPI-BGC) in Jena, Germany, has been asked and agreed to act as the WMO-GAW CCL for stable isotopes in CO2 (only for CO2-in-air measurements).

In this section, the general requirements for WMO CCLs and general issues to maintain calibration of observations by GAW laboratories are discussed. Additional trace gas-specific needs are dealt with separately in subsequent sections.

R1.2 General requirements for Central Calibration Laboratories
a) The CCL maintains the WMO Mole Fraction Scale for the respective gas mixing ratio in air by carrying out regular determinations of this primary scale with an absolute method. The scale is embodied in an adequate set of gas mixtures-in-air in large high-pressure cylinders (called "WMO Primary Standards").

b) The CCL carries out comparisons with independent primary scales, established either through gravimetric, manometric, or other means.

c) While the WMO scale for each trace gas is defined and maintained by an operational designated CCL, WMO and IAEA welcome efforts that monitor, confirm, or improve CCL links to Primary Reference Materials or Fundamental Constants. Such efforts should involve cooperation with National Metrology Institutes (NMI).

d) The WMO-GAW and IAEA Expert committees undertake the responsibility for the evaluation of the effectiveness of such measures and for recommending modifications to existing protocols.

e) The CCL will update its scale when warranted, as the gas mole fractions of the WMO Primary Standards may become better known over time through repeated absolute measurements and comparisons. Revisions of the WMO Scale by the GAW CCL must be
distinguished by name, such as WMO X2005, and the appropriate version number should be included in each standard calibration report. The CCL archives all earlier versions of the WMO scale.

f) The CCL provides complete and prompt disclosure of all relevant data pertaining to the maintenance and transfer of the primary scale, such as manometric calibration procedures and results, and an estimate of the expected uncertainty introduced by the calibration transfer procedure to each individual standard.

g) The CCL provides calibrated reference gas mixtures of gas mixtures-in-air (called “transfer standards”) at the lowest possible cost.

h) The CCL provides for a backup in case a catastrophic event occurs.

i) The CCL, or a designated WMO-GAW World Calibration Centre, organizes round-robin comparisons of laboratory calibrations by distributing sets of high-pressure cylinders to be measured by participating laboratories. The round-robin comparisons are to be used for an assessment of how well the laboratories are maintaining their link to the WMO Mole Fraction Scale. They are not to be used for re-defining laboratory calibration scales, because that would effectively establish two or more traceable paths to the primary scale instead of a single hierarchical path. It is recommended that round-robins are repeated once every two years. However, comparisons of reference gases by themselves are not sufficient to ensure that atmospheric measurements are comparable to the degree that is required (see Section 11).

j) In order to assure comparability of round-robin results, circulation of cylinders is discontinued after two years at latest, and results are evaluated even if not all labs were able to yet analyse the tanks. A new round-robin will then be started with the labs that had not been included before to be first in line. Tracking tank circulation and data submission will be more rigorous than in earlier round-robins with the status of tank circulation and data submission being posted online on a Web Page to be installed and maintained by ESRL. Analysis of CO₂ mole fractions has the highest priority in the round-robins, but laboratories are encouraged to measure multiple species if time (all analyses must be finished in 4 weeks) and air consumption allow for.

R1.3 Maintenance of calibration by GAW measurement laboratories

a) All laboratories that participate in the GAW programme must calibrate and report measurements relative to a single carefully maintained scale, the WMO Mole Fraction Scale for gas mole fractions in dry air, including its version number. Each GAW measurement laboratory must actively maintain its link to the WMO Scales by having its laboratory standards regularly re-calibrated by the CCL. It is recommended that the laboratory primary gases are kept for many years so that a calibration history can be built for each of them.

b) It is recommended that each WMO-GAW measurement laboratory maintains a strictly hierarchical scheme of transferring the calibration of its laboratory primary gases ("laboratory standards") to working standards, and from working standards to atmospheric measurements. Traceability via a unique path will, in principle, enable the unambiguous and efficient propagation of changes (including retro-active changes) in the assigned values of higher-level standards all the way to measured values for atmospheric air.

c) In order to minimise the risk of creating offsets that are coherent among laboratories within the same region, each laboratory should maintain the shortest possible direct link to the WMO-GAW Primary Standards.

d) Because of ongoing improvements in measurement technology it is possible that individual laboratories or groups of laboratories may be able to maintain excellent precision and comparability in scale propagation from their laboratory standards to lower level standards, which could be beyond the precision with which laboratory standards can be tied to the WMO scale. Internal scales of this sort must also remain tied to the WMO scale to the extent possible.

e) Laboratories should, when they find inconsistencies between calibration gases received from the CCL, bring those results to the attention of the CCL.

f) We recommend the use of natural air and that, when trace gases, in particular CO₂, are adjusted in reference air mixtures, the isotopic composition of the cylinder trace gas remains close to that in air. We recommend further a very thorough process of elimination of leaks,
minimization of thermal gradients, and horizontal storage of cylinders in order to minimize
the risk of fractionation between the gas components in the cylinder.

R2. SPECIFIC REQUIREMENTS FOR CO₂ CALIBRATION

a) The primary scale for CO₂ shall range from approximately 180 ppm (covering atmospheric
values in ice cores) to over 500 ppm. The scale is currently embodied in a set of 15 CO₂-in-
air mixtures in large high-pressure cylinders.

b) Since the WMO scale was maintained until 1995 by the Scripps Institution of Oceanography,
comparisons with SIO are especially relevant. It is recommended that remaining
uncertainties associated with the SIO pre-1995 WMO scale and its transfer to NOAA are
resolved.

c) The CCL is encouraged to make available on its web site the calibration results of all GAW
laboratory standards based on previous versions of the scale as well as those based on the
current scale.

d) In order to make possible a level of consistency of ±0.03 ppm or less among the CO₂
calibration scales of laboratories participating in the WMO-GAW programme, the CCL shall
aim to provide the calibrated standards for transfer of the CO₂ scale to secondary and
tertiary standards at that level of consistency.

e) Each WMO-GAW measurement laboratory must actively maintain its link to the WMO Scale
by having its laboratory standards for CO₂ re-calibrated by the CCL every three years.

R3. SPECIFIC REQUIREMENTS FOR CO₂ STABLE ISOTOPE CALIBRATION

R3.1 Background

Efforts for comparing the stable isotopes of CO₂ in air have continued in the last two years
and results were reported during the 14th WMO Meeting of CO₂ Experts (see contributions in this
volume). These intercomparison exercises are indicative of the progress that has been made in
CO₂ stable isotope ratio measurements in air. Moreover, more fundamental issues have been
addressed like release of CO₂ from carbonates, ¹⁷O and N₂O corrections. The results and
arguments presented allow a number of conclusions to be drawn on the sources of measured
isotopic differences between participating laboratories. The implemented intercomparison
programmes (e.g. sausage flasks, high pressure cylinder round-robbins, pure CO₂ ampoules and
whole-air mixtures) are strongly recommended to be continued in the future as a routine
surveillance and quality control tool.

R3.2 Current achievements for CO₂ stable isotope calibrations

a) The possible experimental reasons for systematic offsets in measured CO₂ isotopic
compositions are different for δ₁³C and δ₁⁸O. In δ₁³C, scaling errors seem the most
prominent issue whereas δ₁⁸O suffers from exchange of oxygen with water as well as from
different techniques of generating CO₂ from carbonate reference material.

b) The possible underlying causes must be addressed separately for clean (pure) CO₂ and for
CO₂ in air. Clean CO₂ is developed from carbonates or is available as a calibrated clean gas.
In contrast, CO₂ in air is always accompanied by N₂O. In addition, traces of co-trapped air
from the cryogenic separation as well as issues of trapping efficiency and isotopic
alterations during trapping can change the measured isotopic ratios.

c) There is only one internationally recognized isotope scale for δ¹³C: VPDB. This scale has
recently been refined by IUPAC and IAEA via adding a second fixed calibration point (L-
SVEC Li₂CO₃ = −46.6‰ versus VPDB). As a result, a number of international secondary
reference materials still must be newly evaluated, including reference materials that have
been used for CO₂-in-air isotopic calibration (see 3.3b)). Intercomparability of δ¹³C values of
air CO₂ in the past has mainly suffered from different amounts of cross contamination during
mass spectrometric measurement (eta-effect). The new scaling rule should be able to
adequately address this problem. In order to implement this rule into CO₂-in-air analyses a
practical solution (for instance two air standards with ¹³CO₂ isotopic ratios similar to NBS19
and LSVEC) is needed and suggestions are welcome.
d) To establish a tie to the VPDB scale kept by the IAEA, standards for CO₂-stable isotopes-in-air must be created. MPI-BGC Jena is now able to accurately prepare CO₂ from carbonate material and mix this with CO₂-free air in a fully automated system. These mixtures can now serve as air reference material (‘J-RAS’, Jena Reference Air Set) and will provide the required firm link of air-CO₂ measurements to the VPDB scale (Ghosh et al., 2005, Brand et al., this volume). The long-term integrity of CO₂-in-air isotope results should, however, be based on carbonate material. The future production and dissemination of the J-RAS air-CO₂ anchor to the VPDB scale has been funded by the European Community under the IMMEC project. Given the progress made in the last two years MPI-BGC is asked to take a leading role for unifying the stable isotope scales across the community and act as a WMO-GAW Central Calibration Lab for isotopes (CCL) for these species by providing the J-RAS air-CO₂. BGC Jena has agreed to produce this reference material and provide participating laboratories with a new set of gases at a rate of two per year. Propagation of the scale will be performed only via CO₂-in-air.

e) Comparability of δ¹⁸O data between laboratories remains poor (progress has been made with inter-laboratory precision of close to ±0.2‰, which is still far off the goal of ±0.05‰ (Table 1)). The availability of reference air with assigned isotope values should help to unify reported δ¹⁸O data, irrespective of their accuracy.

f) The major cause for the current discrepancies is not scaling (like for δ¹³C) because air-CO₂ is close to VPDB-CO₂. Progress evidently cannot be made by having the individual laboratories generate CO₂ from NBS19. MSC, NIES and MPI-BGC have reported on progress in our understanding of the underlying causes for the discrepancies. These studies need to be continued and the same partners are asked to further investigate this issue and report on the results during the next meeting. The new findings will enable to establish a more rigorous relation to the VSMOW scale as well.

R3.3 Recommendations for CO₂ stable isotope calibrations

a) Since δ¹³C of atmospheric CO₂ is close to –8‰ on the VPDB scale, any secondary reference material used for high-precision isotope work around this value needs to be re-evaluated. The generation of two pure CO₂ reference materials (NARCIS 1 and 2) by NIES with a composition of NARCIS 1 close to air CO₂ and NARCIS 2 close to NBS 19 has greatly facilitated intercomparison of isotope measurements on pure CO₂ from different laboratories. For establishing a set of recommended values from the intercomparison, more data are required for NARCIS 2. MSC, NIES and MPI-BGC have presented new results comparing these materials with CO₂ generated from the primary references thereby assigning new delta values with very small error margins.

b) The availability and careful calibration of other CO₂ reference materials from NIST (carbon dioxide: RM 8562-8564) has proven to be an independent and reliable resource for tracing offsets between individual laboratory scales. Theses reference materials have already been re-assessed on the 2-point VPDB scale with very small changes to the original values (i.e. RM 8562: δ¹³C= -3.72‰, RM 8564: δ¹³C= -10.45‰, RM 8563: δ¹³C= -41.59‰ (Coplen et al., 2006)). It is recommended to NIST to insure future availability of these materials.

c) Recent findings of the world water pools related fractionation laws for ¹⁸O/¹⁶O and ¹⁷O/¹⁶O require a new ruling for high-accuracy calibration of δ¹³C in air CO₂. The recommendation of the 13th WMO experts meeting to exclusively use the ratio assumption set provided by Assonov and Brenninkmeijer (2003a; 2003b) is endorsed. Mass spectrometry evaluation software as well as individual laboratory software packages should be adapted correspondingly.

d) The need of a calcite reference material with carbon and oxygen isotopic compositions close to atmospheric CO₂ is re-iterated and emphasized. The material is necessary in order to eliminate ambiguities arising from different mass spectrometric scaling factors and other corrections (¹⁷O correction, N₂O correction, etc.).
R4. SPECIFIC REQUIREMENTS FOR RADIOCARBON IN CO₂ CALIBRATION

R4.1 Background

Standardization of radiocarbon analysis has been well established in the radiocarbon dating community for many years, and the new Oxalic Acid Standard (NIST SRM 4990C) has been agreed upon as the main standard reference material. Other reference materials of various origin and ¹⁴C activity are available and distributed by e.g. IAEA.

For atmospheric measurements of \( \Delta^{14}C \) in CO₂, two main sampling techniques are used: High-volume CO₂ absorption in basic solution or by molecular sieve and whole-air flask sampling (typically 1.5-5 L flasks). Two methods of analysis are used: Conventional radioactive counting and Accelerator Mass Spectrometry (AMS). The current level of measurement uncertainty for \( \Delta^{14}C \) in CO₂ is 2-5‰, with a few laboratories at slightly better than 2‰ uncertainty. As atmospheric gradients in background air are currently very small, a target level of 1‰ for inter-laboratory comparability is recommended (Table 1).

R4.2 ¹⁴CO₂ calibration and intercomparison activities and respective recommendations

Calibration with whole-air standards is difficult in the case of large-volume sampling and conventional counting techniques as sample volume is generally larger than 20 cubic meters of air. Therefore, these techniques will still solely rely on the Standard Reference Materials distributed by IAEA. But we recommend that laboratories conducting small-volume flask sampling and AMS analysis should use whole air cylinders as reference material that is similar to the air samples measured.

The first intercomparison activity for \( \Delta^{14}C \) in CO₂ was initiated at the 13th WMO/IAEA Meeting of CO₂ Experts in Boulder Colorado (WMO GAW Report # 168, 2006) and is currently underway. The intercomparison is being managed by University of Colorado and NOAA/ESRL/GMD with support from WMO. Six laboratories are currently participating by sending flasks to NOAA to be filled with air from two whole-air reference cylinders. This intercomparison exercise should report results by the 15th WMO Meeting of Experts.

As the current intercomparison excludes the laboratories using high-volume sampling techniques, we propose the following potential methods for future intercomparison that could include laboratories using either type of sampling technique:

a) Splitting and dissemination of high-volume pure CO₂ samples to the laboratories.
b) Co-located sampling at observation stations.

R5. SPECIFIC REQUIREMENTS FOR O₂/N₂ CALIBRATION

R5.1 Background

Measurements of the changes in atmospheric O₂/N₂ ratio are useful for constraining sources and sinks of CO₂ and testing land and ocean biogeochemical models. The relative variations in O₂/N₂ ratio are very small but can now be observed by at least six techniques. These techniques can be grouped into two categories: (1) those which measure O₂/N₂ ratios directly (mass spectrometry and gas chromatography), and those which effectively measure changes in the O₂ mole fraction in dry air (interferometric, paramagnetic, fuel cell, vacuum ultraviolet photometric). A convention has emerged to convert the raw measurement signals, regardless of technique, into equivalent changes in O₂/N₂ ratio. For the mole-fraction type measurements, this requires accounting for dilution due to variations in CO₂ and possibly other gases. If synthetic air is used as a reference material, corrections may also be needed for differences in Ar/N₂ ratio. By convention, O₂/N₂ ratios are expressed as relative deviations compared to a reference

\[
\delta(O_2/N_2) = \frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{reference}}} - 1
\]
Recommendations

where $\delta$(O$_2$/N$_2$) is multiplied by $10^6$ and expressed in “per meg” units. 1 per meg is a dimensionless unit equivalent to 0.001 per mille. The O$_2$/N$_2$ reference is typically tied to natural air delivered from high-pressure gas cylinders. As there is no common source of reference material, each laboratory has employed its own reference, and hence reports on its own scale.

R5.2 O$_2$/N$_2$ calibration and intercomparison activities

At the 12th WMO CO$_2$ Experts Meeting in Toronto (WMO GAW Report # 161, 2005) the Global Oxygen Laboratories Link Ultra-precise Measurements (GOLLUM) programme was initiated to provide constraints on the offsets between the different laboratory scales and to clarify the requirements for placing measurements on a common scale. There are two components to this programme, a “sausage flask” intercomparison programme, and a “round-robin cylinder” intercomparison programme. The sausage flask programme compares the laboratories’ ability to extract and analyse air from a small flask sample, whereas the round-robin cylinder programme compares the laboratories’ calibration scales, and their methods for extracting air from high-pressure gas cylinders.

Details of the GOLLUM programme can be found in the WMO Technical Document No. 1275. A document was prepared and distributed to the participating laboratories in the GOLLUM programme outlining the required laboratory protocols. The GOLLUM programme has been coordinated by A. Manning at the University of Each Anglia, with the O$_2$ laboratory of R. Keeling at Scripps Institution of Oceanography (SIO) serving as the point of origin for the round-robin programme and the hub for the sausage-flask programme.

The round robin cylinders (2 sets of 3 aluminium cylinders) were prepared in 2004 at SIO and started their worldwide rotations in 2005. At the time of the 14th WMO Experts meeting, two circuits of the round-robin cylinders were completed and three sets of sausage flasks had been distributed. The repeated analyses at SIO, two years after their initial measurement, showed the change in the cylinders was zero to within ±3 per meg, the estimated precision of a trend measurement in the SIO lab.

In addition to preparing cylinders for the GOLLUM programme, the O$_2$ lab at SIO has prepared high-pressure cylinders for a number of laboratories. These cylinders have provided another means to assess laboratory scale differences.

R5.3 Recommendations

a) Continue both, the round-robin cylinder and sausage flask components of the GOLLUM programme for at least two more years.

b) Establish a web page for logistical support and for dissemination of results of the GOLLUM programme.

c) Encourage SIO to continue to provide reference gases to laboratories on request at reasonable cost.

d) Encourage additional efforts, such as overlapping flask sampling from different programmes, to compare O$_2$/N$_2$ scales and methods between programmes.

e) Encourage the standardisation of existing O$_2$/N$_2$ techniques, and particularly to identify and correct weaknesses in laboratories’ current techniques in sample collection, sample analysis, and in defining and propagating calibration scales.

R6. SPECIFIC REQUIREMENTS FOR CH$_4$ CALIBRATION

At the 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, it was agreed that NOAA would assume the role of the WMO-GAW Central Calibration Laboratory (CCL) for methane. The NOAA04 scale was designated as the official calibration scale consisting of 16 gravimetrically prepared primary standards which cover the nominal range of 300 to 2600 nmol mol$^{-1}$, so it is suitable to calibrate standards for measurements of air extracted from ice cores and contemporary measurements from GAW sites. This new scale results in CH$_4$ mole fractions that are a factor of 1.0124 greater than the previous scale (now designated CMDL83) (Dlugokencky et al., 2005). The range of secondary transfer
standards is the same as the range of the WMO Primary Standards. The CCL will transfer the CH₄ scale to calibrated CH₄-in-air standards with an uncertainty of <1 nmol mol⁻¹. All laboratories that participate in the GAW programme must calibrate measurements to relative to the WMO CH₄-in-air mole fraction scale and report them to the WMO World Data Centre for Greenhouse Gases in Japan.

Each GAW measurement laboratory must actively maintain its link to the WMO Scale by having its laboratory standards for CH₄ re-calibrated by the CCL every six years.

R7. SPECIFIC REQUIREMENTS FOR N₂O CALIBRATION

R7.1 Background
Measurements of nitrous oxide are made by a number of laboratories around the world in order to better understand the sources and sinks of this greenhouse gas, also in the frame of the global nitrogen cycle. Systematic differences between mole fractions reported by different laboratories are large compared to atmospheric gradients. The mean interhemispheric difference in N₂O mole fraction is around 1 ppb and the pole-to-pole difference is 2 ppb. These global differences are 0.3-0.6% of the recent mean mole fraction of N₂O in the troposphere. This necessitates not only high measurement precision, but also high consistency among assigned values for standards. Inter-laboratory comparability of 0.1 ppb is needed.

R7.2 Recommendations
a) NOAA/ESRL/GMD serves as the CCL for nitrous oxide. It maintains a gravimetrically-prepared N₂O-in-air standard scale consisting of 13 WMO Primary Standards covering the range of 260 – 370 nmole mol⁻¹ (Hall et al., 2007). The reproducibility of NOAA N₂O calibrations is estimated to be 0.2 ppb at the 95% confidence level. Efforts to improve precision and reproducibility are ongoing.

b) The CCL will include N₂O calibration results in the web-based database maintained by the NOAA Carbon Cycle Greenhouse Gases group.

c) Each GAW measurement laboratory must actively maintain its link to the WMO Scale by having its laboratory standards for N₂O re-calibrated by the CCL every three years.

d) We encourage the development of new or improved techniques, such as optical techniques, that would lead to improvements in precision and reproducibility.

R8. SPECIFIC REQUIREMENTS TO SF₆ CALIBRATION

R8.1 Background
Sulfurhexafluoride (SF₆) is a long-lived trace gas with strong infrared absorbance properties. Emissions of SF₆ are 22800 times more effective than CO₂ on a per-mass basis over a 100-year time scale. The tropospheric mixing ratio of SF₆ has increased steadily, with a current growth rate of about 0.22 ppt yr⁻¹. The steady growth rate and long lifetime (~3000 years) make it a useful tracer of atmospheric transport, including stratospheric “age-of-air determination”. Because SF₆ is almost entirely anthropogenic in origin, used primarily in electrical power distribution, it is a potentially powerful tracer of anthropogenic activity on global and regional scales.

SF₆ is typically measured using GC-ECD techniques in a manner similar to that of N₂O. There are currently three scales in use: NOAA, Univ. of Heidelberg, and SIO. Although there have been few formal SF₆ comparisons, informal comparisons show that scale comparability is generally good. However, to be optimally useful as a tracer of atmospheric transport, consistency of scale must be exceptionally good (on the order of 0.02 ppt). In this regard, a commonly accepted scale does not exist. The formation of a WMO-GAW CCL for SF₆, responsible for maintaining a scale and facilitating the distribution of standards, would benefit the atmospheric (SF₆) measurement community.
R8.2 Recommendations
   a) Establish a WMO-GAW CCL for SF\textsubscript{6}.
   b) Include SF\textsubscript{6} in WMO-GAW round-robin experiments when possible.
   c) Investigations are encouraged to explore advanced techniques to improve measurement precision.

R9. SPECIFIC REQUIREMENTS FOR CO CALIBRATION

R9.1 Background
CO is an important component in tropospheric chemistry due to its high reactivity with OH. It is the major chemically active trace gas resulting from biomass burning and fossil fuel combustion, and a precursor gas of tropospheric ozone. Most atmospheric measurements are based on collected air samples or in-situ analysis although systematic measurements from satellites, aircraft and surface-based FTIRS are improving (WMO GAW/ACCENT Workshop, 2005). Differences among reference scales and drift of standards have been a serious problem for these in-situ CO measurements in the past. Spectroscopic retrieval of CO provides column abundances; wide geographical coverage of CO with some limited vertical resolution is becoming available from several satellite-based sensors (MOPITT-TERRA, SCIAMACHY-ENVISAT, TESS-AURA). The present recommendations will, however, pertain to the calibration of in-situ observation only; the validation of remote sensing data is a complicated separate issue not treated here.

Experience has shown that the accurate calibration of in-situ CO measurements is far from trivial. Mole fractions between 40 and 250 nmol/mol (and higher) should be determined with an expanded uncertainty of ±2 ppb (k=2). Unlike CO\textsubscript{2}, for CO there is a low degree of standardization in analytical techniques deployed (WMO/GAW Report No. 168 (2006)). Specific calibration problems for CO are: a) Available measurement techniques can be non-linear and do not have the stability or precision for long-term measurements of low drift rates. b) Gravimetric mixtures must be diluted to environmental levels, and at these levels CO mixing ratios in high-pressure cylinders may not be stable over time periods of several years. c) The preparation of a gravimetric standard does not a priori guarantee that the actual CO mole fraction corresponds to the assumed one. Careful maintenance of the gravimetric scale and/or inter-comparison with diluted gases from high-concentration cylinders (10 ppm) is regularly required.

R9.2 CO intercomparison activities
NOAA ESRL’s Carbon Cycle Group has on two occasions organized round-robin tests involving 5 to 10 laboratories. This has helped “the international insitu CO measurement community” enormously, but also exposed some drift and inconsistency in the NOAA ESRL calibration scale, as well as the gravimetric technique.

WMO through EMPA and its WMO-GAW WCC for CO has endeavoured to improve the international comparability by implementing an audit system for CO measurements at Global GAW stations. Combining all experience gained so far, it is realistic to expect CO data to be expressed on one single scale that is traceable to a single source. For establishing global trends, and to get a sufficiently accurate estimate of the tropospheric burden, it seems that 1% expanded uncertainty (k=2) is now becoming both analytically attainable and scientifically sufficient.

R9.3 Specific recommendations for CO calibration at the WMO-GAW CCL and at GAW stations
   a) Inter-laboratory comparability for global GAW stations to ±2 ppb (mean bias) and standards to ±1 ppb or 0.5% (whichever is greater, expanded uncertainty, k=2) are needed. Comparisons of CO measurements among laboratories (through round-robins, and other intercomparison sample exchanges) have documented differences in measurements among laboratories. They have proven useful in identifying inconsistencies and/or drift in CO standards and therefore are strongly encouraged.
   b) NOAA ESRL is the CCL for carbon monoxide. In this capacity, they provide calibrated standards to GAW laboratories, and CO calibrations should be traceable to the scale
Recommendations

maintained by NOAA ESRL. Based upon several sets of gravimetric standards this scale was revised in 2000. The WMO-2000 scale still underwent some adjustments, and NOAA ESRL is encouraged to ‘freeze’ the current scale prepared in 2006 as WMO-2006 scale. It is this WMO-2006 scale that GAW stations should refer to. The CCL is responsible for documenting the evolution of the WMO CO scale and for communicating all revisions to the stations as well as to WCC-EMPA.

c) The frequency of the preparation of gravimetric Primary Standards should be increased to a biannual interval to determine any long term drift of the scale. Furthermore the CCL should improve its capability of making accurate dilutions as a second means of assuring the stability of the WMO Primary Scale.

d) Standard drift remains a serious issue for CO measurements. Therefore an annual recalibration of at least one of a station's laboratory standards is strongly suggested.

e) In order to be able to use CO as a tracer for fossil fuel CO₂ at regional GAW or even moderately polluted sites, the CCL should extend its primary scale towards higher mole fractions (up to 1000 ppb).

f) The WMO SAG Reactive Gases' Subgroup on Carbon Monoxide should continue to work on resolving issues of the calibration scale, in particular by giving guidance to stations on how to re-process older data. A SAG Guidance Document on CO measurements is being developed.

g) Currently, no laboratory is conducting absolute volumetric measurements of CO. These measurements would be an extremely useful alternative to dynamic dilution of high-concentration gases for confirming the consistency and potential drift in the WMO primary scale.

h) EMPA is the designated World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA) and is in charge of conducting system and performance audits including intercomparisons at global GAW stations. Audit results and other inter-comparison results should be archived along with CO data at the WDCGG or with GAWSIS.

i) Within the GAW programme, regular inter-comparisons or calibrations by designated calibration centres (with global or regional scope) are necessary to ensure traceability of the observations. Furthermore, regular audits by the WCC are needed as an independent check of the measurements on-site.

j) It should be explored if, in this particular case of a trace gas with large danger of drifting standards, regional round robins could help to maintain the link to the CCL.

k) For many stations, a dynamic dilution system may be an additional means of calibrating their instruments, in particular in cases where non-linear instrument response may be an issue. WCC-EMPA should take the lead in establishing the practicality of such an approach and in assessing the resulting uncertainties for the ambient CO measurements.

l) There is a large number of stations (some of which are regional GAW stations) that are equipped with less sophisticated (or calibrated) CO monitoring equipment. These measurements are currently poorly exploited, in part because some of these data (e.g., from environmental agencies) are not easily accessible and the quality of these observations is not well assessed. There is a need for identification, inter-comparison and improved accessibility of these observations.

R10. SPECIFIC REQUIREMENTS FOR H₂ CALIBRATION

R10.1 Background

Molecular hydrogen plays a significant role in global atmospheric chemistry due to its interference in \( \text{CH}_2\text{-CO-OH} \) cycling. The balance of hydrogen could change with the implementation of a new \( \text{H}_2 \) energy carrier. Therefore, it is important to establish its global budget and atmospheric trend. There is currently no internationally accepted standard scale available for measurements of atmospheric molecular hydrogen nor is there any institution to distribute such standards.
There are different networks of monitoring stations that are linked to independent scales (NOAA, CSIRO-AGAGE, EuroHydros, NIES). These scales have been prepared using different methods, and known biases between these scales exist that have not always been constant in time and include concentration dependencies. Efforts to integrate data from different networks have been undertaken based on results from long-term intercomparison activities (Xiao et al. 2007). While this documents the need to achieve transparent and consistent scales, the reliability of this approach depends on a solid evaluation of these differences. There is a clear need to get consistent data from independent networks and therefore harmonisation of the scale still remains a task of high priority. Molecular hydrogen is recognized as an important target variable to be measured in the WMO-GAW global network and specific tasks are outlined for implementation by the global research community (see the GAW Strategic Plan: 2008-2015; section 7.3.6 referenced in footnote1).

**R10.2 Recommendations**

- **a)** A concerted effort to consolidate the NOAA, CSIRO/AGAGE, EuroHydros and other calibration activities is urgently needed to enable a collaborative global network for hydrogen measurements. These measurement groups are strongly encouraged to establish a common calibration scale. This scale should cover the range from 350-1000 ppb. As part of this effort the existing scales need to be harmonized and the history of their agreement needs to be documented. Links to the BIPM should be explored.

- **b)** In addition, temporal changes of inter-laboratory biases that have not always been related to scale changes, underline the necessity to continue intercomparison of hydrogen data. These exercises have already been made use of and should be expanded with more high-frequency (i.e. at least monthly) comparisons.

- **c)** A major problem most laboratories that measure hydrogen encompass is to ensure the stability of their standards. It is recommended that every laboratory develops a strategy to account for this. This includes appropriate choice of standard gas containers that have been tested successfully (mostly stainless steel cylinders). A set of standard gases in large low pressure glass flasks has proved to be an easy and useful approach. Aluminium cylinders commonly used for other trace gas standard mixtures often show significant growth of hydrogen. Thus, the long-term use of aluminium cylinders as primary standards is discouraged.

- **d)** Appropriate characterization and regular check of the detector response is required given the strong non-linear response of the commonly used HgO reduction detectors.

- **e)** There is currently no WMO-GAW CCL for atmospheric molecular hydrogen. In the course of the scale harmonisation process institutions that are in the position of taking this role should be identified and proposed to attend WMO Experts meetings. The decision on this future CCL should be based on documentation on internal and external measurement consistency of the respective laboratory, its ability to assure the stability of the H$_2$ primary standards, and its ability to supply standards to the community.

**R11. GENERAL RECOMMENDATIONS FOR QUALITY CONTROL OF ATMOSPHERIC TRACE GAS MEASUREMENTS**

The Group of WMO Experts nominates Ken Masarie (NOAA/ESRL) to review the recommendations summarized below at least six months before the next meeting, and remind laboratories to prepare summaries of their current ICP activities as they relate to the respective recommendations.

**R11.1 General**

- **a)** Relating standards to the WMO Mole Fraction Scales: Investigators should follow practices outlined in Section 1.3 of this report for obtaining a sufficient number and range of calibration gases from the respective WMO CCL (laboratory standards) and transferring those calibrations to working and field standards. The data management system in use should allow for easy reprocessing and easy propagation of scale changes from laboratory standards to final measurements.
b) Real-air and modern-CO₂ (and other trace gas) standards: Working standards must have natural levels of N₂, O₂, and Ar to avoid biases e.g. due to different pressure-broadening effects between sample and calibration gases. CO₂ standards should have CO₂ with ambient δ¹³C ratios.

c) Besides round-robin comparisons, more frequent intercomparison activities between pairs of laboratories which incorporate the analyses of actual air samples, such as flask air intercomparison (ICP) experiments or collocated in-situ instruments are strongly recommended. The tremendous benefit of routine intercomparison has been demonstrated (Masarie et al., 2001) and is reinforced. Mutual exchange of air in glass flasks is encouraged as a means to detect experimental deficiencies at an early stage and identify discrepancies in the results quickly.

d) Flask sampling programmes should be implemented at observational sites making continuous measurements as well as automated data processing for these intercomparison projects. A detailed comparison of collocated continuous and flask measurements will be performed until the next WMO Experts meeting which will form the basis to assess the usefulness of such a programme and to decide if audits also for CO₂ need be performed at GAW stations. This would require an instrumental set-up which is easy to ship around.

e) Clear protocols and reports of experience gained in intercomparison projects should be provided. Results should be published and readily accessible. The evaluation of such activities and recommendations for refinement, co-ordination and expansion of such activities has been accepted as a key responsibility of future WMO/IAEA Expert meetings.

f) Defensible uncertainty estimates: Investigators should report uncertainty estimates for their data and provide details of how these estimates are calculated and what activities are used to verify them. ISO nomenclature shall be used for uncertainty estimates and discussions.

g) Deviations from recommendations: We recognize the value of innovation and experimentation with new approaches. However, we stress that deviations from established practices should be fully tested to confirm that the new approach does not introduce bias into the measurements. Furthermore, the results of such experimentation should be reported at future WMO CO₂ Experts meetings and similar venues, and published in the peer-reviewed literature whenever possible.

R11.2 Flask intercomparison

a) Intercomparison programmes distributing to a larger number of laboratories flasks filled in series from tank air as a “sausage” as initiated by the European TACOS project (Levin et al., 2003) are able to increase the benefit of mutual flask exchange.

b) Another possibility to link several laboratories in one single intercomparison exercise is the establishment of Trace Gas Comparison Sites which will take on the task to fill a larger number of flasks regularly and simultaneously with ambient air and distribute them to participating laboratories. The Alert, Mauna Loa and Cape Grim stations have been recommended as such sites. At Alert station this activity has already started with 6 laboratories. At Cape Grim there are 9 labs participating in such a programme.

R11.3 Recommendations for in-situ measurements

a) Continuous in-situ measurements of CO₂ and other trace gases can greatly improve our understanding of regional-scale fluxes. For this reason, and in response to recent advances in technology, the number of investigators and sites carrying out in-situ trace gas measurements is rapidly increasing. Many sound principles for conducting in-situ CO₂ measurements have been described in detail in WMO GAW Report No. 134 (1999). The group recommends that the SAG-GHG initiates a timely update of Report 134 well before the next WMO Experts Meeting in 2009. Preliminary recommendation for CO₂ measurements have been summarized in the 13th WMO Experts recommendation (WMO GAW Report No. 168 (2006)).

b) It is recommended that new robust analytical technologies (e.g., laser-based optical analyzers) are tested. The envisaged new European Infrastructure ICOS (Atmospheric Thematic Centre) may be able to support this activity. A forum should be established to distribute the results and generate discussion among “experts”. New techniques should meet the scientific requirements of accuracy and precision as stated in GAW reports.
Specific areas that need to be investigated are calibration frequency and ability to correct for water vapour dilution or interference with other trace substances, and other artefacts besides sample drying. Manufacturers are encouraged to offer detailed training, perhaps through GAWTEC. The community should identify species for which new technologies are needed and specify which observables should be available for new instruments.

c) Besides recommendations on the greenhouse and associated trace gases mentioned above the WMO Experts identified a strong need for expert guidance to establish an adequate calibration process and intercomparison activity for atmospheric $^{222}$Radon observations. WMO will contact respective specialists to give advice.

R12. RECOMMENDATIONS FOR DATA MANAGEMENT AND ARCHIVING

R12.1 Data management

All GAW measurement laboratories regardless of programme size are required to manage all new and existing atmospheric trace gas and supporting (meta) data using a database management strategy (DBMS) that meets or exceeds the following criteria:

a) Demonstrate that mole fractions / isotope ratios can be unambiguously and automatically reproduced from raw data at any time in the future.

b) Demonstrate that revisions to a laboratory’s internal calibration scale can be efficiently and unambiguously propagated throughout the database.

c) Support routine and automatic database updates of all measurement and meta data.

d) Ensure that all data reside locally, in a single location, and are centrally accessible to internal users.

e) Ensure fast and efficient retrieval of all data.

f) Maximise users’ ability to assess data quality.

g) Facilitate data exploration.

h) Minimise the risk of data loss or corruption due to theft, misuse, or hardware/software failure.

i) Maximise security to primary data (e.g., data from which all processed data is derived).

j) Support routine and automatic backup of all data.

k) Support complete data recovery in the event of catastrophic data loss.

GAW measurement laboratories are encouraged to use WMO/GAW Report No. 150 as a guideline in developing and implementing an atmospheric data management strategy. Laboratories with demonstrated expertise in data management are encouraged to share their expertise.

R12.2 Data archiving

a) Laboratories participating in the WMO-GAW programme must submit their data to the World Data Centre for Greenhouse Gases (WDCGG) (according to WMO, 2007) A co-ordinated annual submission of data, with clearly identified version number of submitted data and calibration scale, as well as supporting details is strongly recommended. The same recommendation holds to other public-access data archive centres such as the Carbon Dioxide Information Analysis Centre (CDIAC).

b) A new version of the WDCGG Guide that includes new data categories, new data submission formats, data submission procedures, and distribution ways of data and products has been published. The adherence to this WDCGG Guide is requested.

c) The WDCGG distributes data in versions consistent with the annual CD-ROM Report and keeps old versions.

R12.3 Co-operative data products

All laboratories making high-quality GHG measurements are strongly encouraged to participate in the Co-operative Atmospheric Data Integration Project which produces the GLOBALVIEW data products. The majority of current participants provide updates in May that include data through December of the preceding year. Data contributed to the GLOBALVIEW project are used to derive the data product. The product includes no actual data.
R13. SUMMARY OF RECENT INTERNATIONAL PLANNING OF ATMOSPHERIC TRACE GAS MEASUREMENT STRATEGIES

This report is prepared in the context of widespread governmental acceptance of climate change (United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto protocol), and leads to new and urgent challenges to the carbon cycle community. Two main objectives justify the deployment of atmospheric observations:

1. To monitor and assess the effectiveness of emission control and/or reduction activities on atmospheric levels, including attribution of sources and sinks by region and sector.
2. To quantify the present state of the fluxes of greenhouse gases and better understand the controlling processes.

An overview of the observational needs for validating GHG emissions and reductions is given in this report (Tans et al.). Recently, new GHG measurement data streams from satellites with global coverage have become available based on a variety of instruments (SCIAMACHY, AIRS, IASI,) and are being integrated into global data assimilation systems (e.g. the GEMS project). However, these new observations lack long-term continuity, are subject to various biases and do not cover with sufficient accuracy the full suite of GHG and associated tracers defined by WMO-GAW. Hence a complementary, long-term, high-quality network of surface-based in-situ, tall tower and total column as well as systematic aircraft observations are indispensable, in order to reliably detect and quantify long-term changes in GHG sources and sinks. Furthermore, these measurements allow an independent assessment of regional trends, as needed by local policymakers.

In addition to the WMO-GAW global programme and its predecessor BAPMoN operating since 1975 and targeting the coordination of systematic atmospheric greenhouse gases observations, there have been international research efforts on understanding the carbon cycle. One has been co-ordinated by the Global Carbon Project (GCP) (http://www.globalcarbonproject.org/) combining the efforts of International Geosphere-Biosphere Project (IGBP), World Climate Research Project (WCRP) and International Human Dimensions Programme (IHDP). The GCP produced in 2003 a Science Implementation Plan dealing with the patterns and variability of carbon fluxes, the associated processes and feedbacks, and the management of the carbon cycle. GCP identified both systematic observations of concentrations in the atmosphere and oceans and process-oriented carbon cycle observations. In parallel, the former Integrated Global Carbon Observing Strategy Partnership (IGOS-P) produced a Theme Report on Integrated Global Carbon Observations (IGCO). It outlined a strategy to coordinate systematic global carbon observational networks that can form the backbone of an integrated carbon cycle monitoring system. It includes GAW for the atmosphere and builds upon earlier planning by GTOS/TCO (Terrestrial Carbon Observations http://www.fao.org/gtos/TCO.html) and GOOS (Global Ocean Observing System http://ioc.unesco.org/goos/). The main role of the IGCO to establish data requirements, design network configurations, and develop advanced algorithms for carbon observations, which will be the core of a future, sustained observing system by 2015 sees the long term efforts of GAW through this WMO/IAEA Expert team and other components of GAW complementing parallel efforts in terrestrial and marine reservoirs. The GAW greenhouse gas observations were also part of a second IGOS-P strategy on Integrated Global Atmospheric Chemistry Observations (IGACO) which includes not only greenhouse gases, but aerosols and ozone. The IGACO strategy (WMO GAW Report #159, 2004) is being implemented through the WMO-GAW Programme and its Strategic Plan for 2008-2015.

In both GCP and IGCO strategies, a strong atmospheric observing component is outlined as indispensable to link land and ocean observing components and to integrate across spatial heterogeneities and temporal variability A modelling strategy for developing Carbon Cycle Data Assimilation schemes that will interpret observations in terms of fluxes is also outlined, based upon a combination of data and models for the different domains: atmosphere, ocean and land, where results from one domain place valuable constraints on the workings of the other two ("multiple constraint").
Two major regional programmes have received funding to increase the density of atmospheric trace gas observations in GAW and terrestrial carbon observations over North America (NACP; http://www.esig.ucar.edu/nacp/) and Europe (CarboEurope-IP http://www.carboeurope.org/; ICOS http://icos-infrastructure.eu). It is important that those regional programmes remain tightly linked to the international WMO-GAW effort and produce regional data sets that can be merged safely into an enhanced global picture of carbon sources and sinks. Lessons from such regional initiatives should be valuable to formulate future atmospheric observing strategies for the remaining under-sampled regions, in particular in the tropics. The strong commitment to build expertise in developing countries by WMO and IAEA, including the establishment of high-quality measurement capabilities, remains a critical issue for achieving adequate spatial coverage of the globe in the coming decade.

The following observational strategies seem to be most promising in this context:

a) Expand aircraft flights over vegetated areas not sampled or under-sampled, with priority to tropical South America, Africa, and South East Asia. Higher altitude flights shall be needed to cope with vigorous convective mixing up to 10 km in the tropics. For that purpose, the use of passenger aircraft such as pioneered in atmospheric chemistry (CARIBIC, MOZAIC programmes) should be promoted.

b) Make the effort to recruit scientists from the under-sampled continents/areas to join the WMO Experts group.

c) Carry out continuous measurements in the boundary layer, in particular on top of high towers, and further pursue the option to use eddy flux towers as a platform for additional precise CO₂ mixing ratio observations. These observations will help us to quantify regional sources and sinks by means of inverse modelling.

d) Develop and implement long-term measurements of total column Greenhouse Gases at a number of sites in WMO-GAW and its partner stratospheric network NDAAC recognising the need for satellite calibration/validation and modelling.

e) Carry out in the vicinity of continuous tower-based boundary layer measurement sites frequent vertical profiles if possible under all weather conditions, which will quantify the vertical mixing of surface sources and sink fluxes.

f) Develop high-quality measurements of carbon cycle tracers that can be used to attribute natural fluxes to their controlling processes (¹³CO₂, O₂/N₂, ¹⁸OCO, stable isotopes in CH₄ and CO) and separate fossil fuel emissions (¹²CO₂, CO…). Along these lines it is absolutely essential that detailed spatially and temporally resolved fossil fuel CO₂ and CO emissions inventories be developed and pursued.

g) Add measurements of characteristic chemical trace substances to the measurement programme or suite of components analysed in flask samples to sort out source contributions of the various GHGs.

h) Develop high-quality measurements of transport tracers (SF₆, ²²²Rn, C₂Cl₄…) to validate numerical models of atmospheric transport (in particular their vertical mixing) including aircraft sampling.

i) Report actual uncertainties on individual data where available. In particular, pursue the development of data products (e.g. GLOBALVIEW) that can include wherever possible information on representativeness, calibration offsets, etc. Take into account station characteristics and catchment area description.

j) Plan atmospheric measurements jointly with terrestrial and oceanic process communities to optimise the link of atmospheric composition change to surface processes. For example, the development of the “virtual tall tower” concept to use short towers as part of atmospheric networks, and the synergetic use of ocean ΔpCO₂ survey programmes to make atmospheric measurements.

k) Encourage and facilitate the development of improved atmospheric tracer transport models. Among the identifiable needs are improving the representation of atmospheric convection, the representation of the surface boundary layer and the need to improve spatial and temporal resolution to better account for sources and sinks variability. Equally as important for assessing the distribution of fluxes is the use of several independently developed models and their frequent intercomparison. Finally, it is important to develop and maintain
community models which are numerically efficient, which can run from standard computer platforms with a modest amount of training, and which are made available to the scientific community as a whole.

References


Recommendations


_________
1.1 Improvements in the WMO/GAW Nitrous Oxide Mole Fraction Scale

Brad Hall
NOAA, Earth System Research Laboratory

1.1 Introduction

The NOAA-2000 mole fraction scale was adopted by the WMO/GAW community of experts as the GAW N₂O reference scale. This scale is based on 17 gravimetrically-prepared compressed gas standards. In recent years we have improved on this scale because a) many of the primary standards used to define the scale were nearing the end of their useful lives, b) some of these primary standards showed inconsistencies in other compounds (dichlorofluoromethane for example), and c) techniques for preparing primary standards have improved. Here the new 2006 mole fraction scale and its relationship to the NOAA-2000 scale are presented. Also included is an improved analysis method for SF₆ and implications for determinations of N₂O and SF₆ by gas chromatography with electron capture detection.

1.1.1 The NOAA-2006 nitrous oxide mole fraction scale

From 2003 to 2005, seven new primary standards were prepared in 5.9-L aluminium cylinders. These were combined with six standards from the NOAA-2000 scale to form a new scale (Hall et al., 2007). The 2006 scale is defined by thirteen ppb-level primary standards (“daughters”) with N₂O ranging from 261-371 ppb. These were prepared from four ppm-level “parents” (2349, 1626, 1461, and 1571 ppm). All ppb-level standards also contain CO₂ ranging from 360 to 380 ppm and SF₆ ranging from 1-10 ppt.

Analysis of the 13 standards shows that they are more internally consistent than those that defined the 2000 scale. A second order polynomial was used to model the ECD response based on peak area. The standard deviation of residuals is 0.29 ppb, compared to 0.8 ppt with the 2000 standards. The agreement among the 13 standards is comparable to the expanded uncertainties associated with their preparation. Further, there is no difference among “cousins”, ie. daughter standards prepared from different parents.

The range of the 2006 scale is 260-370 ppb. This range is smaller than that associated with the 2000 scale. A smaller range was chosen to better define the scale over the range of atmospheric concentrations most often encountered in monitoring programmes. We continue to maintain standards outside this range for special studies, but those standards are not officially part of the 2006 scale.

The 2006 N₂O scale is very similar to the 2000 scale at ambient N₂O levels, differing by only -0.19 ppb at 320 ppb. The largest differences occur above 340 ppb, for which the 2000 scale was poorly defined (Figure 1). The conversion is expressed as

\[ y = -2.20205 \times 10^{-7} x^3 + 1.20704 \times 10^{-4} x^2 + 0.98343x \]  

where \( y \) is N₂O mole fraction on the 2006 scale, and \( x \) is the mole fraction on the 2000 scale.

Figure 1. Difference between the 2006 and 2000 N₂O scales.
1.1.2 Maintaining the scale

The N$_2$O scale is maintained by analyzing six secondary standards (modified natural air) every 3-4 weeks, and analyzing the set of 13 gravimetric standards yearly. All standards are referenced to a single working standard (natural air). With ultra-high-purity nitrogen carrier gas and CO$_2$ dopant added just upstream of the ECD, the ECD response to N$_2$O has remained very stable, showing little variation as cylinders of nitrogen are changed (Figure 2).

![Figure 2. ECD response to an ambient tertiary standard in 2007 (peak area and peak height).](image)

Values assigned to air samples in aluminium and stainless steel cylinders show little variability over 3.5 years (Figure 3). The standard deviation of all measurements of 313 and 318 ppb “target tanks” is 0.09 ppb. This is consistent with differences in N$_2$O determined for tertiary standards used at NOAA observatories. Over the last three years, ten tertiary standards have been analyzed at 2000 psig prior deployment at NOAA observatories and again at 200 psig upon return. The mean N$_2$O difference among these standards (outgoing minus incoming) is 0.12 ppb. The maximum difference is 0.36 ppb. Thus, the reproducibility of N$_2$O calibrations estimated to be ±0.2 ppb. Efforts to improve reproducibility are ongoing.

![Figure 3. Residuals (ppb) based on periodic analysis of several tertiary standards.](image)

1.1.3 Scale comparisons

The NOAA-2006 scale was compared to the SIO-98 scale through the exchange of three modified natural air standards in aluminium cylinders. A difference of only 0.03 ppb was observed at 319 ppb. Differences (NOAA-SIO) of 0.16 and -0.23 were observed at 299 and 310 ppb, respectively.
1.1.4 Improvements in SF\textsubscript{6} analysis

In an effort to improve SF\textsubscript{6} analysis, the method used to measure N\textsubscript{2}O and SF\textsubscript{6} on the main calibration instrument was modified. Prior to the change, N\textsubscript{2}O and SF\textsubscript{6} were separated using a porapak Q column at 56 deg C. The SF\textsubscript{6} peak was Gaussian, but broad, eluting after N\textsubscript{2}O. Precision was typically 1%. By reducing the length of the porapak Q column, increasing the oven temperature to 90 deg C, and adding a 1/8” by 2 foot molecular sieve 5A post column at 185 deg C (Moore et al., 2003), SF\textsubscript{6} now elutes prior to N\textsubscript{2}O (Figure 4). This results in reduced width and increased peak height. The chromatography change resulted in improved SF\textsubscript{6} precision, with precision now typically around 0.3%. The standard deviation associated with a typical SF\textsubscript{6} calibration is 0.02 ppt.

![Sample chromatogram showing N\textsubscript{2}O and SF\textsubscript{6}](image)

**Figure 4.** Sample chromatogram showing N\textsubscript{2}O and SF\textsubscript{6}. Note that CO\textsubscript{2} elutes after N\textsubscript{2}O.

Based on analysis of several tertiary standards (Figure 3) the change in chromatography has not affected the scale or our ability to assign N\textsubscript{2}O values to compressed gas mixtures. The N\textsubscript{2}O measurement precision was not affected (Figure 5).

![History of SF\textsubscript{6} (upper) and N\textsubscript{2}O (lower) precision with a major change in chromatography in mid-2006](image)

**Figure 5.** History of SF\textsubscript{6} (upper) and N\textsubscript{2}O (lower) precision with a major change in chromatography in mid-2006.

References


1.2 Calibration of Atmospheric Hydrogen
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1.2.1 Introduction
Interest in atmospheric hydrogen has increased in recent years as scenarios for a future hydrogen fuel economy are proposed for the coming decades. The balance of hydrogen could change with the implementation of a new H$_2$ energy carrier making it important to establish its current global budget and atmospheric trend. According to global budget estimates sources and sinks of H$_2$ are approximately balanced but there remain large uncertainties. Limitations in the understanding of the global H$_2$ budget partly result from limitations of the measurement data. This was revealed by a long-term intercomparison experiment conducted by NOAA, CSIRO and University of Bristol at common monitoring sites. The three main confounding factors are independent different calibration scales used in different laboratories, problems of instable H$_2$ levels in standard gases and an inadequate characterisation of the non-linear response of the detector (GC-RGA).

In view of these deficiencies the recommendations of the WMO Experts Group encourage to:

- Extend H$_2$ intercomparison activities to keep track of the comparability of different data records
- Test different containers to find cylinders that keep the H$_2$ mixing ratios unchanged
- Develop new methods to produce reference gases

In this context the EUROHYDROS project has started to set up a monitoring network in Europe including 12 continuous measurements sites in Europe, 7 flask sampling sites in Europe and 6 global flask sampling sites. To get a harmonized data set from the EUROHYDROS monitoring network all stations and laboratories are linked to a common calibration scale. Aiming for long-term consistency and comparability of the EUROHYDROS dataset the calibration strategy has tried to address the recommendations outlined above.

1.2.2 EUROHYDROS scale
Responsible for setting up and maintaining the EUROHYDROS calibration scale is the MPI-BGC. This new hydrogen calibration scale extends an already existing scale at MPI-BGC that is based on the CSIRO94 scale. A scale range of 140 to 1200 ppb is covered with a total of twelve standards among which six standards are in the atmospheric range (400 – 600 ppb) (Table 1).

H$_2$ mixing ratio values that exceed the previously calibrated range of 450-665 ppb were assigned to the new standards by a dilution experiment. 39 individual dilutions of the standard gas with the highest H$_2$ concentration have been prepared in glass flasks and then diluted with variable amounts of purified synthetic air (free of H$_2$ and CH$_4$). The dilution factor of each individual sample was then calculated from the ratio of the CH$_4$ concentration in the sample to the CH$_4$ concentration in the undiluted standard as analysed by GC-FID. Diluted samples that contained H$_2$ at a level within the previously calibrated range were then used to recalculate the concentration of the source standard and further the concentrations of all samples from the dilution series. The data points were then fitted by a 3$^{rd}$ order polynomial regression function.

1.2.3 Intercomparisons
Several ongoing intercomparison activities of MPI-BGC serve to check for comparability of the European data with the data from two major monitoring networks (NOAA and AGAGE-CSIRO).

The ongoing CarboEurope "Sausage Flask" intercomparison has been used to compare hydrogen data with CSIRO since 2002. In addition, flask samples from the CSIRO Cape Grim flask sampling programme have also been used for intercomparison also starting in 2002. Figure 1a documents the good agreement in the H$_2$ results. A very minor trend in time apparent in this graph is suggesting a relative increase of H$_2$ results at CSIRO vs. MPI. However, a further investigation revealed that the trend is due to a change in the composition of the intercomparison samples plus a concentration dependent offset between the two groups and not a real trend in time (Figure 1b).
Table 1. Standards defining the EUROHYDROS calibration scale.

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<td>25</td>
<td>05.04.2006</td>
<td>stainless steel</td>
<td>Graeven Met.techn.</td>
</tr>
</tbody>
</table>

Similar intercomparisons were made with NOAA that joined the sausage flask programme in 2005. Since 2006 flasks from the Ochsenkopf monitoring site are analysed at both laboratories. Figure 2a depicts the intercomparison record with NOAA-GMD. The average interlab difference is significantly bigger compared to Figure 1a documenting the offset between the respective calibration scales. This also is evident in the bigger concentration dependent deviation (Figure 2b).

1.2.4 Reference gas stability

The EUROHYDROS standards have been filled into a variety of containers that all have gone through prior tests in terms of keeping a stable hydrogen concentration. This should reduce the risk of an unrecognized small drift of the whole set standards. The cylinders include four types of stainless steel cylinders and one aluminium cylinder. The stability check of the standard hydrogen levels in these different was made by a number of approaches:

- Checking for any relative drift among the different sets
- Checking for any relative drift relative to several quality control standards (two types of steel cylinders, one aluminium cylinder)
- Checking for any relative drift relative to a set of gas samples filled in 5 l glass flasks in 2005
- Intercomparison with CSIRO

All of these methods do not provide a full guarantee of the long-term stability but their combination gives good evidence for the absence of major drifts. To find small drifts over a longer time range an additional check has been made by repeatedly applying a method that allows to make standard mixtures in a highly reproducible way. The procedure has been described and discussed in detail previously and consists of the following steps:

A sample loop of known volume (344 ± 0.3 µl) is filled with H₂ at a known temperature (±0.1 °C) and pressure (±0.05 mbar). This amount of H₂ is then flushed to an evacuated high pressure cylinder with purified nitrogen or H₂ free natural air. The amount of diluent gas is weighed on a calibrated balance (±0.1 g). Calculating the respective moles of H₂ and diluent gas provides the mixing ratio.

None of the above drift tests has indicated any standard instability in the set of standard gases used for the EUROHYDROS scale.
Figure 1a.  CSIRO-MPI flask sample intercomparison record.

Figure 1b.  Concentration dependence of H₂ intercomparison with CSIRO.

Figure 2a.  NOAA-MPI flask sample intercomparison record.
1.2.5 Preparation of new reference standards

Initial results of reference gases generated with this mixing procedure showed an offset to the CSIRO94 based scale of more than 3%. Therefore, potential factors that might bias this method were thoroughly explored and accounted for. This made the approach valid for preparation of reference gases with accurate mixing ratios in absolute terms.

In total more than 80 reference mixtures of hydrogen in nitrogen were prepared and analysed. Figure 3 shows the residuals of the actually mixed H₂ contents minus the values measured. While there is a general difference of about 3.5% this difference is not a constant factor but the residuals have a systematic non-linearity. This reveals that the detector response is not adequately described by a cubic curve over the given concentration range.

One basic requirement for the accuracy of the method is that the diluent gas does not contain any H₂. The employed nitrogen did not have any detectable H₂ blank. It was purified further using two different kind of purifying cartridges (Aeronex, SAES Getters) that are specified for a purity < 1ppb. Dilution air is made from purified from ambient atmospheric air. For this the air is compressed in high pressure cylinders at a flow rate of 70 l/min through a cartridge filled with 400g Sofnocat 423. This air...
normally contains 150 ppb H$_2$. When preparing the reference gas mixtures it is then passed through a second cartridge filled with another 400 g Sofnocat 514 at a flow rate of 2 l/min. This removes the residual hydrogen.

Hydrogen of standard gases mixed in nitrogen produced 0.6 % higher instrumental signals at the RGA than the same hydrogen levels in air. This cannot be explained with a higher H$_2$ blank in the nitrogen. To investigate this effect additional gas mixtures of hydrogen were prepared in pure oxygen and in air/nitrogen and air/oxygen mixtures with varying ratios of oxygen and nitrogen. In Figure 4 the deviation of the H$_2$ signal height of these mixtures relative to the signals of the respective H$_2$ in N$_2$ mixtures are plotted as function of the O$_2$ content of the diluent gas. Oxygen clearly reduces the detector response. In the chromatographic method for H$_2$ and CO analysis the peaks of oxygen, nitrogen and hydrogen of an air sample injected on the RGA are not well separated chromatographically. This co-elution of oxygen and hydrogen may result in a scrubbing effect of the Hg that is produced from HgO reaction with hydrogen by reconversion to HgO through oxygen. This finding implies that air sample analysis with this kind of detection principle must be calibrated with real air reference gases rather than with mixtures of hydrogen in nitrogen or other gases.

![Figure 4. Influence of oxygen content of a reference gas mixture on instrumental response.](image)

### References


1.3 Preparing and Maintaining of CO₂ Calibration Scale in National Institute for Environmental Studies – NIES 95 CO₂ Scale

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² Global Environmental Forum, Tsukuba, Japan

1.3.1 Preparing the primary standard gases

The National Institute for Environmental Studies (NIES) employed the CO₂ calibration scale in 1995 based on 10 CO₂-in-air standard gases in 10L aluminium cylinders prepared by Nippon Sanso Corp. The pure CO₂ gas was diluted with purified air by gravimetric 3-step dilution method. The CO₂ mole fractions were determined from measured masses of the pure CO₂ and the purified air. The accuracy of the CO₂ mole fraction was estimated to be about 0.3ppm [Tanaka et al., 1987]. The relationship between the gravimetric CO₂ mole fractions and response of NDIR (XURA-207, Shimadzu, Japan) for the 8 cylinders were fitted by a least square method with a quadratic function and the gravimetric values were adjusted to fit the quadratic function. All of the corrections were less than 0.1ppm (Figure 1). Then we regarded the corrected values of 320.01, 330.03, 340.01, 350.03, 360.16, 369.88, 379.56 and 390.90ppm as NIES 95 CO₂ calibration scale for atmospheric air. Remaining two cylinders with their CO₂ values of 249.96 and 470.00ppm were also NIES 95 standard gases used for oceanic pCO₂ measurement. Mixing ratios and purpose of NIES95 primary cylinders are summarized in Table 1. We used these ten cylinders as primary standard gases for calibrating working standard gases used for CO₂ measurements at ground based stations, on the ship, on the aircraft and flask measurements in the laboratory.

![Figure 1. Relation between the gravimetric CO₂ mole fractions and response of NDIR for eight cylinders (upper panel) and the residuals from the fitting curve (lower panel).](image)

<table>
<thead>
<tr>
<th>Cylinder#</th>
<th>CO₂[ppm]</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPB08589</td>
<td>249.96</td>
<td>Ocean pCO₂</td>
</tr>
<tr>
<td>CPB08595</td>
<td>320.01</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>CPB08596</td>
<td>330.03</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>CPB08597</td>
<td>340.01</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>CPB08598</td>
<td>350.03</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>CPB08599</td>
<td>360.16</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>CPB08602</td>
<td>369.88</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>CPB08603</td>
<td>379.56</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>CPB08604</td>
<td>390.90</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>CPB08669</td>
<td>470.00</td>
<td>Ocean pCO₂</td>
</tr>
</tbody>
</table>
1.3.2 Internal stability of the Primary cylinders

To avoid rapid consumption of the primary standard, we have established standard gas hierarchy, primary, secondary and working standard. Secondary and Working standards were prepared by manometric method and stored into aluminium cylinders.

Primary standard gases were analysed repeatedly at a frequency of 0.5-2 years by NDIR and their responses were compared each other to check the CO₂ drift in individual cylinder. The time series of residuals from the quadratic fit of CO₂ values and the NDIR responses are plotted in Figure 2. Most of the residuals are within ±0.05 ppm in these 12 years. The relationship between primary and secondary standard gases have been also stable for more than 10 years.

Figure 2. Time series of residuals from the quadratic fitting of CO₂ values and the NDIR responses by primary standard.

1.3.3 Inter-laboratory comparison

NIES 95 scale was compared with other CO₂ scales in Round-Robin (RR) inter-comparison project. Based on the results from RR 1995/1996, differences in the CO₂ between WMO scale and NIES 95 scale varied from −0.02 to +0.12 ppm in a range between 343 and 372 ppm (Figure 3) [Peterson et al. 1999]. While the difference between NIES 95 scale and WMO scale were −0.14 to −0.10 ppm in a range between 355 to 385 ppm based on the preliminary results of RR 2002/2007 inter-comparison (Figure 4) [L. Zhou, personal communication, October 2007]. These changes are mainly due to the revision of CO₂ calibration scale by WMO Central Calibration Laboratory [Tans et al., 2006].

When we extract the relationship of the CO₂ scales employed by NIES, Tohoku University [Tanaka et al., 1987] and Meteorological Research Institute, Japan (MRI) [Inoue et al., 1995] from the results of RR 1995/1996 and 2002/2007, the differences can be plotted in Figure 5. Both Tohoku and MRI prepared their own gravimetric CO₂ scales and maintained individually. We can conclude that the relationship between 3 laboratories have been maintained from 1996 to 2002.

1.3.4 Future NIES CO₂ scale

To extend the NIES scale for atmospheric CO₂ to higher than 390 ppm, we plan to employ a new CO₂ scale based on cylinders prepared gravimetric method in one-step dilution. The one-step dilution method has two advantages: (1) reduction of dilution steps may reduce the uncertainty associated with mass determination and gas handling processes, and (2) the standards prepared by the one-step dilution method are independent of each other [Tohjima et al., 2006].
Figure 3. Difference of the CO$_2$ scale employed by each laboratories from WMO scale based on the Round Robin 1995-1996.

Figure 4. Difference of the CO$_2$ scale employed by each laboratories from WMO scale based on the Round Robin 2002-2007.

Figure 5. Differences of the CO$_2$ scale employed by Tohoku University, MRI and NIES based on the Round Robin 1995-1996 and 2002-2007.
References


2.1 Activities in QA/SAC and WCC in Japan
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Tokyo, Japan

2.1.1 Introduction
The Japan Meteorological Agency (JMA) operates the QA/SAC for Asia and the South-West Pacific in CO₂ and CH₄ (QA/SAC Japan). The JMA also operates the WCC in Asia and the South-West Pacific for CH₄ (WCC Japan). This report focuses on the activities of these centres after the previous meeting.

2.1.2 Activity in the QA/SAC Japan
Some of the roles of QA/SACs are to provide advice and support for the local QA system at individual GAW sites, and to provide training, long-term technical help for station scientists (WMO, 2007).

In 2002, the QA/SAC Japan was asked from the Malaysian Meteorological Department (MMD) for technically support on an establishment of CO₂ observation at Danum Valley (in Borneo) in Malaysia. The QA/SAC Japan visited the MMD in Kuala Lumpur and a planned observation site in Borneo in January 2003. During the visit, the QA/SAC Japan made some presentations for general knowledge for CO₂ observation and observation environments, and suggested specifications of observation system and operation procedures for CO₂ observation at Danum Valley.

Figure 1. Locations of Danum Valley observation station (left) and a tower and laboratory for CO₂ observation at Danum Valley.

The MMD started CO₂ measurement at Danum Valley using a sampling tower (~100 m) in 2004. As a following up QA/SAC activity of CO₂ observations at Danum Valley, the QA/SAC Japan invited an expert of CO₂ observation from the MMD. The expert visited the QA/SAC Japan in November 2005, and the centre held the discussions on the Danum Valley CO₂ observations. In conclusion, the CO₂ observation system is generally well designed with no major faults that could prevent high precision CO₂ measurements. The QA/SAC Japan made the QA/SAC report on CO₂ observation in Malaysia including some recommendations and sent it to the MMD and the WMO. The CO₂ data at Danum Valley from September 2004 through May 2005 are archived in the World Data Centre for Greenhouse Gases in the JMA. However, the CO₂ observation system at Danum Valley was damaged by lightning and floods. The system is restored recently with assistance from the manufacturer. However, further checks are necessary for regular operation.
2.1.3 Activity in the WCC Japan

Round-robin comparisons (inter-comparison experiment) of laboratory standards and comparisons of field measurements and samples over the last decade have regularly shown differences larger than the target comparability for merging data from different field sites. These systematic differences contribute to uncertainties in the location and magnitude of surface fluxes derived from atmospheric composition measurements (WMO, 2006).

The WCC Japan has conducted the Round-Robin inter-comparison of CH₄ standard gases in Asia and the South-West Pacific since 2001. During 2001-2002, the inter-comparison experiment was conducted for the China Meteorological Administration (CMA) and the Korea Meteorological Administration (KMA). During 2002-2003, the inter-comparison experiment was conducted for the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia and National Institute of Water & Atmospheric Research Ltd. (NIWA) in New Zealand. During 2002-2003, the inter-comparison experiment was conducted for Tohoku University and National Institute for Environmental Studies (NIES) in Japan. During 2005-2007, the second inter-comparison experiment was conducted for CMA, KMA, CSIRO, and NIWA. The results are shown in Figure 2.

![Figure 2. Results of the Round-Robin inter-comparison of CH₄ standard gases. JMA: Japan Meteorological Agency, CMA: China Meteorological Administration, KMA: Korea Meteorological Administration, CMDL: Climate Monitoring and Diagnostics Laboratory, CSIRO: Commonwealth Scientific and Industrial Research Organization, NIWA: National Institute of Water & Atmospheric Research Ltd., TU: Tohoku University, NIES: National Institute for Environmental Studies, KRISS: Korea Research Institute of Standards and Science. Some participants show relatively different results due to the differences of using scales.](image)

The CH₄ WMO primary standard was established by NOAA/ESRL/GMD in 2005. The WCC JMA corrected the past inter-comparison experiment results in accordance with the WMO primary standard in June 2007.

The results of Round Robin Inter-comparison have also been posted on the WCC Japan website (http://gaw.kishou.go.jp/wcc/ch4/comparison.html). The Round Robin Inter-comparison is effective for check of measurement techniques and data consistency. The WCC Japan appreciates the participants’ cooperation. The CH₄ inter-comparison in Asia will be continued by the WCC Japan hereafter for maintenance and enhancement of observation technique.
References
2.2 NOAA Comparison Activities: Are We Closer to the Required Measurement Accuracy?
Ken Masarie, P. Tans, A. Andrews, T. Conway, A. Crotwell
D. Worthy (EC), A. Gomez (AEMET)

Global carbon cycle inverse modelling studies have produced a wide range of estimates of the spatial and temporal distribution of carbon emissions. Debate is ongoing about the percentages of carbon taken up by the ocean and the land biosphere, and where uptake is occurring. Despite their differences, these studies all agree on one point, the need for more observations. However, more observations are only helpful if they can be merged into a cooperative global network of observations with consistency meeting or exceeding target levels as defined by current research topics [WMO TD No. 1359, 2006]. Researchers must now complement their observations with comparison activities designed to determine the level of confidence at which their data can be merged with data from other labs. Several strategies exist within our community and include comparisons of 1) measurements of air from the same high-pressure cylinders; 2) measurements from glass flasks filled from the same high-pressure cylinders; 3) measurements from low-pressure cylinders decanted from high-pressure cylinders; 4) measurements of air from the same ambient samples; and 5) measurements from the same location using different methodologies. What we learn from the different comparison strategies varies greatly and depends on experiment design, comparison frequency, and level of automation.

2.2.1 Introduction
The NOAA ESRL carbon cycle observing programme includes discrete and quasi-continuous sampling from surface sites, aircraft, tall towers, and baseline observatories. While all projects are managed by a single group, sampling and analytical strategies can vary considerably. And while all measurements are traceable to WMO calibration scales, we cannot assume internal consistency with respect to calibration. Thus a critical component of our operation is quality assurance, specifically, procedures designed to assess the level of consistency among measurements made within NOAA. We use the strategies mentioned above to compare measurements made using different methodologies within our lab and also to compare our observations with observations made by other labs. Many of these strategies are fully automated and web-based. But are these efforts producing results? Are NOAA observations internally consistent and comparable with observations made by other labs to the levels required to address current carbon cycle questions?

Here we assess the comparability of NOAA ESRL CO₂ measurements. The objective is to achieve and maintain comparability between independent records to within 0.1 ppm. We present comparisons of measurements made solely within NOAA (intra-laboratory) and comparisons between NOAA and other laboratories (inter-laboratory).

2.2.2 Comparison experiments
NOAA participates in several comparison experiments each designed to assess some aspect of the measurement process. The diagram in Figure 1 shows basic components of the measurement process and identifies where several of our comparison activities are located within this process. The WMO/IAEA sponsored Round Robin (RR) experiments, for example, assess the level to which a laboratory scale is tied to the WMO CO₂ mole fraction scale. RR experiments are not designed to assess the level of comparability among atmospheric measurements made by different laboratories or using independent methods. Comparisons of measurements from colocated but independent sampling methods perhaps provide the best estimate of the level of consistency between two independent atmospheric records because the experiment incorporates all aspects of the measurement process. However when differences are observed, this comparison, by itself, makes it difficult to identify possible causes. Thus, our comparison activities must complement each other in order to maximize our ability to understand the cause of problems leading to inconsistencies.
NOAA comparison experiments become critical quality control tools when the comparisons are frequent (≤ weekly) and the results are readily available. Timely access to the comparison results provides the best opportunity to detect problems shortly after they develop. Table 1 summarizes current NOAA comparison experiments.

**Table 1. Current NOAA comparison Experiments.**

<table>
<thead>
<tr>
<th>Intra-Laboratory</th>
<th>Collaborating Lab</th>
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</thead>
<tbody>
<tr>
<td>Boulder Flask Analysis Systems – flasks and cylinders (same air)</td>
<td>NOAA</td>
</tr>
<tr>
<td>Baseline Observatories – insitu and flask (co-located)</td>
<td>NOAA</td>
</tr>
<tr>
<td>Baseline Observatories – flask and flask (co-located)</td>
<td>NOAA</td>
</tr>
<tr>
<td>Tall Towers – insitu and flask (co-located)</td>
<td>NOAA</td>
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</table>

<table>
<thead>
<tr>
<th>Inter-Laboratory</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>weekly flasks from Cape Grim (same air)</td>
<td>CSIRO</td>
</tr>
<tr>
<td>weekly flasks from Alert (same air)</td>
<td>EC</td>
</tr>
<tr>
<td>weekly flasks from Oschenkopf (same air)</td>
<td>MPI-BGC</td>
</tr>
<tr>
<td>weekly flasks from Mace Head (same air)</td>
<td>LSCE</td>
</tr>
<tr>
<td>insitu/flask at Niwot Ridge (co-located)</td>
<td>NCAR</td>
</tr>
<tr>
<td>insitu/flask at Izaña (co-located)</td>
<td>AEMET</td>
</tr>
<tr>
<td>insitu/flask at Oklahoma, U.S. (co-located)</td>
<td>LBNL</td>
</tr>
</tbody>
</table>

2.2.3 *Intra-laboratory comparison experiments*

In 2005, the ESRL flask analysis system in Boulder was operating at full capacity. In 2006, we introduced a second near identical system with the idea that surface network flasks and Programmable Flask Packages (PFP) could be analyzed on either system without introducing errors into the long-term observational records. To monitor the level of comparability between the two analytical systems (M1 and M2), we initiated several long-term comparison experiments. Daily, we analyze a pair of flasks filled with air from a well-calibrated cylinder on both systems (test flasks). At approximately monthly intervals, we measure air from a well-calibrated high-pressure...
cylinder on both systems (target gas). Figure 2 shows differences between measurements of target gas cylinder CC71583 made on M1 and M2 and the value assigned by our calibration lab. For the period shown, the differences are -0.01 ± 0.03 (N=17) and -0.01 ± 0.02 (N=21) respectively and suggests we are able to propagate our scale to within 0.05 ppm. We also measure weekly flask sample pairs collected at Kumukahi, Hawaii (KUM) on both systems. KUM comparison results for the period June 2005 through July 2007 (not shown) suggest that we can analyze surface network flasks on either analytical system with a confidence level of < 0.1 ppm. These experiments are ongoing to ensure that we can continue to measure atmospheric samples on either system without introducing bias into our long-term records.

![Figure 2. Differences between measurements made on MAGICC1 (M1) and MAGICC2 (M2) and the assigned value of the target gas as determined by our calibration laboratory.](image)

Quasi-continuous measurements of CO₂ are made at the 4 GMD baseline observatories and tall towers. Weekly discrete samples are also collected at these sites and returned to Boulder for analysis. Comparison of these independent records provides a good estimate of the true uncertainty of a NOAA data set. Figure 3 shows a comparison between weekly discrete samples and in situ measurements for the hour corresponding to when the flask was sampled for the most recent 10-year period at Barrow, Alaska (BRW). The discrete samples and in situ system share the same intake line. The average difference over this time period is zero. On shorter time intervals, however, there are periods when the two records do not agree. Departures from the average may indicate a problem with either of the two systems. The discrepancy in the two records at Barrow during 2004 is most notable where discrete measurements are more than 1.0 ppm lower than the in situ values. A second comparison at Barrow between the in situ record and another flask record whose intake line is completely independent of the in situ setup (not shown) shows a similar offset suggesting the problem may be due to either the analysis of flasks in Boulder or the in situ system. Additional comparisons designed to evaluate the performance of the flask analysis system in Boulder (not shown) suggest the problem is likely with the in situ system. Because we do not know the cause with certainty, neither the flask nor in situ data during this period have been flagged as rejected.
Comparisons of in situ measurements and co-located discrete flask samples from our tower network are more difficult to interpret because CO$_2$ is highly variable due to each tower’s proximity to areas with active vegetation and urban populations. Differences in the records could be attributed to actual differences in the atmospheric air measured in situ and sampled by the flasks. Figure 4 shows flask minus in situ CO$_2$ differences from the tall tower at Moody, Texas (WKT). The comparison is between in situ measurements sampled at the 122 m intake level and PFP samples also collected at this level but using an independent intake line. Differences during 2006 show no systematic offset between the two records (0.02 ± 0.32 ppm, N=126). In 2007, however, there are several instances where flask values are low relative to the in situ record. This result is consistent with a possible leak in the PFP collection system. The PFP has since been replaced and agreement is again back to 2006 levels. The ~0.3 ppm variability in the 2006 result is comparable to the estimated total uncertainty (analytical uncertainty and atmospheric variability) of individual in situ measurements and is likely the best outcome we can expect using the current tower configuration.

Figure 3. Differences between NOAA flask and in situ measurements at Barrow, Alaska. The time at which the flask air samples were collected is indicated by the symbol colour.

Figure 4. Comparison of NOAA flask and in situ measurements from the 122 m level at the WKT tower. The time at which the PFP flask samples were collected is indicated by the symbol colour.
2.2.4 Inter-laboratory comparison experiments

NOAA participates in several ongoing comparison experiments with other laboratories. Inter-laboratory comparisons are essential to our assessment of how well our measurements agree with those from other laboratories. The assessment is typically based on comparisons of NOAA and the collaborating laboratory measurements of air from the same atmospheric samples [e.g., Masarie et al., 2001] or co-located samples collected or measured at a single location. If we are able to establish and maintain consistency to within 0.1 ppm over several years, we then assume all records derived from the two labs are consistent to this level. We believe this assumption to be reasonable but perhaps not always valid.

Figure 5 shows comparison results between NOAA and EC measurements of the same air from weekly discrete samples collected in NOAA flasks at Alert, Nunavut, Canada (open circles). Agreement during this period is 0.04 ± 0.11 (N=578) and appears consistent with results from two RR experiments (1997 and 2005) and available results from the ongoing bi-monthly EC Sausage comparisons [Levin et al., 2003]. Figure 6 shows a complementary comparison between EC measurements of the NOAA (ICP) flask and EC flasks sampled at approximately the same time. This result suggests that for much of the comparison period the EC measurement of the NOAA flask is consistently higher than EC measurements of their own flasks. This discrepancy based on the complementary comparison is still under investigation.

Figure 5. Comparisons between measurements made by EC and NOAA from discrete samples collected at Alert, Canada (open circles). Results from RR experiments (“R”) and bi-monthly EC Sausage fillings (“S”) are also shown.

Figure 6. Differences between EC measurements of the NOAA (ICP) flasks and EC measurement of EC flasks collected at approximately the same time at Alert are shown as red triangles. For comparison, agreement among pairs of EC flask samples collected at Alert is shown as cyan circles.
AEMET (formerly INM) has been making high-precision in situ CO₂ measurements at Izaña Observatory (IZO) since 1984. In collaboration with AEMET, NOAA has been collecting weekly air samples at IZO since the early 1990s. Figure 7 shows differences between the NOAA flask measurements and AEMET hourly averages for the hour corresponding to when the NOAA flask was sampled. Prior to 2003, the majority of NOAA samples was collected in the evening between 1800-2300 LT. In early 2003, the collection of the NOAA samples was moved to mid-day (1200-1700 LT). Since this change, we see improved agreement and reduced variability between the AEMET and NOAA measurements. However, it is important to note that this change in the NOAA sampling protocol introduces an inconsistency within the NOAA long-term IZO record. This is evident in Figure 8 where we compare the long-term trends (seasonal cycle removed) from the two records. The observed shift in the NOAA trend in early 2003 coincides with the change in sampling time-of-day and is consistent with the measurement of air that has been influenced by local vegetation and likely transported to the station during upslope flow conditions.

Figure 7. Comparison of NOAA flask and AEMET in situ measurements at Izaña Observatory. The time at which the NOAA samples were collected is indicated by the symbol colour.

Figure 8. Comparison of the long-term trend (seasonal cycle removed) in the AEMET in situ and NOAA flask records from Izaña.
2.2.6 Conclusions

Ongoing intra-laboratory and inter-laboratory comparisons play a key role in the NOAA observing programme. The only way to truly assess the quality of our data sets is to compare them with other independent records. Without these comparison experiments we might tend to assume our measurements are better than they actually are. Averaged over several years, NOAA CO₂ records are internally consistent to within 0.1 ppm, however, there are periods where systematic differences exceed the target level. Comparisons with other labs also show that the level of agreement between two CO₂ records typically varies with time. Only after we consider results from both intra- and inter-laboratory comparisons can we make a reasonable assumption about the level of consistency among data from different networks. When the comparison is frequent and ongoing, and the results are readily available, the experiment also serves as an important quality control tool that can help us detect and correct problems shortly after they develop.

References


L.X. Zhou1, D. Kitzis2, P.P. Tans2

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2.3.1 Introduction

As recommended by the WMO/IAEA Meeting of Experts on Carbon Dioxide and Related Tracers Measurement Techniques, all participating laboratories are urged to contribute the results of all systematic investigations of gas handling protocols and materials, whether the results were positive or negative. The purpose of the WMO Round-robin reference gas intercomparison would be NOT to distribute calibration scales, but rather to determine the precision of the current practice of international calibrations.

2.3.2 Protocol and experiment

The protocol of the fourth intercomparison during 2002-2007 was similar to that used for the previous ones held during 1991-1992, 1995-1997 and 1999-2000. An important difference, however, would be that all participants should also report values for several gases in addition to CO2, if they have the capability to do so. Mr Duane Kitzis and Dr Pieter Tans served as the coordinator; Dr Lingxi Zhou served as the referee. Twenty-seven laboratories from fifteen countries in total participated and they were divided into three globally-distributed groups. The NOAA ESRL (WMO CCL) prepared nine high pressure cylinders (three sets) for the intercomparison. Each laboratory was instructed to treat each cylinder as containing gases of unknown mixing ratios and to analyze the three cylinders as if they were “working tanks” within their programmes. The results were reported to the referee, who kept the results confidential until all laboratories had reported. Each set was analyzed first and last at NOAA ESRL to determine if there was any change in mixing ratios while the cylinders were circulating.

2.3.3 Participating laboratories and reported species

For the intercomparison report, there were 26 laboratories reporting CO2 (details in Table 1) and 12 laboratories reporting CH4 (details in Table 2). Besides, 8 laboratories reported CO, 2 laboratories reported H2, 6 laboratories reported N2O and SF6, and 7 laboratories reported δ13C and δ18O in CO2. Calibration histories for CO2, CH4, CO, H2, N2O, and SF6 by the NOAA ESRL and CO2 stable isotopes by the CU INSTAAR have been circulated among the participants in advance and discussed at the 14th Expert Meeting in Helsinki. Description of CO2 and CH4 standard scale reported by each participating lab was requested and shown in Table 1 and 2 -- we could then hope that labs on the same scale produce similar results. Intercomparison results of the other species such as CO, H2, N2O, SF6, δ13C and δ18O in CO2 have not been reported here (available to the participants only).

2.3.4 WMO mole fraction scale for CO2 and CH4

Under the WMO calibration system, several calibration scales exist for CO2 data, e.g. X74, X85, X87, X93, and WMO Mole Fraction Scale (WMO-X2005 and WMO-X2007). Because the mole fraction of CO2 contained in high-pressure cylinders can potentially change with time due to adsorption or production within the cylinder or regulator, or through other effects, a laboratory’s internal scale may potentially change with time relative to the WMO scale, which itself is anchored through absolute manometric determinations. Without routine recalibration by the CCL to re-establish direct traceability to the WMO-X2005 scale, laboratories contribute CO2 data that are no longer directly traceable to the WMO scale. Many laboratories compare their standards bilaterally or multilaterally among themselves. For CH4, participating laboratories are encouraged to provide either measurements calibrated with the NOAA 2004 scale (the WMO CH4 Mole Fraction Scale) or a multiplicative adjustment factor based on intercomparisons of their scale with the NOAA 2004. A number of the CH4 scales reported to the Referee are shown in Table 1. A multiplier factor is used
to adjust CH4 values to a common scale. A few laboratories have not yet intercompared their scales with the CMDL83 or the NOAA 2004 scales.

Table 1. Standard scales reported to the Referee by a few participating laboratories. A multiplier factor is used to adjust CH4 values to the NOAA 2004 scale

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Standard scale</th>
<th>Multiplier factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>US – NOAA</td>
<td>NOAA 2004</td>
<td>1.0</td>
</tr>
<tr>
<td>JP – NIES</td>
<td>NIES Gravimetric</td>
<td>0.997</td>
</tr>
<tr>
<td>JP – AIST</td>
<td>TU Gravimetric</td>
<td>1.0003</td>
</tr>
<tr>
<td>DE – UBA, FR – LSCE</td>
<td>CMDL83</td>
<td>1.0124</td>
</tr>
</tbody>
</table>

2.3.5 Preliminary results of the CO2 and CH4 intercomparison

The participating laboratories shown in the Table 2 and 3 are listed in chronological order of analysis for each set of tanks. Preliminary CO2 and CH4 results are those initially reported directly to the referee by each participant and are listed as the difference from NOAA value for that set (the NOAA value was subtracted from the Laboratory value). The NOAA value used here is the mean of the values reported by them at the beginning and at the end of the intercomparison. Using the NOAA value here as a reference does not imply that their numbers have absolute accuracy.

As shown in the Tables, not all the participating laboratories that have had cylinders calibrated by the CCL reported in revised calibration assignments based on the new scale. A few laboratories reported measurements relative to some other scale. Several other laboratories have had their standards calibrated by the CCL but have not maintained a routine recalibration schedule.

The results of the fourth intercomparison for CO2 and CH4 were generally encouraging – For example CO2, the majority of participating laboratories agreed to within 0.1 μmol mol⁻¹. However, the intercomparison results reported here should be considered as "preliminary" concentrations. Any drift of Laboratory standards and/or changes in their Scale have not been accounted for. Some Laboratories had very recent ties to the WMO CCL scale whereas others did not. Consequently, some institutions have already stated that their final analyses will change significantly and they should have an opportunity to submit updated numbers. Some of the participants had not yet been completed as this report was finished.

References


**Table 2. 2002 - 2007 WMO Round-Robin Intercalibration Results**

<table>
<thead>
<tr>
<th>Laboratories</th>
<th>Analysis Date</th>
<th>Report Date</th>
<th>TANK #</th>
<th>Differences (Lab minus NOAA) CO₂, μmol mol⁻¹</th>
<th>Description of reported standard scale</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GROUP ONE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US – NOAA average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4532</td>
<td>368.14</td>
<td>384.81</td>
</tr>
<tr>
<td>Korea – KMA (KGAWO)</td>
<td>Mar./Jun.2004</td>
<td>July.2004</td>
<td>354.47</td>
<td>368.02</td>
<td>384.73</td>
</tr>
<tr>
<td>US – SCRIPPS (CMM)</td>
<td>June.2005</td>
<td>June.2005</td>
<td>355.14</td>
<td>368.31</td>
<td>385.01</td>
</tr>
<tr>
<td>US – SCRIPPS (ECM II)</td>
<td></td>
<td></td>
<td>355.01</td>
<td>368.16</td>
<td>384.83</td>
</tr>
<tr>
<td><strong>GROUP TWO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US – NOAA average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4542</td>
<td>368.35</td>
<td>384.60</td>
</tr>
<tr>
<td>IT - Monte Cimone</td>
<td>Oct.2002</td>
<td>Oct.2002</td>
<td>355.93</td>
<td>368.37</td>
<td>384.57</td>
</tr>
<tr>
<td>IT – ENEA, Lampedusa</td>
<td>Nov.2002</td>
<td>Mar.2003</td>
<td>355.90</td>
<td>368.20</td>
<td>384.34</td>
</tr>
<tr>
<td>IT – Plateau Rosa, CESI.CNR</td>
<td>Dec.2002</td>
<td>Dec.2002</td>
<td>355.83</td>
<td>368.35</td>
<td>384.55</td>
</tr>
<tr>
<td>HU – HMS</td>
<td>Feb.2003</td>
<td>Sept.2003</td>
<td>355.91</td>
<td>368.14</td>
<td>384.54</td>
</tr>
</tbody>
</table>
The CH₄ differences (Lab minus NOAA) are all computed by simply averaging the NOAA calibrations analyzed first and last and subtracting that from the values from other labs. We didn't use the closest NOAA calibration value or an interpolation scheme.
3.1 Ten Years of High-Precision Methane Isotope Data for Mace Head and London: The Influence of Canadian and European Sources

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3.1.1 Introduction

Time-series of methane mixing ratio and high-precision carbon isotope ratio ($\delta^{13}C_{CH_4}$) have been maintained for air samples collected at the Mace Head site, western Ireland, and at Royal Holloway, University of London, Egham (EGH), UK, for the period 1995-2004. The data have been subdivided using back trajectory analysis and arrival direction of the air masses to assess source contributions. Comparison of the two sites shows that since 2000 there is a very close correlation between the records, particularly in summer. In winter the London site is influenced by the prevailing North Atlantic weather systems and winter methane averages correlate strongly with the winter NAO Index. During summer the SW London site can be a more representative Atlantic background site than Mace Head, on the occasions when the Azores high does not track far enough North to influence Mace Head. Combining background sector data for both sites allows the derivation of an Atlantic background $\delta^{13}C$ curve for 45-60°N.

3.1.2 Mace Head and SW London time series

Average mixing ratios have been calculated for each of the 12 months for the period 1995-2004 to compare the bi-weekly Mace Head ‘clean sector’ samples collected for the isotope study with the AGAGE quasi-continuous and NOAA flask sampling records for Mace Head. This confirms that our sampling over the 10-year period was representative (Figure 1a) and identifies a seasonality of 30-35 ppb with minimum mixing ratio in July. The time-series of $\delta^{13}C$ for Mace Head shows clear seasonality, but is not synchronous with the mixing ratio cycle. (Figure 1c). The amplitude of the seasonal $\delta^{13}C$ cycle when a 10-year average for each month is taken is 0.32‰ with maximum enrichment in April at –47.24‰ and depletion in September at –47.56‰. Taken on an individual year basis the seasonality is larger, between 0.4 and 0.5‰, with the exception of 1995 at 0.8‰ and 2004 at 0.6‰.

The 10-year averaged seasonal cycle for our SW London site is 39 ppb, slightly more than for Mace Head, due largely to the influence of air masses passing over parts of the UK on route to SW London and to incomplete break up of inversions in winter. There is a maximum of 1863 ppb in December and a minimum of 1824 ppb in July. The seasonal cycle in $\delta^{13}C$ when a 10-year average for each month is used is 0.34‰, similar to Mace Head, with maximum enrichment in March at –47.11‰ and depletion in September at –47.45‰. Taken on an individual year basis the seasonality is larger, between 0.5 and 0.6‰, with the exception of 1995 at 1.0‰ and 2004 at 0.8‰, slightly larger than for Mace Head, but with the same exceptional years. Since 1999 the tank sampling at RHUL has focussed predominantly on western sectors. Prior to this the sampling was less constrained and seasonality is less clearly defined although local sources within 3 km also hindered ‘clean air’ sampling during the early (1995-1998) period. The mixing ratio annual cycles for individual years since 1999 have been approximately 80 ppb.

3.1.3 Differences between the two records

Comparisons between the two datasets reveal monthly excesses over Mace Head for the Egham site of up to 17 ppb, most significantly in March, April and October (Figure 1b). This excess is associated with enrichment in $^{13}C$, for all months except July, of up to 0.2‰ (Figure 1c).
Figure 1. Comparison between the 10-year averaged seasonal cycles of methane mixing ratio and $\delta^{13}C$ for Mace Head and Egham stations for the 1995-2004 period: a) Comparison of 3 different Mace Head mixing ratio time-series, b) and c) Comparison between Mace Head and Egham time series from RHUL tank sampling.

Averaged over 10 years there is an excess of 13 ppb and enrichment of 0.12‰ in ‘clean sector’ air masses sampled in SW London. This suggests a source with a $\delta^{13}C$ signature of -34‰. Although this signature is typical of North Sea gas emissions from the distribution network (see Lowry et al., 2001), the errors are large and the signature varies from month to month, encompassing the range of values of vehicle emissions (-20‰), domestic gas boilers (-25‰) and landfill (-53‰). Overall the predominant source of CH$_4$ excess in the urban atmosphere compared to the background station is fossil fuels and their combustion. More detailed analysis of diurnal changes in $\delta^{13}C$ is identifying source variations with time of day with combustion sources higher during periods of high traffic density and high domestic gas consumption.

There is a strong correlation between the ‘clean sector’ time series for the two localities (Figure 2), particularly in the isotope record since 1999. In 1998 the SE London record was influenced by a persistent gas leak from a shallow buried supply pipe outside campus, resulting in higher mixing ratios and enrichment in $^{13}C$ by addition of the –34‰ gas. Summer minima in $\delta^{13}C$ are very closely correlated between the two sites, with a slight $^{13}C$-enrichment persisting in SW London winters before 2002.
The strongest correlation between the mixing ratio records is at the time of annual minima in July. In 1998, 1999, 2002 and 2003, the lowest mixing ratio of the year for the sampled tanks was at the SW London site (Figure 2). By careful selection of data from the SSW-WSW sector for both sites it should be possible to produce a $\delta^{13}$C Atlantic background curve for 45-65°N to assist with understanding emissions in western European regions influenced by the same air masses.

Both Mace Head and SW London sites had relatively constant annual $\delta^{13}$C means from 1995-2001. At Mace Head this was $-47.37 \pm 0.04\%$. From 2001 to 2004 there was a shift toward $^{13}$C enrichment by more than $0.2\%$ at both sites, consistent with high biomass burning emissions in the Northern hemisphere from mid-2002 through 2003. The INSTAAR – NOAA collaboration have maintained an isotope record for Mace Head on bi-weekly samples since mid-2003. These correlate well during the 2003-4 overlap period suggesting that there is a near seamless record for Mace Head from 1995-present.

![Figure 2. Comparison between Mace Head and SW London time-series for the non-continental ('clean') sectors. The correlation is very strong from 1999 onwards since when the focus of sampling at RHUL has been airmasses from the identified 'background' sector (202-282°). The pale grey line represents closest to background conditions. Highlighted period of higher mixing ratio and $^{13}$C-enrichment during 1998 can be related to persistent local area gas leaks. Mace Head and SW London trend line data supplied by Ken Masarie, NOAA CMDL.](image)

### 3.1.4 Source identification

Source mixes in Canada, Ireland and Continental Europe have been identified. All are depleted in $^{13}$C relative to background over a 10-year average, but closer comparison of source region and background trajectories in the same season reveals far more complexity.

The source mix for Western Europe changed from $-54.1\%$ in 1996 to $-55.6\%$ in 2000 (see also Levin et al., 1999). This shift is consistent with known reductions in emissions from coal mining, better landfill practice and a shift from predominant use of North Sea gas (relatively enriched in $^{13}$C) to Siberian gas (relatively depleted).
Air sourced in the Atlantic background sector but passing over SW Ireland on route to Mace Head is significantly depleted in $^{13}$C implying a source mix at –65‰ representative of ruminant and wetland emissions. Air masses from the Hudson Bay and Quebec region of Canada paint a more complex picture. The predominant summer / autumn scenario is a small relative depletion in $^{13}$C related to a wetland source in the –65 to –60‰ range, but in 1998 and 2002 there were notable autumn enrichments in $^{13}$C related to late summer boreal forest fires emitting methane with $\delta^{13}$C of CH$_4$ around –26‰.

Local emissions in SE England (London vicinity) can be assessed during extreme diurnal build-up of methane under anticyclonic conditions at the SW London site, which reveals local natural gas (–34‰) and landfill (–52.5‰) sources (Lowry et al., 2001; Fisher et al., 2006).

3.1.5 Summary
The main findings of the isotope and mixing ratio time series for the 2 stations are listed below:

1) The SW London site records CH$_4$ levels which can be typical of background or continental Europe depending on season and winter NAO index.

2) Careful sampling at the SW London site can produce a background $\delta^{13}$CH$_4$ isotopic time-series to complement that for Mace Head, particularly during summer.

3) Trajectory analysis of the two time series, allows their division by source sector. This has identified methane emissions in Mace Head air from Canadian wetlands and fires, from Irish bogs / cows, and a changing European source mix.

4) Higher resolution high precision isotopic time series at Mace Head (daily) has great potential for better understanding of temporal variations in CH$_4$ emissions around the N. Atlantic, particularly in separating the contribution of biomass burning from that of wetland (see also Morimoto et al., 2006).

5) When assessing the contributions from these two sources it is important to study the complementary CO data. CO anomalies can influence OH with a knock on effect on methane.

Although the complementary high precision $\delta^{13}$CH$_4$ time series for Mace Head and Egham have provided much useful information, far more sites making these measurements are required, particularly in the European realm to give better spatial and temporal understanding of the changing sources and a possibility to independently verify European emissions. Development of rapid continuous flow analysis techniques for $\delta^{13}$CH$_4$ are allowing air from more sites to be analysed and are now approaching the precision levels and degrees of automation required for background stations.

References


3.2 Inter-Laboratory Calibration of CO₂ Produced from NBS19 Calcite, Calibration Of Narcis-II, and CO₂-Isotopes in Synthetic Air

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† EC (Climate Research Division, Atmospheric Science & Technology Directorate/STB, Environment Canada), 4905 Dufferin St., Toronto, ON, Canada,
‡ NIES (Global Carbon Cycle Research Section, Center for Global Environmental Research, National Institute for Environmental Studies), 16-2 Onogawa, Tsukuba, Ibaraki 305 Japan

Abstract

Starting from NBS19 calcite a number of CO₂ preparations were made, distributed and analysed in three laboratories. The results from the different types of preparations were compared to a common reference CO₂, Narcis-II, which allowed us to study the isotopic variability of CO₂ generated by the calcite acid digestion reaction.

The agreement for δ¹³C among our laboratories was within a standard error of ±0.003‰. For Narcis-II, a δ¹³CVPDB value of -1.923‰ was found. For δ¹⁸O, with the temperature dependence of the acid digestion reaction for calcites and the associated oxygen exchange with residual water, the agreement was less satisfying, with a maximum δ¹⁸O deviation of 0.13‰. In agreement with previous determinations a mean δ¹⁸OVPDB-CO₂ value of -2.580‰ for Narcis-II was found which, however, requires further studies.

In a second series of experiments, larger amounts of CO₂ were prepared from NBS19 at MPI-BGC, analysed for the resulting isotopic composition and then mixed into CO₂-free air. The resulting artificial air samples then were analysed by the same three laboratories for the stable isotopic composition of CO₂ using locally established extraction lines and protocols. Comparison of the results with the pure CO₂ values revealed additional systematic differences in between our laboratories owing to the CO₂ extraction process and to local data evaluation and standardization issues. For δ¹³C the results showed a rather narrow and satisfying range of deviations (±0.012‰). For δ¹⁸O, however, cumulative disagreements up to 0.11‰ were observed.

3.2.1 Introduction

All carbon stable isotope ratio measurements must be reported on a common scale formerly defined via a calcite material, PDB (‘Pee Dee Belemnite’). The exhaustion of the original material as well as homogeneity issues required a redefinition of the scale which resulted in the VPDB scale. This scale is based on the well characterized calcite material NBS19 which was prepared by Irving Friedman in 1982.

The origin of the VPDB scale has been set by defining a deviation of +1.95‰ (δ¹³C) and -2.2‰ (δ¹⁸O) for NBS19. These NBS19 isotope values defining the VPDB scale refer to the isotopic compositions of the elements in the calcite mineral. In order to perform a precise and accurate measurement a conversion step to transfer the isotope ratio information to a gaseous material is required. Usually, CO₂ is liberated from the calcite material via reaction with orthophosphoric acid under well controlled experimental conditions.

For air-CO₂, a (cryogenic) extraction step is necessary to produce pure CO₂ (+ N₂O) which then is compared with the CO₂ from the reference calcite for obtaining δ¹³CVPDB and δ¹⁸OVPDB-CO₂. During cryogenic extraction, a number of small experimental effects such as trapping efficiency, fractionation upon thawing, co-trapping of traces of air etc. can lead to substantial errors in isotopic determination when comparison is made to a clean CO₂ gas as the primary reference. It has therefore been recognized that for highest precision analysis and consistency in long term records comparison should be made to an air reference gas which goes through the same preparation.

a Author, to whom correspondence should be addressed: wbrand@bgc-jena.mpg.de
steps as the samples to be analyzed\textsuperscript{8, 11-14}. This approach, however, leaves the task of creating an appropriately calibrated anchor to the VPDB scale which is robust, accurate, and stable within the required precision range. This is among the tasks this paper tries to address.

### 3.2.2 Experimental details and results

#### 3.2.2.1 Inter-laboratory comparison of pure CO\textsubscript{2} data; CO\textsubscript{2} from NBS19

The acid digestion reaction was performed using ortho-phosphoric acid, H\textsubscript{3}PO\textsubscript{4} (d = 1.91 – 1.93 g/ccm). At EC, a set of more than 20 ampoules of CO\textsubscript{2} were prepared at 25 ± 0.1 °C using a classical McCrea type preparation\textsuperscript{6, 9} and sent to the other two laboratories for analysis. Likewise, CO\textsubscript{2} was generated from NBS19 at NIES using a similar setup for local analysis. At MPI-BGC Jena, CO\textsubscript{2} was prepared using the previously described Aramis\textsuperscript{6} line. The gas amount of the latter experiment was large enough to allow for mixing the CO\textsubscript{2} with CO\textsubscript{2}-free air after initial isotopic analysis. The resulting air mixtures have been distributed for isotopic comparison.

As a common reference material a pure CO\textsubscript{2} gas was required enabling us to draw direct conclusions about the carbonate digestion process. An ideal common reference could have been one big CO\textsubscript{2} sample directly released from NBS19. As a close approach, the reference material Narcis-II, a large set of pure CO\textsubscript{2} samples in 6-mm break-seal tubes with isotopic compositions close to the desired gas provided by NIES\textsuperscript{15} satisfied these requirements. With Narcis-II prepared by one of us (HM) to match the isotopic composition of CO\textsubscript{2} from NBS19, this enabled us to study the variability of CO\textsubscript{2} preparation from calcites avoiding other systematic errors due to mass spectrometric scaling effects ('\(\eta\) effect')\textsuperscript{16, 17} or due to the necessary correction for \(^{17}\)O when the respective gases have larger differences in isotopic composition\textsuperscript{18-20}.

As a first intercomparison, Narcis-II samples were directly compared with the NBS19 ampoules prepared at EC by measurement against a common reference gas. Each lab analyzed five sets of the samples (i.e., five Narcis-II against five NBS19 pure CO\textsubscript{2}). Table 1 holds the final results for this 3-laboratory intercomparison; prior results by EC from 2004 using the same preparation are also included.

<table>
<thead>
<tr>
<th>Date</th>
<th>Analyzing Laboratory</th>
<th>#</th>
<th>(\delta^{13}\text{C}_{\text{VPDB}})</th>
<th>(\delta^{18}\text{O}_{\text{VPDB-CO2}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 2004</td>
<td>EC</td>
<td>(5)</td>
<td>1.919 ± 0.011</td>
<td>-2.488 ± 0.020</td>
</tr>
<tr>
<td>Sep 2006</td>
<td>EC</td>
<td>(5)	extsuperscript{b}</td>
<td>1.930 ± 0.020</td>
<td>-2.513 ± 0.016</td>
</tr>
<tr>
<td>Nov 2005</td>
<td>NIES</td>
<td>(5)</td>
<td>1.924 ± 0.003</td>
<td>-2.504 ± 0.028</td>
</tr>
<tr>
<td>Nov 2005</td>
<td>MPI-BGC</td>
<td>(5)</td>
<td>1.922 ± 0.005</td>
<td>-2.510 ± 0.027</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>1.924 ± 0.004</td>
<td>-2.504 ± 0.011</td>
</tr>
</tbody>
</table>

Combining the results from the three laboratories a \(\delta^{13}\text{C}\) value of 1.924 ± 0.004‰ and a \(\delta^{18}\text{O}\) value of -2.504 ± 0.011‰ versus VPDB have been found for Narcis-II. This average value is based on 20 independent NBS19 preparations all made in the same laboratory (EC), using the same equipment.

\textsuperscript{b} Five preparations and analyses of NBS19-CO\textsubscript{2} for \(\delta^{13}\text{C}_{\text{VPDB}}\) and \(\delta^{18}\text{O}_{\text{VPDB-CO2}}\), four analyses of Narcis–II for \(\delta^{13}\text{C}_{\text{VPDB}}\) and five analyses for \(\delta^{18}\text{O}_{\text{VPDB-CO2}}\) were valid.
In a similar set of experiments, Narcis-II was analyzed locally against NBS19-CO₂ either prepared at MPI-BGC Jena or at NIES during 2003-2006. The mean values of these experiments are listed in Table 2.

Summarizing these results for the pure CO₂ experiments in our laboratories, an excellent agreement has been achieved for δ¹³C originating from different preparations of NBS19-CO₂ made in Toronto, Jena and Tsukuba when using Narcis-II as the crucial test substance for comparing the data. Based on these independently observed results a δ¹³CVPDB value of +1.923‰ is proposed to be assigned to Narcis-II with a combined uncertainty of ± 0.003‰. Our results confirm the excellent quality of NBS19-calcite as the primary reference material for the δ¹³C-VPDB scale at an accuracy level of better than ±0.01‰.

| Table 2. Results for Narcis-II using NBS19-CO₂ prepared and analyzed at NIES and MPI-BGC Jena, respectively. |
|-----------------------------|-----------------|---------------------|-----------------|
| Narcis-II                   | δ¹³CVPDB      | 1σ δ¹⁸OVPDB-CO₂      | 1σ #             |
| NBS19-CO₂ prepared and analyzed at | %‰ | %‰ | %‰ |   |
| NIES                        | mean +1.923   | 0.006 -2.598        | 0.012 (3)c       |
| Jena                        | mean +1.923   | 0.003 -2.637        | 0.016 (11)d      |

The results for δ¹⁸O are mixed, with a difference of 0.133‰ between Toronto and Jena and 0.039‰ between Tsukuba and Jena. These differences reflect the known and often observed difficulties in the acid digestion reaction of calcites relating to temperature and to water exchange issues. As a consequence, a reliable δ¹⁸O scale at an accuracy level of ±0.02‰ cannot be achieved by defining the reference material NBS19 as the scale anchor alone. Additional agreements are necessary in terms of unified and accepted experimental details of the acid digestion reaction which need to be worked out in the near future.

3.2.2.2 Inter-laboratory comparison of δ¹⁸O and δ¹³C from NBS19-CO₂ mixed into CO₂-free air

The preparations of CO₂ gas from calcite powder at MPI-BGC have been made in such amounts that the gas could directly be used for mixing with CO₂-free air following isotopic analysis. The CO₂-free air was custom made for MPI-BGC from ultra pure gases, with a composition of 21.0% O₂, 1% Ar, and 0.39 ppm N₂O, filled to 100% with pure N₂. The final gas was checked for CO₂ impurities using GC and MS with no appreciable detectable amounts. For every preparation of a 40 mg NBS19 CaCO₃ sample, three 5-L glass flasks were filled to 1.5 bar (absolute) with the artificial air produced in this fashion. The 5-L flasks and filling procedure were similar to the procedure described elsewhere for the J-RAS set of standard air. In total, 15 5-L flasks were filled with air containing CO₂ prepared from NBS19 in Jena (five separate filling procedures using CO₂ from one of the previous NBS19 preparations made at temperatures ranging from 32 - 42 °C). Prior to distribution all flasks were analyzed at MPI-BGC for isotopic composition on the fully automated BGC-AirTrap setup and compared with the prior values from the pure CO₂ gases before mixing. Four of the 5-L flasks were then shipped to each of the laboratories in Toronto and Tsukuba for isotopic analysis; the other flasks were set aside in Jena for future experiments.

3.2.2.3 Air-CO₂ data MPI-BGC

The MPI-BGC δ¹³C and δ¹⁸O results for CO₂ from NBS19 measured before mixing with CO₂-free air and afterwards are denoted in Table 3. The prior results are those from the MPI-BGC Jena

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c Total number of Narcis-II analysis versus at least two separately prepared NBS19-CO₂ samples

d Number of separate Narcis-II analyses against 10 separately prepared NBS19-CO₂ samples
experiments described above (with the averages given in Error! Reference source not found.). The scale for the CO₂ extracted from air mixtures (J-RAS) has been established and described earlier⁸. It is based on a number of NBS19 preparations in the Aramis line conducted during 2003 and 2004. The CO₂ from the preparations in this case was directly mixed into CO₂-free air; no isolation of the CO₂ for a prior isotopic determination had been made at the time.

### Table 2. MPI-BGC Jena: δ¹³C and δ¹⁸O from NBS19: Comparison for pure CO₂ and CO₂ mixed into CO₂-free air.

<table>
<thead>
<tr>
<th>MPI-BGC Jena</th>
<th>NBS19-CO₂ in air vs. pure NBS19-CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ¹³C</td>
<td>δ¹⁸O</td>
</tr>
<tr>
<td>average differences (CO₂-in-air minus pure CO₂):</td>
<td>#</td>
</tr>
<tr>
<td>Mean</td>
<td>0.001 ‰</td>
</tr>
<tr>
<td>std dev</td>
<td>0.010 ‰</td>
</tr>
</tbody>
</table>

The data in Table 3 exhibit an excellent agreement for δ¹³C to within the precision level required. The average values for the prior analysis and the post-mixing and extraction analysis differ by only 0.001‰ with a precision of 0.010‰. Assuming absence of compensating effects this finding shows that the mixing process followed by automated extraction and measurement of CO₂ including correction for the N₂O interference is free from artifacts and produces δ¹³C values correctly anchored to the VPDB scale as defined through the data in Table 1 and Table 2.

Not unexpectedly, the oxygen isotope data in Table 3 do not show such a near-ideal scenario. The preparations were made at different temperatures, hence the range of results for NBS19. Versus the prior δ¹⁸OVPDB-CO₂ results obtained for the set of pure CO₂, an average offset of -0.047 ‰ was observed for the same CO₂ specimen after mixing and analysis as routine air samples. This difference reflects the offset between the (Jena) JRAS scale⁸ used for assigning the air-CO₂ results which was anchored to VPDB earlier using air mixtures exclusively, and the scale represented by the Jena results in Error! Reference source not found., based on preparation and isolation of pure CO₂ at MPI-BGC. We attribute the observed difference in δ¹⁸O to two improvements we have made to the BGC-Aramis reaction system since 2004: (1) The sample dropping into the acid has been automated, so that the reaction vessel can remain in the temperature controlled area all the time and (2) the temperature stability and accuracy have been improved using a better heat insulation and a calibrated thermometer and temperature control inside the acid. In light of the many sources of possible errors in preparing CO₂ from calcite reliably and reproducibly for δ¹⁸O determination we consider the observed difference small; it may yet be significant and may eventually require a δ¹⁸O scale modification for JRAS. The precision of the data is acceptable (± 0.019‰).

#### 3.2.2.4 Air-CO₂ data EC and NIES:

At NIES four samples of NBS19-CO₂ in air prepared in Jena in 5-L flasks were analyzed as if they were ordinary air samples. In the same fashion, EC extracted and analyzed CO₂ from their four 5-L flask samples of NBS19-air. In Table 4 the differences between these results relative to the prior (MPI-BGC) values are given. The latter are the data from the air extraction, not the measurements of the pure CO₂ prior to mixing.
The $\delta^{13}$C differences of ~0.025‰ are small, yet probably not negligible, whereas the $\delta^{18}$O air differences of NIES and EC versus MPI-BGC are -0.028‰ and +0.092‰ respectively. The relation to the pure-CO2 values can be inferred from the target data.

The expected target offset for $\delta^{13}$C is zero because of the excellent inter-laboratory agreement observed for Narcis-II plus the negligible difference between plain CO2 and CO2-in-air value at MPI-BGC (Table 3). The $\delta^{13}$C values from both laboratories are more negative than the original CO2 prior to mixing and the values measured from the mixture in Jena. The mean offsets (-0.026‰ and -0.024‰) are identical for both laboratories suggesting that the Jena assignments may be slightly off. However, since the pure-CO2 $\delta^{13}$C data and the extraction values at MPI-BGC have exhibited perfect agreement, the offsets in both cases (if significant) must be attributed other sources, possibly the extraction processes or the post-analysis evaluation. The latter is a somewhat critical point as it includes correction for N2O, which is co-trapped with CO2 when extracting air. The artificial air has an unusual amount of N2O (0.39 ppm) compared to present day air (~0.32 ppm). This correction has to be established for every mass spectrometer, in fact every setting of the ion source, and the ionization efficiency must be adjusted from air mixtures, not only from the pure gases11, 22. The total correction for ambient present day air is about 0.21‰; an error of 10% in this number is usually unlikely. However, due to the unusual amount of N2O relative to CO2 in the samples, the error in this case may be larger. The other main sources of error include co-trapped air, in particular traces of N2 and O2, which can interfere with the isotopic analysis10, and a non-quantitative trapping efficiency which can be associated with an isotope effect. The effects related to trapping can have multiple causes including a variable level of liquid nitrogen during trapping. The multiple sources of error and the problems in keeping the experimental artifacts at a well controlled level are one of the reasons why referencing for high accuracy isotopic analysis can be made with better precision when air is used as the daily reference instead of pure CO2.11, 23 Also the N2O mass balance correction tends to cancel in this case because any errors arising in this procedure apply to the reference and the sample in an equal fashion (provided both are air or close to air materials).
For δ18O the situation is more complex. Figure 1 illustrates the relationship of the different data in a graphical form. The air-CO2 intercomparison results for δ18O relative to the Jena values are rather different for the two laboratories (Δδ18O = -0.028‰ for NIES and +0.092‰ for EC). Considering the -0.047‰ offset of the Jena air-CO2 results the target values against the pure CO2 results from Jena should have been +0.047‰. Considering further the individual δ18O offsets observed for the pure NBS19-CO2 (+0.133‰ between EC and MPI-BGC and +0.039‰ between NIES and MPI-BGC) the target values for the air-CO2 differences observed in δ18O would have been +0.180 ‰ for EC and +0.086 ‰ for NIES. These are the values expected if the local scales for the first, pure CO2 experiment and the ones for CO2 extraction from artificial air were consistent. These target values for δ18O are clearly missed by a wider margin. The air-CO2 versus pure CO2 scale discrepancies of -0.114 ‰ for NIES and -0.088 ‰ for EC listed in the last line of Table 4 seem larger than expected from further experimental evidence. They are based on the accuracy of the Aramis-related δ18O offset of -0.047 ‰ which needs further attention and confirmation. The observed offsets might reflect further differences between our laboratories in sample handling, data generation, but there are only few remaining sources of error left, some of which are the same as for δ13C: The extraction process and the N2O correction. The latter, however, can not account for larger deviations. A more δ18O-specific source of contamination is co-trapped N2 and O2. From these, NO2 can arise in the ion source, comprising a possible isobaric interference at the m/z 46 ion current. As the ‘usual suspect’, oxygen exchange with residual water adhering to the walls of the extraction units can not be ruled out completely. Similarly, δ18O alterations inside the flasks between analyses in Jena and at EC or NIES, respectively, may still play a role in spite of the efforts to get the flasks water-free by keeping them at 60 °C under vacuum for 72 hours. A last candidate for δ18O variations is a prominent, 18O-specific isotope effect of CO2 during thawing which, however, can only play a role when transfer rates are considerably below 100%. This should not be the case in the experiments described above.

References


4.1 Installation of a New Gas Chromatograph at Izaña GAW Station (Spain) to Measure CH₄, N₂O, and SF₆
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Observatorio Atmosférico de Izaña, Instituto Nacional de Meteorología (INM, Spain)

Abstract
We have installed a new GC at Izaña Global GAW Station (Tenerife, Spain) with two detectors: a FID (to measure CH₄, this compound has been measured at Izaña with another GC-FID since 1984) and an ECD (to measure N₂O and SF₆). Each detector has associated a set of precolumn, maincolumn, and 10-port-2-position valve to allow for backflushing. Additionally, there is a 4-port-2-position valve to avoid the flow of O₂ through the ECD. Routinely continuous background measurements (with this new GC) started on June 14, 2007. In this presentation, the setup of the GC system, injection procedures and associated chromatograms, integration methods, sampling and traceability strategy, and data processing procedures are described. We also obtain the power spectrum of the chromatograms (noise plus signal) and briefly discuss the sources of uncertainty in peak integration. Finally, we briefly study the response functions of the detectors, associated uncertainties, and repeatabilities.

4.1.1 System configuration, time sequences and chromatograms

Figure 1. GC configuration scheme. For valves V1, V2, and V3, the depicted positions of the valves are indicated in red colour.

We have installed a GC Varian 3800 with two detectors (ECD and FID) at Izaña Observatory. Figure 1 shows the GC system configuration. The general ambient air inlet, which is situated on top of the building tower (30 m height) and provides ambient air for all instruments that analyze it, is a 8 cm I.D. stainless steel pipe and has a high flow rate. A tube branches from the general air inlet toward a pump that provides ambient air to the GC. Valves V4 and V5 are 3-port-2-position valves. MPV is a Valco multiposition valve with 1 outlet and 16 inlets connected to the ambient air inlet, the working tanks and the laboratory standards. MFC is a mass flow control. Valves V1 and V2 are 10-port-2-position valves, with positions inject and backflush as showed in Figure 2. EFC4s are electronic flow controls that regulate flow maintaining a prescribed pressure above ambient. AuxFCs are auxiliary flow controls (with values fixed by analogical controls). Valve V3 is a 4-port-2-position valve, with positions bypass and no-bypass. There are a few meters of PTFE tube at the vent of V5 and at the loops outlets to prevent any diffusion from the laboratory.
The Ar/CH₄ carrier flowing through the vents of EFC4 and V3 is conducted out of the laboratory. For ECD safety, AuxFC allows carrier flow even if the GC is turned off (EFC4 does not). The electronic and battery that controls V3 (bypass valve) are configured in such way that V3 commutes to bypass position in the case that the GC is turned off (e.g. AC supply interruption) and therefore the very hot ECD is not damaged by carrier flow interruption.

![Diagram of GC system](image)

**Figure 2.** Scheme with the connections and the flow direction (blue arrows) for two valve positions: Inject and Backflush.

<table>
<thead>
<tr>
<th>Table 1. GC configuration.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ECD</strong></td>
</tr>
<tr>
<td>Oven temperature</td>
</tr>
<tr>
<td>Sample Loop</td>
</tr>
<tr>
<td>Precolumn</td>
</tr>
<tr>
<td>Maincolumn</td>
</tr>
<tr>
<td>Carrier gas</td>
</tr>
<tr>
<td>Oxygen/Moisture Trap</td>
</tr>
<tr>
<td>Carrier direct flow</td>
</tr>
<tr>
<td>EFC4 set pressure</td>
</tr>
<tr>
<td>(above ambient)</td>
</tr>
<tr>
<td>Carrier Backflow</td>
</tr>
<tr>
<td>Valve Oven</td>
</tr>
</tbody>
</table>

**DETECTOR:**
- **Temperature**: ECD 380 °C, FID 150 °C
- **Make up flow**: 0 ml/min
- **Air flow**: 300 ml/min
- **H2 flow**: 30 ml/min

Table 1 provides details about the GC system configuration. The indicated flows, non corrected for $T$ and $p$, have been measured with an external Varian digital flowmeter (laboratory temperature=21.3 °C, typical Izana pressure: 770 hPa). Additionally, the FID Carrier direct flow for low flow is 30.6 ml/min, which only happens in Backflush position (11.5 psi). Table 2 provides the time sequences (cycle of 7.5 minutes) for the GC-FID and the GC-ECD subsystems. 30 seconds before a sample loop injection, valve V4 stops flushing (commuting to the other loop) to allow temperature (oven) and pressure (ambient) equilibration. Valve V5 directs pumped air towards the cryocooler (flask of approximately 300 ml) whenever there is an ambient air injection and each cycle between minutes 3.15 and 6.15.
Table 1. Time sequences. For each subsystem, some events have been denoted with letters a, b, and c.

<table>
<thead>
<tr>
<th>Minute</th>
<th>ECD</th>
<th>Minute</th>
<th>FID</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>Stop sample loop flushing (V4)</td>
<td>0.50</td>
<td>Start sample loop flushing</td>
</tr>
<tr>
<td>0.50 a</td>
<td>Inject (V2)</td>
<td>1.44 a</td>
<td>Increase of carrier flow</td>
</tr>
<tr>
<td>1.50 b</td>
<td>Start of ECD Bypass (V3)</td>
<td>1.50</td>
<td>Stop sample loop flushing (V4)</td>
</tr>
<tr>
<td>3.00 c</td>
<td>Backflush &amp; End of Bypass</td>
<td>2.00 b</td>
<td>Inject(V1)</td>
</tr>
<tr>
<td>6.50</td>
<td>Start sample loop flushing</td>
<td>4.00 c</td>
<td>Backflush &amp; Decrease of carrier flow</td>
</tr>
</tbody>
</table>

Figure 3. Obtained ECD and FID chromatograms. Events marked with red letters as indicated in Table 2.

Figure 4. Yellow line: ECD chromatogram without bypass. Blue line: ECD chromatogram with the usual time sequence for valves.
Figure 3 shows the obtained ECD and FID chromatograms. Figure 4 shows ECD chromatograms with the usual bypass (to avoid the flow of O\textsubscript{2} through the ECD) and without bypass. As Gomez-Pelaez shows, what is detected in the ECD between times c and d, is the O\textsubscript{2} present in the main column (very weak tail). Abrupt decrease d happens when there is no more O\textsubscript{2} inside the main column.

The cryocooler temperature is -32 °C. Working and laboratory standards, which are very dry (H\textsubscript{2}O < 5 ppm), do not flow through the cryocooler, whereas ambient air does, achieving the saturation water vapour content for this temperature. The saturation water vapour pressure (e\textsubscript{i}) at -32 °C is 0.3078 hPa (e.g. Iribarne&Godson). The relation among r\textsubscript{xd}, mixing ratio (mole fraction) of compound x in dry air, and r\textsubscript{xe}(T), mixing ratio when water vapour is added till saturation (which depends on T), is given by:

\[
\frac{e_i}{p_d} = \frac{r_{sd} - r_{xe}}{r_{xe}} \equiv \frac{r_{sd} - r_{xe}}{r_{sd}} = \text{relative bias}
\]

The relative bias is 4.00 \times 10^{-4}, taking into account the typical atmospheric pressure at Izana (p = 770 hPa). The GAW N\textsubscript{2}O recommended Inter-Laboratory comparability is ± 0.1 ppb, which relative to 320 ppb has a value ± 3.125 \times 10^{-4}. Therefore, we have to correct our ambient air measurements for this systematic error produced by dilution, and consider the associated uncertainty. Probably, in the future, we will use a more powerful cryocooler. Backflush prevents from any undesired effect of water vapour (which has a large retention time) inside the GC.

### 4.1.2 Data acquisition and integration methods

The sources of uncertainty in (isolated) peak integration (e.g. Dyson) are: a) Sampling frequency (to decrease time resolution, averaging from a higher resolution chromatogram, does not affect area but affects height); b) Signal digitalization (A/D converters). In our GC, \(\Delta V = 0.001 \text{ mV}\); c) Placement of baseline under the peak (the uncertainty for area is larger than for height).

In our system, the sampling frequency is 10 Hz, averaging from a 40 Hz signal. We think that the decrease of peak height is negligible. The area uncertainty is dominated by c), whereas for height uncertainty there is also a significant contribution of a). For CH\textsubscript{4} integration we use area because a FID is a mass sensitive detector and the peak is asymmetric. For N\textsubscript{2}O and SF\textsubscript{6} integration we use height. We store raw chromatograms. At present, we are using the Star Varian integrator. We selected parameters to get good integration repeatability. We force a Valley Baseline between the N2O and SF6 peaks, which is used when necessary (rarely).

### 4.1.3 Chromatograms power spectrum

Figure 5 shows the power spectrum of the ECD and FID chromatograms. The integer k defines the linear frequency: \(f_k = k / (n \Delta t)\) (e.g. see Press et all for the definition and properties of the power spectrum). As Figure 5 shows, these power spectra allow a clear separation between signal and noise. The ECD power spectrum has been obtained for the time interval 3.85-6.45 minutes, 10Hz, 1557 points padded till n=2048, and the noise threshold is identified at k=27 (1/f=7.6 s). The FID power spectrum has been obtained for the time interval 2.75-4.00 minutes, 10Hz, 750 points padded till n=1024, and the noise threshold is identified at k=37, 1/f=2.8 s. The RMS noise estimation obtained from the power spectrum is 0.036 mV for the ECD, and 0.0022 mV for the FID. But these are not final values because: 1) we have used a Fast Fourier Transform, so padding with a constant value till the nearest and larger power of 2; and 2) we need to analyse the power spectrum of a large number of chromatograms.
4.1.4 Sampling, traceability, and calibrations

Valve V4 allows the introduction of distinct samples in the ECD and FID loops within the same run. Table 3 shows the one hour cycle we use for ambient air measurements.

Table 2. One hour injection cycle for ambient air measurements. Notation for injections: ambient air (amb), working gas for CH4 (wch4), and two working gases for N2O and SF6 (wns1 and wns2).

<table>
<thead>
<tr>
<th>Min:Seg</th>
<th>00:00</th>
<th>07:30</th>
<th>15:00</th>
<th>22:30</th>
<th>30:00</th>
<th>37:30</th>
<th>45:00</th>
<th>52:30</th>
</tr>
</thead>
<tbody>
<tr>
<td>FID</td>
<td>wch4</td>
<td>Amb</td>
<td>wch4</td>
<td>amb</td>
<td>wch4</td>
<td>amb</td>
<td>wch4</td>
<td>amb</td>
</tr>
<tr>
<td>ECD</td>
<td>wns1</td>
<td>wns2</td>
<td>amb</td>
<td>amb</td>
<td>wns2</td>
<td>amb</td>
<td>wns1</td>
<td>amb</td>
</tr>
</tbody>
</table>

We are still not using a target gas. With Varian Star software, we have to use “Sample Lists” with cycles of 1 or 24 hours (among other inconveniences). The working gases are periodically calibrated, and the response functions of the detectors obtained, using the sets of Izana standards (WMO Tertiaries, provided by NOAA, CCL): 5 standards for N2O and SF6, and 2 (3 in the near future) standards for CH4. Within a calibration, the repeatability for a tank is around 0.3 ppb for N2O and 0.06 ppt for SF6. We have programmed Fortran 90 numerical codes to read run reports and write data in a more compact format, and to process calibrations and ambient measurements.

AJGP is grateful to Eckhart Scheel, Ed Dlugokencky, Brad Hall, and Armin Jordan for providing to him some information two years ago when he was a beginner in GC. Both authors acknowledge J. Perez-delaPuerta, C. Lopez, and V. Garcia-Ayala for some help during the installation.

References


4.2 A Brief Overview of the Theory of Flow Along GC Packed Columns and Some Practical Consequences for Measuring Atmospheric CH₄, N₂O, and SF₆
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Abstract
First, I present a brief and compact overview of the theory of flow along GC packed columns using: the Darcy’s Law of flow through porous media, the continuity equation for the carrier gas (assuming stationary flow), and the continuity equation for the trace gas of interest with a diffusion term and a source/sink term due to the transfer of trace gas molecules between the mobile and the stationary phases (it is assumed that this transfer obeys a linear partition isotherm). Using these equations, the pressure profile, the compressibility factor, the relation between the retardation factor and the distribution constant, and the relation between plate height and diffusivity are easily obtained. Second, I present a study (new in the scientific literature) of the behaviour of two packed columns (precolumn and maincolumn) GC systems after a sample injection and the subsequent applied carrier gas pressure ramp. Finally, several features of the chromatograms for atmospheric CH₄ (obtained with a FID) and for N₂O and SF₆ (obtained with an ECD) are explained using the previous formalism.

4.2.1 Fundamental equations for flows along GC packed columns

We assume \textit{slab geometry} (quantities only depend on \(x\): the length along the column) and \textit{isothermal flow} (the column is inside an isothermal oven at temperature \(T_c\)). The column, of internal cross-section \(A\) and length \(L\), is filled with a packed grainy material, called \textit{stationary phase} in the following. The gas flowing through the column is called \textit{mobile phase}, and it has two components: \textit{carrier gas} and \textit{solute}s (trace gases of interest, which are assumed \textit{very dilute}). The volume within the column, \(V_T\), has two addends: the volume occupied by the packed material \(V_S\), and the void volume \(V_M\) (intergrain plus pores-in-grains volumes). \textit{Porosity}, \(\phi\), is defined as \(\phi = V_v / V_T\). \textit{Solute}s are \textit{adsorbed and desorbed} by the \textit{stationary phase}. \(c_M\) is the concentration of solute \(i\) in the mobile phase, \(c_S\) is the concentration of solute \(i\) in the stationary phase.

\textbf{Continuity equation for the carrier gas} flowing in stationary state (constant in \(t\) : time):
\[
\rho u = \frac{\rho F}{A \phi} = \frac{\rho_{out} F_{out}}{A \phi} = \text{constant} \quad (1),
\]
where \(\rho\) is the carrier density, \(u\) is the carrier average linear velocity along \(x\), \(F\) is the volumetric flow, and subindex \textit{out} denotes the magnitude of a quantity at the end of the column (\(x = L\)).

\textbf{Darcy’s Law of flow through porous media} (e.g., Giddings)
\[
u = \frac{K}{\phi \mu} \frac{\partial p}{\partial x} \quad (2),
\]
where \(K\) is the permeability of the porous media, \(p\) is the carrier pressure, and \(\mu\) is the carrier dynamic viscosity (that, for an ideal gas, depends on \(T_c\) but not on \(p\), e.g. see section 1.7. of Batchelor).
Ideal gas equation for the carrier gas:

$$p = R_c \rho T_c$$  \hspace{1cm} (3),

where $R_c$ is the specific gas constant of the carrier.

Continuity equation for solute $i$ in the mobile phase with a diffusion term and a source/sink term due to the transfer of solute molecules between the mobile and the stationary phases:

$$\frac{\partial c_{Mi}}{\partial t} + u \frac{\partial c_{Mi}}{\partial x} + c_{Mi} \frac{\partial u}{\partial x} = D_i \frac{\partial^2 c_{Mi}}{\partial x^2} - \frac{V_s}{V_{Mi}} \frac{\partial c_{Mi}}{\partial t}$$  \hspace{1cm} (4),

where $D_i$ is the diffusivity of solute $i$ in the carrier gas (which includes molecular diffusion, multipath around grains, and non-instantaneous partition among phases; and depends on $u$).

Note that this equation is the same than that for trace gases in the atmosphere (e.g. see equation 17.1 of Seinfeld & Pandis). Note that the expansion term (third addend on the left hand side) must be taken into account in gas (no in liquid) chromatography (however, this term is “forgotten” by some authors, e.g. eq. 2.65 of Conder & Young).

Linear partition isotherm:

$$c_s = K_{ci}c_{Mi}$$  \hspace{1cm} (5),

where $K_{ci}$ is the distribution constant for solute $i$ (which depends on temperature and chemical composition of the stationary phase and the solute $i$).

After a straightforward integration of equation (2) using equations (1) and (3):

$$\rho(x) = \rho_{out} \sqrt{1 + \frac{B}{A} (L-x)}$$  \hspace{1cm} (6),

$$\rho(x) = \rho_{out} \sqrt{1 + \frac{B}{A} (L-x)}$$  \hspace{1cm} (7),

$$u(x) = u_{out} / \sqrt{1 + \frac{B}{A} (L-x)}$$  \hspace{1cm} (8), with

$$B = \frac{2 \mu F_{out}}{\kappa p_{out} A}$$  \hspace{1cm} (9).

The (column) average carrier velocity, $\bar{u}$, is defined as $\bar{u} = L/t_M$, where $t_M$ is the hold-up time: the time required for the carrier to pass through the chromatographic column (e.g. Miller). Taking into account that $t_M = \int_0^L \frac{dx}{u}$ and using equations (8), (1), and (3), it can be showed that $\bar{u} = j u_{out}$ and therefore $F = j F_{out}$, where $F$ is the (column) average volumetric flow, and $j$ is the compressibility factor:

$$j = \frac{3}{2} \left[ \frac{(p_{in}/p_{out})^2 - 1}{(p_{in}/p_{out})^2 - 1} \right]$$  \hspace{1cm} (10).

Using equation (5), equation (4) can be rewritten as:

$$\frac{\partial c_{Mi}}{\partial t} + u_i \frac{\partial c_{Mi}}{\partial x} + c_{Mi} \frac{\partial u_i}{\partial x} = \chi_i \frac{\partial^2 c_{Mi}}{\partial x^2}$$  \hspace{1cm} (11),

where $u_i(x) = u(x)/(1 + K_{ci} V_s / V_{Mi})$ and $\chi_i = D_i / (1 + K_{ci} V_s / V_{Mi})$. Note that $u_i$ is the effective advection velocity of the solute $i$, and it is lower as larger is $K_{ci}$ and therefore as larger is the fraction of solute $i$ adsorbed by the stationary phase. Note that equation (11) is valid even when the carrier flow is not stationary, that is, when equation (1) does not hold.

The retardation factor, $R$, can be defined as $R = t_R / t_{Ri}$, where $t_R$ is the total retention time (e.g. Miller): the time required for the solute $i$ to pass through the chromatographic column. Taking into account that $t_R = \int_0^L \frac{dx}{u_i}$ and using previous equations, it can be showed that

$$R = 1/(1 + K_{ci} V_s / V_{Mi})$$.
Equation (11) only can be solved using numerical methods (out of the scope of this presentation). However, it is instructive to look at the solution of a very simplified form of equation (11): there is no expansion term, and \( \nu_i \) and \( \chi_i \) are constants (and boundary conditions \( c_{\text{fl}}(x, t) = 0 \) at \( x = \pm \infty \)). For the particular initial condition of the form \( c_{\text{fl}}(x, t = 0) = S \delta(x) \), (where \( \delta \) is the Dirac delta function) which means a very narrow initial peak with the integral of concentration equal to \( S \), the solution is (e.g. see section 17.5 of Seinfeld&Pandis):

\[
c_{\text{fl}}(x, t) = \frac{S}{\sqrt{2\pi \sigma(t)}} \exp \left[ -\frac{(x - \nu_i t)^2}{2\sigma^2(t)} \right]
\]

(12), where \( \sigma^2(t) = 2\chi_i t \). So, the peak is a Gaussian that is advected at \( \nu_i \) speed and has a spatial \( \sigma \propto \sqrt{t} \) (due to diffusion). For a general initial condition, the solution is the convolution product of solution (12) and the general initial condition (e.g. see section 5.4. of Guenther & Lee).

Plate height can be defined as \( H_i = \sigma^2(t_i)/L \) (e.g. see equation 3.25. of Miller). So, using the previous equations, the following relation can be obtained:

\[
H_i = \frac{2\chi_i}{\nu_i} = \frac{2D_i}{\sigma}
\]

(13)

4.2.2 Transient behaviour of two packed columns GC systems after sample injection and some practical consequences for measuring atmospheric CH4, N2O, and SF6

We consider two packed columns (precolumn and maincolumn) GC systems. In particular, for numerical examples, we consider the new GC installed at Izaña Global GAW Station (see Gomez-Pelaez & Ramos), and chromatograms obtained with that instrument (see Figures 3 and 4 of Gomez-Pelaez & Ramos). Figure 2 of Gomez-Pelaez & Ramos shows the internal GC configuration for Inject and Backflush valve positions.

Let be \( \Delta p_{\text{in}} = p_{\text{in}} - p_{\text{out}} \). An EFC4 regulates column flow maintaining a prescribed \( \Delta p_{\text{in}} \) (using a fraction of a set maximum flow, the non used fraction is vent). To obtain the desired \( F_{\text{out}} \), the appropriate value of \( \Delta p_{\text{in}} \) is found empirically changing \( \Delta p_{\text{in}} \) till measure the desired \( F_{\text{out}} \) with an external flowmeter. Indeed, the external flowmeter measures \( F_{\text{mea}} \), which is related to \( F_{\text{out}} \) through the relation \( F_{\text{mea}} = F_{\text{out}} T_L/T_c \), where \( T_c \) is the laboratory temperature (\( T_L = 294.4 \text{ K} \) and \( T_c = 353.1 \text{ K} \)). In the following, we present a sketch of some preliminary results we have obtained.

**Figure 2.** This graphic shows the pressure (units: psi) distribution along the sample loop, the precolumn, and the maincolumn for two valve positions: Inject (blue curve) and Backflush (red curve). It shows actual values for the ECD subsystem of the GC installed by Gomez-Pelaez & Ramos.

We neglect pressure drops along the short S.S. tubes 1/16” O.D. that connects columns and valves, except downstream of the ECD precolumn in Backflush position because there is a
tube of 8 m length, for which we compute a pressure drop of 1.9 psi (using the solution of the classical Poiseuille problem, e.g. section 6.3. of Streeter, Wylie & Bedford; using \( F_{\text{max}} = 32.2 \) ml/min, I.D. = 0.8 mm, and \( \mu = 2.54 \times 10^{-4} \text{ N} \cdot \text{s} / \text{m}^2 \)). The flow is laminar in all tubes, including 1/4” O.D. sample loops (Reynolds number is far below the critical one).

Unfortunately, manufacturers of packed columns do not provide \( \phi, \kappa, K, (T_e), \) nor \( D_i(u) \). Using equation (7), we compute \( B = 5.87 \text{ m}^{-1} \) for the ECD maincolumn in Backflush position (\( L = 3 \) m, \( \Delta P_{\text{in}} = 37.0 \) psi, and \( P_{\text{atm}} = 11.2 \) psi, the typical atmospheric pressure at Izaña Observatory). Using that value of \( B \), equation (7) predicts \( \Delta P_{\text{in}} = 50.4 \) psi for the ECD pre and maincolumn in Inject position (both columns are of the same type, and \( F_{\text{out}} \) is the same in Inject and Backflush positions; \( L = 5 \) m). That value is in relative good agreement with the empirical one: \( \Delta P_{\text{in}} = 50.0 \) psi. Again using equation (7), we compute \( B_i = 3.03 \text{ m}^{-1} \) for the FID maincolumn in Backflush position and high flow (\( L = 1.83 \) m, \( \Delta P_{\text{in}} = 17.4 \) psi, and \( F_{\text{max}} = 52.4 \) ml/min). For the FID maincolumn in Backflush position and low flow (\( F_{\text{max}} = 30.6 \) ml/min), and using \( B_i = 1.77 \text{ m}^{-1} \) (obtained from \( B_i \) taking into account the dependence of \( B \) on \( F_{\text{out}} \)), equation (7) predicts \( \Delta P_{\text{in}} = 11.8 \) psi. This value is in relative good agreement with the empirical one: \( \Delta P_{\text{in}} = 11.5 \) psi.

Figure 2 shows the pressure distribution along the ECD columns and loop for Inject and Backflush positions. Curves of the same shape are valid for the carrier density, due to equations (6) and (7). Let be \( p_L \) the atmospheric pressure in the laboratory. Sample loop flushing is stopped 30 seconds before injection to allow the sample loop achieve \( p_L \) and \( T_e \). For achieving a stationary flow when switching from Backflush to Inject (which needs a larger \( \Delta P_{\text{in}} \) ), a fast \( \Delta P_{\text{in}} \) ramp is set in the GC method (100 psi/min, with a set maximum flow of 500 ml/min for several seconds). So, during this transient (several seconds), the precolumn and the loop are filled with carrier and pressurized till achieve the pressure distribution given by the blue curve in Figure 2. During this transient, equation (11) is still valid, and the sample is compressed and introduced in the precolumn. However, it can happen that only part of the sample is introduced in the precolumn during the transient, and the part that remains in the loop suffers a different diffusion than the part inside of the precolumn, producing an asymmetric peak. To discriminate between both cases, it is useful to compute the amount of carrier volume, \( V_{\text{ol}} \), at \( p_L \) and \( T_e \), that is contained in each column for each valve position. It can be showed that:

\[
V_{\text{ol}} = R_i T_e \int_0^L A \phi(\xi) d\xi = \frac{2 p_{\text{atm}} A\phi}{3 p_L B} \left( \frac{p_{\text{atm}}}{p_{\text{in}}} \right)^3 - 1 \tag{14}
\]

For our GC, we compute:

<table>
<thead>
<tr>
<th></th>
<th>Maincolumn</th>
<th>Precol-Inject</th>
<th>Precol-Back</th>
<th>Available in Precol</th>
<th>Loop</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECD</td>
<td>19.7</td>
<td>20.8</td>
<td>12.4</td>
<td>8.4</td>
<td>10</td>
</tr>
<tr>
<td>FID</td>
<td>10.2</td>
<td>10.9</td>
<td>5.5</td>
<td>5.4</td>
<td>10</td>
</tr>
</tbody>
</table>

So, almost all the content (one half) of the sample loop is introduced in the precolumn during the transient for the ECD (FID). This can explain why \( \text{N}_2\text{O} \) peak is symmetric whereas \( \text{CH}_4 \) is asymmetric. Note that the high asymmetry on the top of the CH4 peak does not seem produced by a non-linear isotherm. For simplicity, we neglect the small volumes of the short S.S. tubes 1/16” O.D. that connect columns. It can be showed that for a given \( L_p + L_m \) (precolumn and maincolumn lengths), the maximum available volume in the precolumn happens when \( L_p = L_m \). When switching from Inject to Backflush, there is an excess of carrier gas in the precolumn (equal to the previous defect) that is vented in a few seconds. So, it can be showed that for having an effective backflush,
it is necessary to have in the precolumn a larger integrated flow (in time) in the backflush direction than in the direct direction (it holds in our system).

It can be showed (computing and comparing hold-up time and O₂ retention time) that between arrows c (switch from Inject to Backflush) and d on left panel of Figure 3 of Gomez-Pelaez & Ramos, what is detected in the ECD is the O₂ present in the maincolumn (very weak tail). Abrupt decrease d happens when there is no more O₂ inside the maincolumn.

Finally, we point out that changes in \( p_i \) do not only change the moles of sample collected in the loop, but also change the mass flow \( F_{out} \rho_{out} \). It can be showed that if \( \Delta p_{in} \) is kept constant, it holds

\[
\frac{d \left( \frac{F_{out} \rho_{out}}{F_{out} \rho_{out}} \right)}{F_{out} \rho_{out}} = \frac{2}{BL} \frac{\Delta p_{in}}{p_{out}} \frac{dp_{out}}{p_{out}} \quad (15),
\]

where \( d \) indicates a small increment of the quantity. For our ECD maincolumn in Backflush position, a 1% relative change in \( p_i \) produces a 0.37% relative change in mass flow.

References
4.3 Measuring Selected Atmospheric Trace Gases Using Gas Chromatography and a Valco Pulsed Discharge Ionisation Detector

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In CSIRO's GASLAB (Global Atmospheric Sampling LABoratory), and at the Cape Grim Baseline Air Pollution Station, packed column gas chromatography (GC) has been used for many years as a technique for making measurements of atmospheric trace gases. For measurements of methane, the detector of choice has been the flame ionisation detector (FID). For GC measurements of carbon dioxide, the FID has also been used as the detector, but a high temperature (400°C) nickel catalyst is used for conversion of the column-separated carbon dioxide to methane. Carbon monoxide and hydrogen have been measured using the Trace Analytical heated mercuric oxide detector, while nitrous oxide has been measured using the electron capture detector (ECD). While these detectors have proven to be reliable in these applications over many years, some limitations are becoming apparent.

In this presentation, the experiences so far in trials of the Valco pulsed discharge helium ionisation detector (PDHID), as a potential replacement for the FID, ECD, and mercuric oxide detector, in measurements of methane, carbon dioxide, carbon monoxide, hydrogen, and nitrous oxide by packed column GC will be described. Briefly, the PDHID has the advantage of being highly sensitive, and effectively behaves as a universal detector. But the universal response has introduced difficulties which are not so severe with the other detectors. In particular, the large (and tailing) chromatographic peaks for nitrogen and oxygen present challenges for improved column separation for those species eluting soon after the oxygen and nitrogen. The strong response of the PDHID to oxygen and nitrogen make the technique particularly sensitive to leaks anywhere in the GC system. The response of the PDHID to the noble gases present in the atmosphere requires very good column resolution to avoid interferences with the targeted species. Good temperature control of the detector and key plumbing components is required for best results. Very high purity helium is critical for this detector, as is the use of purge housings on valves.

Results are presented for measurements of hydrogen, which show great promise. Hydrogen elutes prior to oxygen and nitrogen on the selected packed columns, and so is not subject to the difficulties of the tailing oxygen and nitrogen peaks. Using a Shincarbon 2m micro-packed column (Restek), species separated and identified by their retention times were: hydrogen, neon, carbon dioxide, nitrous oxide and carbon tetrafluoride (refer Figure 1).

Figure 1. PD-HID chromatogram using Shincarbon 2-meter micro-packed column (Restek).
Our long-term experience with measuring hydrogen on the Trace Analytical RGA3 system in GASLAB, shows a consistent repeatability of about 0.3% (or about +/- 1.5 ppb, at current ambient atmospheric mixing ratios in the range 500-600 ppb). Using the Valco PD-PID a repeatability of about 0.05% can be achieved, at similar hydrogen mixing ratios (or about +/- 0.3 ppb). Also importantly, a linear response over a 20-fold range in hydrogen mixing ratios has been found (refer Figure 2.).

![Figure 2. PD-HID linear response function for hydrogen.](image)

Progress towards the measurement of methane, carbon dioxide, nitrous oxide, and carbon monoxide using this detector is also presented. Using a HayeSep-D 30’x 1/8” packed column (2ml Cape Schanck dry air sample), methane separation can be achieved (refer Figure 3.). The resolution of peaks of species eluting after the oxygen and nitrogen peaks require the use of the GC “heart cutting” pre-column technique, whereby the large oxygen and nitrogen peaks can be separated to vent via a pre-column, allowing the pre-column effluent to then be switched to the detector via the main column. Using this method, good separation and detection has been achieved for carbon monoxide (refer Figure 4.).

![Figure 3. PD-HID chromatogram using Haysep D column.](image)  
![Figure 4. PD-HID chromatogram using heart-cut technique (74 ppb CO in Cape Schanck air sample).](image)

Work is progressing to optimise chromatography parameters, and to design a final column and valve configuration for deployment in the GASLAB GC system.
4.4 High Precision Continuous Measurement System of the Atmospheric O$_2$/N$_2$ Ratio Using a Fuel Cell Oxygen Analyzer

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4.4.1 Introduction

Simultaneous observations of the atmospheric O$_2$/N$_2$ ratio and CO$_2$ concentration for a long time make us possible to estimate land biotic and oceanic CO$_2$ sinks separately (e.g. Manning and Keeling, 2006). A seasonal cycle of the atmospheric O$_2$/N$_2$ ratio also contains information about marine biological production (Keeling and Shertz, 1992; Bender et al., 1996). To obtain a better understanding of global carbon cycle based on the atmospheric O$_2$/N$_2$, it is indispensable for measuring its ratio precisely. Several laboratories have developed high precision measurement systems of the atmospheric O$_2$/N$_2$ ratio by employing various methods (Keeling, 1988; Bender et al., 1996; Manning, 1999; Tohjima et al., 2000; Stephens et al., 2003, 2007). We have also newly developed a continuous measurement system using a fuel cell analyzer. In this report, we will describe an outline of our new system.

4.4.2 Continuous measurement system of atmospheric O$_2$/N$_2$ ratio

Our continuous measurement system developed newly for the atmospheric O$_2$/N$_2$ ratio is schematically shown in Figure 1. To measure the atmospheric O$_2$/N$_2$ ratio continuously and precisely, we adopted a Sable Systems Oxzilla/FC2 differential oxygen analyzer. The analyzer has two symmetrical flow paths of air, and each path is equipped with a fuel cell as a detector. Sample air is taken from an aspirated intake using a diaphragm pump through a Dekabon tube with an inner diameter of 4 mm. The aspirated intake is used to prevent from thermal fractionation of O$_2$ and N$_2$ due to solar radiation (Blaine et al., 2005), and the flow rate of the sample air is kept at about 35-40 L/min.

The sample air is introduced into a buffer loop (4 m-length, 4 mm-inner diameter) to minimize pressure fluctuations induced by a vibrating diaphragm of the pump, after removing water vapour contained in the sample air using a Perma Pure dryer (Perma Pure LLC, MD Series) with a dew point of -40°C. Then, the sample is further dried using two cold traps immersed into a -80°C ethanol bath. By controlling a flow regulation valve (PV; HORIBA STEC, PV-1000) with the signal from a pressure gauge (P; Honeywell, 40PC Series) at the outlet of the water trap, the sample pressure in the cold traps is maintained at 0.1 MPa. Such a pressure regulation improved the measurement precision of the O$_2$/N$_2$ ratio significantly.

High and low standard air calibrated against our primary standard, are filled in 48L high-pressure aluminium cylinders. These standard air and the sample air are introduced into one flow path of the analyzer with a rate of 80 ml min$^{-1}$ in order, and dry reference air always flows through the other path at the same rate. The two flows are switched every 3 minutes, and the switching is made once and 8 times for each standard air and sample air, respectively, to compensate for different output drifts of the respective fuel cells. The difference between the fuel cells’ outputs before and after the switching is read as a measure of partial pressure difference of O$_2$ between the sample (or standard) air and the reference air.
For high precision measurements of the O$_2$/N$_2$ ratio, different fractionations of O$_2$ and N$_2$ of the sample air, caused by fluctuations of pressure and temperature, (Keeling et al., 1998) should be minimized. To stabilize the air pressures in the fuel cells, a precise differential pressure gauge (Setra239) is set at both outlets of the Oxzilla analyzer, and the flow regulation valves (HORIBA STEC, PV-1000) at the respective analyzer inlets are controlled to minimize pressure differences between the air filled in a P. Volume (see Figure 1) at 20 kPa and the air in the flow paths. By
employing this method, the pressure fluctuations of the sample and reference air are minimized to be an order of $10^{-3}$ Pa. In addition, the Oxzilla analyzer and the pressure regulation system are not only insulated but also kept at 32°C by controlling their temperatures. The measurement system is installed in an air-conditioned room and surrounded by a plastic sheet to reduce the influence by short-time fluctuations of room temperature. As a result, the temperatures inside the analyzer are maintained within an order of $10^{-3}$ °C at least for 24 hours.

The standard air cylinders are positioned horizontally in a thermally insulated rack to minimize thermal and gravitational separation of O$_2$ and N$_2$ in the cylinders. To convert the measured partial O$_2$ pressure to the O$_2$/N$_2$ ratio, the dilution effect by CO$_2$ included in the sample air is corrected by measuring the CO$_2$ concentration simultaneously using a NDIR analyzer (LICOR LI-6252; see Figure 1), The dilution effect by H$_2$O is neglected, since the dew point of the sample air is lowered to -80°C using the two cold traps.

The measurement system developed by this study provides 7 data every 36 minutes for the O$_2$/N$_2$ ratio of ambient air, and the analytical reproducibility, defined by one standard deviation of repeated analyses for the same air, is evaluated to be ±2.5 per meg.

4.4.3 Application to the atmospheric O$_2$/N$_2$ measurements

Continuous measurements of the atmospheric O$_2$/N$_2$ ratio using the system developed by this study began actually in the suburbs of Sendai (38°N, 140°E), Japan in February 19, 2007. As seen in Figure 2, the measurement results show that the rate in change of the O$_2$/N$_2$ ratio relative to the CO$_2$ concentration (oxidation ratio) is -1.33 ppm/ppm (R=0.97) for February 19-28, 2007 and -1.18 ppm/ppm (R=0.99) for July 19-28, 2007. The former oxidation ratio is close to -1.39 ppm/ppm which is expected from fossil fuel burning (Keeling, 1988), and the latter ratio is in agreement with -1.1 which is expected from land biospheric activity (Severinghaus, 1995). These observed ratios would be plausible, since the observation site is situated on a hilltop not being away from the Sendai urban area and surrounded mainly by deciduous shrubs. However, from late March to early April of 2007, we sometimes observed the oxidation ratios of lower than -2.0. The trajectory analysis of air parcels suggests that such low values are caused by a rapidly exchanged oceanic O$_2$ in the Sea of Japan. Continuous O$_2$/N$_2$ measurements with the same system also started at Japanese Antarctic station, Syowa in January 2008.

![Figure 2. Relationship between the O$_2$/N$_2$ ratio and the CO$_2$ concentration observed in the suburbs of Sendai, Japan on February 19-28, 2007 and on July 19-28, 2007.](image_url)
References
5.1 REPORT OF THE WCC-N₂O  
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5.1.1 Introduction

The World Calibration Centre for N₂O (WCC-N₂O) has been established as a central GAW facility according to requirements of the GAW Strategic Plan 2001–2007 (WMO/GAW Report No. 142). Its overall goal is the improvement of N₂O data quality and comparability. The WCC-N₂O (http://imk.fzk.de/wcc-n2o/) is hosted by the Forschungszentrum Karlsruhe, IMK-IFU, and its activities are conducted under supervision and through funding by the Quality Assurance/Science Activity Centre (QA/SAC) Germany, operated by the German Environment Agency (UBA). Among the major tasks of the WCC-N₂O are the development of quality control procedures, conducting audits at stations and round-robin experiments as well as providing training and technical advice to GAW station personnel. This presentation reports primarily on WCC-N₂O activities performed since the 13th Experts Meeting of September 2005.

5.1.2 Activities of the WCC-N₂O

5.1.2.1 Contributions to GAW documents

Editing work on Measurement Guidelines (MGs) for N₂O has been continued in 2007. The MGs for N₂O are part of a future WMO/GAW report containing Data Quality Objectives (DQOs) and Measurement Guidelines for both CH₄ and N₂O (Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance). Thanks to the input from a number of GAW participants and external experts, the draft of the report is now at an advanced stage and was submitted for approval to the SAG GG prior to the SAG meeting in September 2007.

The WCC-N₂O has contributed to the WMO/GAW Glossary of QA/QC-Related Terminology, which originally started out as a spin-off from a glossary section of the MGs. After further editing and formatting by QA/SAC Switzerland, this document is now available on the web (http://www.empa.ch/gaw/glossary.html). Refinements made to the glossary during the final editing phase were thereafter recirculated to the respective section of the MGs. It is noted that the web version of the glossary is intended as a dynamic process, which will yield enlargement depending on future input by its users, also from outside the greenhouse gas community.

Based on the joint input from QA/SAC Switzerland, WCC-Empa and WCC-N₂O an Audit Questionnaire (Gases) was compiled. It serves for collecting all relevant information during audits at stations. Moreover, the WCC-N₂O has been involved in the editing of an Audit SOP, which was based on an outline by WCC-Empa. Both audit documents have been approved by the SAG GG.

5.1.2.2 Comparisons of standards

In the laboratory of the WCC-N₂O, extensive comparisons of standards were conducted, several of them as pre- and post-audit checks of the travelling standards involved. The standards of the WCC-N₂O are linked to the GAW standard scale maintained by the Central Calibration Laboratory for N₂O, operated by NOAA ESRL in Boulder (USA). While the primary and secondary standards of the GAW N₂O scale are maintained at the CCL, the standards ranking highest within the WCC-N₂O (laboratory standards) are on the tertiary level of the hierarchy. At the beginning of 2007, an intercomparison was conducted between the CCL and the WCC-N₂O. It was based on five travelling standards previously used for audits, with N₂O mole fractions ranging between 290 and 350 ppb. The intercomparison established an important internal quality check. Analysis results reported by the CCL showed agreement within a range of ± 0.1 ppb for four of the five cylinders (Table 1). The greater deviation (0.37 ppb) found for the lowest mole fraction could be attributed to one of the WCC-N₂O laboratory standards, for which the assigned value had already previously been assumed to be possibly too high by 0.3 ppb.
Table 1. Results of a CCL–WCC intercomparison experiment based on 5 WCC-N₂O travelling standards (10-L cylinders) analyzed by the CCL.

<table>
<thead>
<tr>
<th>N₂O [ppb] as assigned by WCC-N₂O</th>
<th>CCL results (intercomparison 2007) [ppb]</th>
<th>Difference.: WCC – CCL [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Based on NOAA-2000 scale</td>
<td>Converted to NOAA-2006 scale</td>
<td></td>
</tr>
<tr>
<td>296.30</td>
<td>296.26</td>
<td>0.37</td>
</tr>
<tr>
<td>306.03</td>
<td>305.95</td>
<td>0.06</td>
</tr>
<tr>
<td>319.12</td>
<td>318.97</td>
<td>0.07</td>
</tr>
<tr>
<td>332.91</td>
<td>332.65</td>
<td>-0.12</td>
</tr>
<tr>
<td>347.90</td>
<td>347.47</td>
<td>0.12</td>
</tr>
</tbody>
</table>

5.1.2.3 Audits

Currently, the main criteria for the selection of stations to be audited by the WCC-N₂O are: (i) N₂O measurements were only started recently, (ii) a station is not directly part of well-established global networks (such as NOAA/ESRL or AGAGE), or (iii) major changes, in particular upgrade of N₂O instrumentation, were made since the last audit.

Two audits were conducted at global GAW stations, one at Zugspitze (ZSF, as part of the global station Zugspitze/Hohenpeißenberg) in December 2005 and the other at Jungfraujoch (JFJ) in July 2006. At both stations, the N₂O analytical setup is based on state-of-the-art instrumentation using the same type of gas chromatograph. The stations’ working standards were linked to the Scripps SIO-98 scale. Although rather similar equipment was being used, the audits have revealed interesting differences in the performance. These pertain to the separation of N₂O within the chromatogram, reproducibility of N₂O mole fractions, handling of the 1-level calibration applied for routine operation, and finally differences in the results obtained for the intercomparison of five travelling standards (range 290 – 350 ppb, WCC-assigned mole fractions in NOAA-2006 scale).

While there is excellent separation of the N₂O peak from interfering CO₂ and SF₆ signals at Jungfraujoch, the N₂O analysis at Zugspitze was optimised for short cycle time at the expense of N₂O peak separation. On the other hand, the reproducibility of N₂O results at ZSF is superior to the one achieved under comparable GC conditions at JFJ. Since the ECD response curve is non-linear and usually does not go through zero, a 1-level calibration for calculating mole fractions is only applicable if the working standard is very close to the N₂O level in the unknown sample, as it was in the case of ambient air at JFJ and one of the five travelling standards (Fig. 1, right).

Figure 1. Differences between reported and assigned N₂O mole fractions for an intercomparison of 5 travelling standards at the stations Zugspitze and Jungfraujoch. Results are shown for cases without non-linearity correction (steeper slope of the regression line) and with corrections applied.
For the other four standards significant systematic errors remained even after non-linearity had been accounted for, since the response curve was not known exactly enough. In contrast, the non-linearity and CO₂ interference corrections made at ZSF proved to be well suited. However, a small bias of ~ 0.5 ppb over the entire range was found, with one outlier being discarded for the regression (open circle in Fig 1, left).

5.1.2.4 Contributions to training courses
In recent years, the WCC-N₂O has contributed to four GAWTEC courses in the form of lectures given in 2005 and 2006. The courses of the GAW Technical Education Centre took place at the Environmental Research Station Schneefernerhaus located at the Zugspitze mountain (http://www.schneefernerhaus.de/ufs.htm). While there was no demand for specific N₂O training so far, the need of improving the data visualisation skills of the participants had already been noticed at an early stage of GAWTEC. Therefore one lecture dealt with "Graphical Presentation of Measurement Data", while the other one, entitled "GAW Terminology and ISO Definitions", was intended as an introduction to current and future requirements set out by GAW according to its Strategic Plan.

5.1.3 Summary and outlook
In the period 2005 – 2007, the WCC-N₂O has continued its involvement in the preparation of GAW documents related to QA/QC matters for trace gases, notably CH₄ and N₂O. An intercomparison of five travelling standards with the Central Calibration Laboratory has verified the link of the WCC-N₂O to the GAW scale. Audit results have revealed minor problems with N₂O measurements that need to be addressed by the respective stations. Post-audit contacts by the WCC-N₂O with the stations should be intensified. The WCC-N₂O will make plans for future intercomparisons, including round-robin experiments. Furthermore, contributions of the WCC-N₂O to GAWTEC training courses will be continued.
5.2 Calibration and Network Monitoring Performance of LOFLO Continuous CO₂

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Results are presented from a series of high precision calibration experiments which have been conducted to investigate the propagation of CO₂ mole fraction mixing ratios using dry, CO₂-in-air standards (Luxfer, aluminium cylinders). At the CSIRO GASLAB (Global Atmospheric Sampling LABoratory), a primary laboratory LoFlo CO₂ analyser (NDIR) calibration suite, consisting of seven standards, each of which has been calibrated by the WMO CCL (NOAA ESRL CCGG), has been used to propagate the CO₂ calibration scale to additional LoFlo calibration suites using the central GASLAB LoFlo (“LoFlo 2B”).

The calibration standards (and all working reference gas cylinders) are prepared using clean, dry (< 0.1 ppm H₂O – Meeco analyser), natural air from the marine boundary layer (Cape Schanck, Victoria, Australia), to minimise any potential background air matrix effects. The calibration range spans 320 to 460 ppm CO₂, with δ¹³C-CO₂ range from -7.8 to -8.3‰, thereby minimising NDIR isotopic effects (variable ¹³CO₂ NDIR response). The seven calibration cylinders are attached directly to the LoFlo analyser, eliminating the need for additional hierarchical calibration levels. This avoids potential scale propagation errors when using a hierarchical calibration scheme. Due to very low gas consumption rates, the calibration cylinders have an extended working life (greater than 50 years), avoiding the need for scale adjustments when replacing working calibration cylinders.

The inherent high precision of the LoFlo is demonstrated in Figure 1, which represents the progressive CO₂ assignment of a working reference gas cylinder during the course of a standard calibration sequence. In general, the initial calibration pyramids are removed from the calibration processing until a stable reference gas CO₂ concentration is obtained (drifts due mainly to “regulator conditioning” effects). The uncertainty in this assignment is very small (<0.01ppm) and is also repeatable, to the same precision, during subsequent calibrations over the lifetime of the working reference gas cylinder (refer Figure 2.).

![Figure 1](image1)

Figure 1. LoFlo typical reference gas calibration sequence (18 calibration pyramids).

![Figure 2](image2)

Figure 2. Typical working life calibration history of LoFlo reference gas.
The calibration history of the GASLAB LoFlo 2b instrument has proven to be very stable over an extended period as shown in Figure 3 (note: two periods of instability when the instrument was removed to Cape Grim to be used in an overlap experiment and then returned to Aspendale). These results show no discernible drift in any of the calibration cylinders, although this cannot be confirmed until the cylinders are returned to the WMO CCL for re-calibration. This same calibration history is summarised in Figure 3b, which reveal the very low uncertainty in each calibration residual mean value. This figure also demonstrates the existence of a “quadratic fitting routine effect” forming a non-random residual pattern. This is caused by the two end points of the quadratic function constraining the remaining five calibration points, in effect having an enhanced weighting effect on the quadratic fitting function. A range of different weighting schemes and alternate cubic fitting routines have been attempted to reduce this effect.

This quadratic fitting routine effect is potentially significant given the high values of some of these residuals (-0.07ppm for calibration cylinder#6), relative to the WMO recommended global network precision targets of 0.05ppm CO₂ (Southern Hemisphere). However, while this quadratic effect is still present when the LoFlo 2B primary laboratory suite is used to propagate the CO₂ calibration scale to additional LoFlo instruments (operated in the observation network), the impact of this quadratic effect is essentially removed as the LoFlo propagated calibration residuals are all
less than 0.01ppm (refer Figure 4.). This could be explained by the ability of the LoFlo instrument to more precisely characterise the relationship between the primary laboratory calibration cylinders (constituting this derived CO₂ scale) relative to that of the WMO CCL primary calibration scale.

A contributing impact is also likely from two of the primary LoFlo laboratory calibration cylinders (cylinders #3 & #6), both of which show drifting consecutive analyses in the original WMO CCL assignments conducted in 2002 (refer Figure 5).

Apart from this issue, the integral precision of the LoFlo analyser combined with the ability to propagate a CO₂ calibration scale with very high precision, promotes confidence in the potential for a LoFlo based observation network (combined with inversion modelling techniques) to resolve small regional CO₂ fluxes, such as in the important Southern Ocean region. This is demonstrated in the repeatability in calibration profiles for multiple LoFlo instruments using a single calibration suite (Refer Figure 6).

It has also been demonstrated in an overlap experiment using two LoFlo analysers (LoFlo 2b and LoFlo 2a) to measure the same ambient air from a shared air intake (and shared intake pump manifold), which was conducted at Cape Grim in 2005/2006. The LoFlo analysers have individual calibration suites: the WMO CCL calibrated LoFlo 2b suite, and the LoFlo 2a suite propagated from the 2b suite.

Figure 4. LoFlo propagated suite calibration history (2A propagated from 2B).

Figure 5. WMO CCL calibrations of LoFlo 2B calibration cylinders (#3, #6).
These results demonstrate the very high precision achievable measuring both CO2-in-air gas standards and atmospheric CO2 with the LoFlo technology, which could potentially allow the successful resolution of small atmospheric CO2 spatial gradients across a Southern Ocean LoFlo monitoring network and the inference of CO2 fluxes in this region.

Figure 8 shows a preliminary comparison between continuous atmospheric LoFlo CO2 measurements from the Cape Grim Baseline Air Pollution Station, in northwest Tasmania and a recently installed (March 2005) LoFlo CO2 analyser system at the remote Macquarie Island (54.48°S, 158.97°E) in the Southern Ocean.
Figure 8. Preliminary comparisons between Cape Grim and Macquarie Island LoFlo analysers.
5.3 The Publication of WDCGG Data Submission and Dissemination Guide
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5.3.1 Introduction
The World Data Centre for Greenhouse Gases (WDCGG), first established in 1990, has now been operated by the Japan Meteorological Agency for more than 15 years. The current operations of the WDCGG are composed of the following four functions:

- To gather measurement data and associated metadata of greenhouse and related trace gas species from various platforms of the GAW observation network and relevant international research programmes.
- To archive the data of known quality for long-term use after validation.
- To make the archived data available to users via the Internet.
- To disseminate value-added products and user support information in order to facilitate more reliable monitoring and data analysis.

A schematic diagram of data submission, dissemination, and the data flow in the WDCGG is shown in Figure 1.

Figure 1. Schematic diagram of data submission, dissemination, and data flow in the WDCGG.

The amounts of observation data submitted to and information provided by the WDCGG have increased markedly with recent developments of GAW measurement network and the Internet (Figure 2). Regarding these enhancements of the data exchanges, the WDCGG would like to express deep appreciation for cooperation of data submitters and users. However, under these
circumstances, the data management of the WDCGG and information demands on the WDCGG have changed. Therefore, the “DATA REPORTING MANUAL of the WMO World Data Centre for Greenhouse Gases”, which described the data submission formats and was published in 1991, has become unsuitable for the current operations of the Centre.

The WDCGG revised the DATA REPORTING MANUAL, and newly published it as the WDCGG Data Submission and Dissemination Guide (WMO, 2007). The objectives of this Guide are as follows:

- To make better use of Archived data, the overall activities of the WDCGG in responding to the social demands of observers, scientific communities, and the public are introduced.
- To gather more appropriate observation data and associated metadata, the purposes, function, and operational courses of the WDCGG are clarified.

The new WDCGG Data Submission and Dissemination Guide can be downloaded on the WDCGG website (http://gaw.kishou.go.jp/wdcgg/products/publication.html). The points of the new Guide are as follows:

5.3.2 Definition of observation categories
Measurement data are classified into six observation categories according to the observation platforms or methods used.

1. Air sampling observation at ground-based stations.
2. Air sampling observation for vertical profile (e.g. multi heights observation using a tower).
3. Air sampling observation by mobile platforms (e.g., aircraft, ships, etc.).
4. Ice core observation.
5. Surface seawater and overlying atmosphere observation.
6. Hydrographic sampling observation by ships.

5.3.3 Data format
After the publishing the DATA REPORTING MANUAL in 1991, the gathering data in the WDCGG become to have various species and types, which caused the dissemination file formats of Archived data diverging. As a result, this situation causes complicated data handling for
computer, consequently degraded the usability of the WDCGG. To improve this situation, the WDCGG has established new data dissemination file formats aiming at the facilitation of use of Archived data in the WDCGG. The new data dissemination file formats are computer familiar FORTRAN fitting formats.

To simplify the new formats, each file contains mole fraction values of only one parameter; mole fraction data and ancillary meteorological data are separated; all information to read the data file is included in the header part.

The WDCGG prepared a sample program to read the Archived data file, and this program is available on the WDCGG website.

5.4.4 Metadata
Accurate metadata of observation is crucial for data users. However, the former WDCGG metadata in the WDCGG was insufficient. The WDCGG arranged the metadata items and established new metadata formats to expand their items to more comprehensive. The WDCGG converted old metadata to new metadata format, but the new metadata formats require additional station and measurement information. The WDCGG is asking Contributors to complete your metadata in the new Metadata Edit Menu on the WDCGG website. Please contact the WDCGG to open the Metadata Edit Menu if you would like to edit your metadata.

5.4.5 Archive of all versions of data
After the publishing the new Guide, a new data version is assigned when existing data are replaced by new data that have different quality. All versions of Archived data are available (only by FTP for the moment) as well as the latest Archived data on the WDCGG website. The version of the Archived data is maintained by the file name. Please refer “WDCGG_filename_format.pdf” on the website. Past WDCGG CD-ROMs data are also available on the WDCGG website.

The WDCGG also has a FTP server on the new website. The users will be able to download data by accessing the FTP server as an anonymous user. Please refer http://gaw.kishou.go.jp/wdcgg.html.

5.4.6 Submission-data plausible check before acceptance
In the GAW new strategic plan, one of the terms of reference (TOR) of WDC is described as “Ensure that data collected and archived by WMO/GAW WDCs are of known quality, adequate for their intended use and documented comprehensively”. The WDCGG is developing a check method for data plausible check before acceptance. In some cases, the WDCGG performs trail checks, and has begun to communicate with some stations. However, The WDCGG is now accumulating cases to be checked. We need more time for research. In future, the WDCGG would propose check methods to SAG for GG and the measurement community for discussion.

5.4.7 Overall improvement of WDCGG website
In July 2007, The WDCGG improved the website (Figure 3). The new website equips following functions:

- User can download the Archive data by FTP.
- The new website has easy search system for targeted stations and data “Quick plot” has a function to produce figures with both PNG and PDF formats. Quick plot is produced in consideration of data quality flag.
Welcome to the WDCGG Web Site

The World Data Centre for Greenhouse Gases (WDCGG) is one of the WDCs under the GAW programme. It serves to gather, archive and provide data on greenhouse gases (CO2, CH4, CFCs, N2O, surface ozone, etc.) and related gases (NOx, SO2, VOC, etc.) in the atmosphere and ocean, as observed under GAW and other programmes.

This web site provides information on greenhouse gases, including WDCGG publications and measurement data contributed by organizations and individual researchers around the world.

If you would like to submit data for the first time, please refer to the WDCGG Data Submission and Dissemination Guide.

Figure 3. New Home page of the WDCGG website (http://gaw.kishou.go.jp/wdcgg/).

References
5.4 The Global Analysis Method by the WDCGG using the Archived Data
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5.4.1 Introduction
The Japan Meteorological Agency operates the World Data Centre for Greenhouse Gases (WDCGG) that supports scientific researches, assessments and correspondence policy for environmental issues such as global warming, ultimately to contribute towards reducing societal environmental risks, and to meet the requirements of related environmental conventions (WMO, 2007). As a result, the WDCGG is charged with producing reliable global analyses using GAW network data together with the SAG for Greenhouse Gases.

The WDCGG calculates the inter-annual variations of global-mean mole fraction of greenhouse gases (Fig. 1) using the archived data in the WDCGG for the WMO Greenhouse Gas Bulletin (http://www.wmo.int/pages/prog/arep/gaw/ghg/ghgbull06_en.html) and the WDCGG Data Summary (http://gaw.kishou.go.jp/wdcgg/products/publication.html).

![Figure 1. Globally averaged CO₂ (left) and its growth rate (right) from 1983 to 2006.](image)

Two problems are associated with global analyses of greenhouse gases using observational data from multiple measurements programs. First, the measurements have to be on the same measurement scale derived from a common reference standard (otherwise, they cannot be compared). Second, measurement data from all stations have to be synchronized for the observation period. However, the observation period for each station, particularly beginning of observation, is usually different. Furthermore, many stations have gaps in their observation time series due to instrument malfunctions or other reasons. If global analyses are performed without considering these problems, the results may be biased by the particular stations used and the availability of data. In the contrast, if only stations that have long observation periods are selected, data from many stations in recent years would not be included in global analyses. For global analyses, it is practical to prepare a dataset of uniform quality without gaps and that is not biased by variation in station and data number.

5.4.2 Procedures for global analyses
To calculate the global mean, the WDCGG produces the WMO traceable and period synchronized dataset without any gap. After that, the WDCGG calculates the latitudinal means, hemisphere means, and the global mean. All calculations are performed using monthly mean data. The steps of CO₂ calculation by the WDCGG are below.

Step 1: Stations for global analysis are selected by the WMO traceability.
Step 2: For selection for background station, a latitudinal distribution of the annual-mean mole fractions normalized with respect to the South Pole is fitted with the LOESS
model curve. Stations with mole fraction lying more than ±3σ from this curve are rejected and this process is iterated until all of the remaining stations lay within ±3σ from the fitted curve.

Step 3: Integration of plural data in the same station (in the case that both continuous and flask sampling datasets exist).

Step 4: For each station, using the longest data, a station’s own seasonal variation expressed by the Fourier polynomial up to third degree is derived.

Step 5: The linear interpolation is performed for data from which the own seasonal variation is subtracted. The complete variation is then retrieved by adding the own seasonal variation to the interpolated periods (Fig. 2).

Step 6: Extrapolation for synchronization is then performed for the long-term trend as its growth rate traces the zonal mean growth rate calculated from the other stations’ interpolated data in the same latitudinal zone (30°). Subsequently, the synchronized complete variation is retrieved by adding the own seasonal variation.

Step 7: The zonal mean mole fractions are calculated using the synchronized dataset in the each latitudinal zone.

Step 8: Global and hemispheric means are calculated by averaging the zonal means, taking into consideration the area ratio of the each latitudinal zone. The deseasonalized long-term trend and growth rate for the globe, both hemispheres and each latitudinal zone are calculated again with the low-pass filter from the global, hemispheric and zonal means.

For CH₄ and N₂O, since the WMO primary standard has not yet prevailed, the stations where the WMO standard is used or stations whose difference between the station standard and the WMO standard is scientifically known are employed as Step 1.

Figure 2. Original (left) and synchronized (right) monthly mean CO₂ mole fractions of stations used for global analysis illustrated in colours that change with mole fractions. Stations are arranged from north to south.

5.4.3 Summary
A synchronized dataset with no gaps in the observation period that is traceable to the WMO reference standard is practical for global analyses of greenhouse gases. The WDCGG produces such a dataset using data from the GAW global observation network and following procedures:

- Station selection based on traceability to the WMO reference standard.
- Integration of parallel data from the same station.
- Selection of stations suitable for global analyses.
- Interpolation of data gaps.
- Extrapolation of data for synchronization throughout the observation period.
Using the synchronized dataset, the WDCGG calculates monthly means, long-term trends and the growth rates for each latitudinal band. Subsequently, the global mean and other global statistics are calculated using latitudinal values weighted according to area.

References
6.1 Quarter Century of Atmospheric CO₂ Monitoring and Research in Hungary

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6.1.1 Hungarian CO₂ monitoring programmes

Continuous monitoring of atmospheric carbon dioxide mixing ratio was started at the regional background air pollution monitoring station of the Hungarian Meteorological Service, K-puszta (46°58’N, 19°33’E, 125 m asl), on 5 June, 1981 (Haszpra, 1999a). Air intake was located at 10 m above the grass covered sandy ground and a Siemens Ultramat 3 CO₂ analyzer was installed applying the so-called Köhler’s method (Köhler, 1974). Instead of a freeze out trap a constant water vapour level was maintained for the analyzer. Due to the lack of funding, the measuring program was ceased at the end of June, 1999. In the meantime, another, up-to-date monitoring site could be established at Hegyhátsál (46°57’N, 16°39’E, 248 m asl), West Hungary, 220 km away from K-puszta, in co-operation with NOAA (Haszpra et al., 2001). Using a TV-transmitter tower continuous monitoring of CO₂ concentration was started at four elevation levels from 10 m to 115 m on 29 September, 1994. The station is also a co-operating NOAA flask sampling site for greenhouse gases (code: HUN) where samples have been taken every week since 2 March, 1993. The flask samples offer a possibility for the quality control of the in-situ measurements. In spring 1997 an eddy covariance system monitoring the surface-atmosphere CO₂ exchange was also installed on the tower at 82 m elevation. Both K-puszta and Hegyhátsál are as free from direct anthropogenic influence as it is possible in Central Europe. The ground based monitoring program has been completed by regular (1 flight/20 days) aircraft flask sampling over the tower up to 3000 m since 2001, and an intensive (1 flight/4 days) in-situ CO₂ mixing ratio profile measuring campaign in 2006-2008.

6.1.2 Long-term trend in atmospheric CO₂ mixing ratio

The almost 5 years long parallel measurements at K-puszta and Hegyhátsál proved that the nighttime concentration values were strongly influenced by the local conditions (soil and vegetation types, regional meteorology), while the difference between the early afternoon values were small and the correlation between them was high. The conclusion was that the early afternoon values from the two stations (10 m sampling elevation also at Hegyhátsál) can be combined into a single, more or less homogeneous time series (Haszpra, 1999b).

Figure 1 shows the mixing ratio trend based on the early afternoon (12-16 h LST) values without any further data selection. 43 ppm increase has been recorded since the beginning of the measurements. We started at 343 ppm in June, 1981, and reached 390 ppm by the end of 2007. The average deviation of the Hungarian measurements from the marine boundary layer reference mixing ratio taken from GLOBALVIEW (GLOBALVIEW-CO₂, 2007) is 4.3 ppm with a significant fluctuation. The average deviation can be explained by the contribution of the European anthropogenic sources surrounding the mid-continental Hungarian sites, while the fluctuation may be caused by the fluctuation in the biospheric activity. The growth rate correlates well with that in the global background and with the Southern Oscillation Index. The lag-time to the Southern Oscillation Index is about 9 months, similarly to most of the northern hemispheric continental sites. The range of the fluctuation is wider at the Hungarian sites than in the oceanic background indicating that the continental biosphere plays a crucial role in the global atmospheric carbon budget.
6.1.3 Shorter term fluctuations in atmospheric CO$_2$ mixing ratio

The overall trend and the fluctuation in the growth rate are similar to the global values but the details also show regional features. During the period between the beginning of the measurements at Hegyhátsál (1994) and 2003 there was a significant difference between the spring and summer mixing ratio trends. The spring trend was lower (1.54 ppm/year) than that of the annual values (1.80 ppm/year) while the summer one (2.22 ppm/year) was well above that. These years were increasingly warm and dry. The earlier start of the growing season can explain a more intensive biospheric uptake during the spring months resulted in a lower than average concentration increase, while the hot and dry summers decreased the net uptake of the biosphere. From 2004 the climate has returned to normal, it has become relatively cooler and wetter in Eastern Central Europe. It almost balanced the spring-summer difference on the 13-year time scale (spring: 1.76 ppm/year, summer: 1.92 ppm/year, annual: 1.95 ppm/year). It is indicated in Figure 2 that the summer mixing ratios have hardly increased since 2003.
The effect of the climate anomaly lasted until 2003 is well presented by the biosphere-atmosphere CO₂ exchange measurements. Higher biospheric uptake resulted in decreasing net release in March and significantly decreased net uptake in summer, especially in July and August (Figure 3). From 2004 the situation has changed drastically, parallel with the changing regional climate.

![Figure 3. Temporal variation of the daytime (8-16 h LST) net ecosystem exchange (NEE) measured by the eddy covariance system located at Hegyhátsál at 82 m elevation. Note, the lines in the figure are not trend lines, they only indicate the direction of the changes. (March – dashed line, July – thin solid line, August – thick solid line).](image)

The length of the CO₂ deficit season, when the mixing ratio is lower than the annual average, is increasing. The beginning of the period is moving earlier in the year, while its end hardly changes. Supposing a linear trend, the length of the CO₂ deficit season has become almost 9 days longer between 1995 and 2007. The earlier start of the CO₂ deficit season may be caused by the generally warming climate, by the earlier start of the growing season. In principle, warming could also prolong the growing season and move the autumn zero-crossing towards the end of the year. However, the earlier harvest and/or the increasing respiration caused by the higher autumn temperature can prevent it (Piao et al., 2008).

The regional scale climate fluctuation influenced the biospheric activity in general as it is reflected by the biosphere-atmosphere CO₂ exchange measurements at Hegyhátsál. From the beginning of the measurements (1997) until the extremely hot and dry 2003, parallel with the increasing temperature and decreasing precipitation amount, the net biospheric uptake characterized by the net ecosystem exchange decreased, and the region became a net source of carbon on an annual time scale (Figure 4). However, since 2004 the regional biosphere has taken up more carbon annually than ever before since the beginning of the measurements. In Figure 4 it seems as if the precipitation amount were the main controlling factor, but in fact, there are a lot of others like the amount of water accumulated in the soil during the winter, the timing of the wet and dry, hot and cold periods, etc. The identification of the governing environmental parameters and processes needs further study.
Figure 4. The net ecosystem exchange (NEE) of the region of Hegyhás, as well as the precipitation amount and the mean temperature characteristic for the growing seasons.

Acknowledgments

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References


6.2 CO₂ Isotopic Composition in the Upper Troposphere: the Project CARIBIC
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6.2.1 The approach
Many programmes worldwide aim at greenhouse gas monitoring covering different geographical scales, from very local, via regional to global (background stations). Commonly boundary layer air is assayed this way, close to CO₂ sources and sinks, whereas only a few stations are on mountains in the free troposphere. There also are a few programmes using ocean ships and vertical profiling by small research aircrafts (NOAA/ESRL). In particular aircraft sampling is relatively expensive. Basically most global networks do cover remote areas (particularly the tropics) only sparsely, and much less information is available at altitude, although satellite observations are filling in some gaps in observation. In view of incomplete global monitoring, the 13th CO₂ Expert Meeting recommended [1] to promote programmes using commercial aircraft (altitudes of ~10 km). To provide information about CO₂ (including isotopic composition) in background air, in the free tropical troposphere and in the tropopause region, far from CO₂ sources and sinks, aircraft-based observational platforms are really important. The project JAL (Japan) studies CO₂ concentrations by flights from Japan to Australia, and recently other designations have been added. CO₂ isotope measurements by JAL have been started [2]. The project CARIBIC (http://caribic-atmospheric.com) started in 1997 and aims to study atmospheric chemistry and composition by measuring many compounds and species in the upper troposphere around the globe. CARIBIC has two phases, CARIBIC-1 and CARIBIC-2 (CARIBIC-LUFTHANSA).

6.2.2 CARIBIC-1
The instrument container onboard a Boeing 767 operated by LTU (Düsseldorf, Germany) included instruments for on-line analyses of O₃ and CO, aerosol measurements as well as air sampling system (twelve SS canisters of 20 l, air pressurised to ~17 bar) for trace gas analyses in lab conditions. Analysed were CO₂, CH₄, N₂O, SF₆, NMCH, halogenated organic compounds as well as CO and CO isotopes, including ¹⁴CO. The CO extraction by means of CO → CO₂ oxidation required a quantitative extraction/stripping of tropospheric CO₂ prior to the oxidation step. Isotope analyses presented in this paper were performed on a MAT-252 at the Max Planck Institute for Chemistry (Germany), on the cryogenic extracts obtained from processing ~300 l air. Originally CO₂ isotope analysis was not a main focus of CARIBIC-1. Large δ¹⁸O(CO₂) scatter at the beginning of CARIBIC-1 (Figure 1) indicated CO₂-water isotope exchange. For canisters no. 1, 6 and 9 the problem persisted longer than for others. Also the MAT-252 calibration was optimised for CO measurements rather than for CO₂ isotope analyses. Despite of these problems and thanks to the high quality extraction, robust IRMS performance, and having extremely large samples, CO₂ isotope results are considered to be very reliable (examples are presented below). This success stimulated us to continue CO₂ isotope measurements for CARIBIC-LUFTHANSA.

6.2.3 CARIBIC-2
The new instrument container, operating onboard an A360-600 of Lufthansa (Frankfurt, Germany), performs monthly flights from Frankfurt to remote designations such as China, South America and Canada. The container includes an extended range of instrumentation (O₃, CO, NOx, H₂O and others, adsorption cartridges for NMHC, aerosol measurements etc. see http://caribic-atmospheric.com, [3]). The sampling system consists of two collector boxes (TRACs) each with 14 glass containers (2.7 l volume, pressure ~3 bar) being filled within a minute, giving much better sampling resolution than in CARIBIC-1 (20 minutes, or ~250 km). After a flight, the TRACs are sent to participating institutions. A specially designed CO₂ extraction line was installed at IRMM (Geel, Belgium) and measurements started in May 2007. Preliminary CARIBIC-2 data indicate that δ¹⁸O(CO₂) scatter is small, indicating excellent preservation of δ¹⁸O(CO₂), due to use of glass containers. We particularly focus on quality δ¹⁸O(CO₂) data which give information about CO₂ exchange with oceans, soils and biosphere [4], being a long-term indicator of global changes in the...
CO2 cycle as well as oceans' feedback. (Positive feedback on temperature increase, namely CO2 release from oceans is not an improbable scenario.)

6.2.4 Examples of CARIBIC-1 data and interpretation.

Fights at cruising altitudes of 10 to 12 km at mid latitudes frequently cross the tropopause (UT/LS region). Also large convective plumes (biomass burning and anthropogenic signals) are intercepted. In the lowermost stratosphere mixing determines CO2, δ13C(CO2) and δ18O(CO2) values in a different way, depending on season, transport, mixing and residence time of air in stratosphere. Besides this, by reaction with ozone via CO3 in the stratosphere CO2 oxygen (both δ17O and δ18O) becomes modified. The anomalous isotopic enrichment of O3 is partly transferred to CO2. To interpret CO2 isotope data and understand effects related to UT/LMS mixing, one needs to combine chemical tracers, back-trajectories and, in future, atmospheric circulation models.

First we demonstrate how O3 data can be used as a filter for the LMS component, in order to interpret CO2 isotope data and separate samples containing upper-tropospheric air, not affected by the LMS component. Based on the O3 and CO anti-correlation, Zahn et al. [5] proposed the concept of chemical tropopause and introduced its O3 seasonality. Both O3 (in the UT/LMS region) and CO2 are long-lived tracers. Use of O3, a long-lived chemical tracer appears to be more appropriate than the use of tropopause tracers having a pure physical nature (PV levels, temperature), also because the O3 measurements are carried out continuously.

Two fights (33 and 34) which were close in time (May-14 and May-19, 2001) and sampled nearly the same latitude-longitude region have been combined for analyses. O3 data linearly correlate with 14CO (both produced in stratosphere) implying mixing of LMS and UT components (Figure 2), with their end-member composition being similar for all samples. CO2, N2O, CH4 and SF6 anti-correlate with O3 – that has 2 well known reasons: N2O and CH4 decompose in the stratosphere whereas CO2 and SF6 were lower in the past. δ13C(CO2) correlates well with the O3-excess above the chemical tropopause and with the inverse of the CO2 contents (Figure 2), confirming usefulness of O3 data as LMS-filter as well as a similarity of air masses sampled by the two flights separated by 5 days.

Interestingly, δ18O(CO2) observed for the LMS samples are within the values demonstrated by UT samples from these two fights (Figure 2). No correlation between δ18O(CO2) and O3 excess or the inverse of the CO2 contents is seen. At a first glance the latter implies a small effect of LMS-mixing on δ18O(CO2), which needs to be considered in more detail. For LMS air with 14CO≈115
molec/cc STP, $\delta^{17}$O(CO$_2$)≈0.5 ‰ was found [6]. Because maximal $^{14}$CO values among CARIBIC samples are around 100 molec/cc STP, we consider $\delta^{17}$O(CO$_2$)≈0.5 ‰ as a maximal value for LMS component sampled. Next, for stratospheric CO$_2$ it was found [7] that $\delta^{17}$O(CO$_2$)=1.7•$\delta^{18}$O(CO$_2$). Thus, for samples being most enriched in the LMS component, the $\delta^{18}$O(CO$_2$) shift relative to $\delta^{18}$O(CO$_2$) of air entering the stratosphere is not higher than 0.5/1.7=0.3 ‰. For samples less affected by the LMS component, the $\delta^{18}$O-shift is smaller. Similar to the $\delta^{13}$C(CO$_2$) vs. O$_3$ trend we observed, the agreement between $\delta^{18}$O(CO$_2$) of UT and LMS samples (Figure 2) depends on the $\delta^{18}$O(CO$_2$) seasonality at the UT region sampled, seasonality at the equator (where most air enters the stratosphere) and the age for LMS air. However we suggest that air samples with low O$_3$ values have $\delta^{18}$O(CO$_2$) being pristine to the UT region sampled. Next is to answer whether the positive $\delta^{17}$O(CO$_2$) of the LMS component can affect $\delta^{13}$C(CO$_2$) determinations by mass-spectrometry ($^{13}$C and $^{17}$O contribute to the same m/z 45). The answer is no. Because $[\delta^{15}$C(CO$_2$)-bias]≈$\delta^{17}$O(CO$_2$)/14, and because $\delta^{17}$O(CO$_2$)<0.5‰, $[\delta^{15}$C(CO$_2$)-bias]$ cannot exceed 0.03‰ for most LMS-enriched samples and be much lower for UT samples having low O$_3$. In the later case the bias is close to or below than the $\delta^{13}$C comparability target (0.01‰ [1]) with is limited by analytical uncertainty.

Figure 2. Samples taken on May 14 and May 19 2001 (was-33 and was-34) demonstrate LMS-UT mixing.

All in all we consider that O$_3$ data can be used as a reliable filter for the LMS contribution, in order to filter out UT air and characterize CO$_2$ composition in the UT region. Of course, fast convection and biomass-burning plumes need to be recognised as well, e.g. by elevated CO and NMCH. (We do not demonstrate that in this manuscript).

Having considered only UT air samples (O$_3$ below the chemical tropopause level) and separated data into several latitude bands, we observe that $\delta^{13}$C(CO$_2$) values of UT air for the equatorial area, the 0-15°N band, are similar to ground-based observations and to JAL data (Figure 3), with discrepancy increasing at higher latitudes. That observation basically reflects air transport and mixing in the troposphere, as well as the fact that most ground stations at high NH latitudes are on continents, close to CO$_2$ sinks and sources with a strong seasonality.
\(\delta^{18}O(CO_2)\) data provide a similar agreement (data not plotted here), but the number of reliable \(\delta^{18}O(CO_2)\) data of CARIBIC-1 is limited and more data are needed to obtain a more consistent picture. A few CARIBIC-1 samples at low NH latitudes shown \(\delta^{18}O(CO_2)\) being higher than the values demonstrated by ground stations. However for these samples back trajectories go to SH, implying some contribution of SH air with \(\delta^{18}O(CO_2)\) being higher than in NH.

\[\text{Figure 3. } \delta^{13}C(CO_2) \text{ data of CARICIC-1 are compared with data produced by NOAA/ESRL ground stations and the JAL. Left panel - latitude band of 0 to } 15^\circ \text{ N, right panel - 35 to } 45^\circ \text{N.}\]

6.2.5 Summary
1. CARIBIC-1 demonstrated that use of commercial aircraft can provide isotope CO\(_2\) data for the free tropical troposphere and the UTLS region. CARIBIC-2 has an expanded instrument package in the container and performs regular fights. More data will become available, also allowing studies of convection and biomass burning plumes.
2. Combination of chemical tracers, meteorological data and air back-trajectories is a promising approach. O\(_3\) data can be used as a reliable filter to recognise and filter out samples affected by LMS/UT mixing.
3. A chain of reasoning implies that \(\delta^{18}O(CO_2)\) in the UT area is little affected by admixture of CO\(_2\) from stratosphere where both \(\delta^{18}O(CO_2)\) and \(\delta^{17}O(CO_2)\) are photo-chemically modified. Possible artefacts/biases for \(\delta^{13}C(CO_2)\) for the UT samples are close to or below the analytical uncertainty.
4. CO\(_2\) isotope data for UT samples (filtered by O\(_3\) data) demonstrate that UT air in low latitudes has \(\delta^{13}C(CO_2)\) and \(\delta^{18}CO(CO_2)\) values that are similar to ground stations, whereas discrepancies are at higher latitudes. The CARIBIC data thus provide valuable background data for the higher latitudes.

Acknowledgements
We thank W. Brand for his kind advice during installation of the CO\(_2\) extraction line at IRMM and H. Matsueda for providing CO\(_2\) data by JAL.

References
Machida T et al. (2007) Presentation on 14th Meeting of Experts on Carbon Dioxide.
Recommendations of 13th Meeting of Experts on Carbon Dioxide.
7.1 Greenhouse Gases Monitoring in India
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7.1.1 Introduction

The quantification of interactions among the atmosphere, biosphere, hydrosphere and lithosphere i.e. bio-geo chemical cycle is necessary to accurately estimate sources and sinks of Greenhouse Gases (GHGs). It requires accurate determination of concentration of these gases and their trends with adequate spatial coverage so as to improve estimates of radiative forcing needed for addressing the climate change issues under UN Framework. About one half of the carbon emitted by combustion remains in the atmosphere, while the other half is taken up by the oceans and terrestrial biosphere. Based on measurements of CO$_2$ abundance, its stable isotopes of carbon and oxygen, and O$_2$/N$_2$ ratios, IPCC 2001 estimated that average uptake was 1.7±0.5 Pg / yr by the oceans and 1.4±0.7 Pg/yr by the land biosphere for the 1990s [Houghton et al., 2001]. These are net fluxes while, gross fluxes between atmosphere and oceans, and atmosphere and terrestrial biosphere (photosynthesis and respiration), are of the order of 100 Pg per yr. Since this partitioning of fossil CO$_2$ between the oceans and biosphere has policy implications, it is important to reduce uncertainties to make better estimates on regional scales (e.g., using inverse modelling to estimate regional fluxes).

Methane is emitted to the atmosphere by natural and anthropogenic sources. Natural sources include wetlands, vegetation, termites, oceans, and geologic sources (e.g., hydrocarbon seeps, hydrates, mud volcanoes). Anthropogenic sources include fossil fuel exploitation, rice agriculture, landfills, domestic ruminant animals, landfills, municipal waste treatment, and biomass burning. Emission rates from many sources are difficult to quantify from the top-down perspective using atmospheric measurements, because fluxes are small, diffuse, and vary by orders of magnitude, both spatially and temporally.

The major natural sources of N$_2$O to the atmosphere are the ocean and soil processes while anthropogenic sources are agriculture, through use of nitrogen fertilizers, biomass burning, industrial processes (nylon and nitric acid production), and cattle feedlots. Though the major sources have been identified, but the uncertainties in emissions from each are still large. Two major sink processes are responsible for N$_2$O removal from the atmosphere, both of them in the stratosphere: photolysis and reaction with electronically excited oxygen atoms (WMO GAW 2007).

The Indian sub-continent and surrounding seas with more than 1.1 billion people and unique natural resources have a significant impact on regional and global environment but lack a comprehensive observational network. India Meteorological Department (IMD) has embarked upon an extensive programme to establish a permanent network of stations in India to monitor atmospheric concentrations of greenhouse gases (CO$_2$, CH$_4$ and N$_2$O) and aerosols in order to quantify source and sink potentials.

7.1.2 Monitoring philosophy

The two main phenomena that affect GHGs variations over the Indian region are the influence of subtropical highs and monsoon wind reversal. The former influences much of the northern parts of the country while the latter would have discernable impacts over the peninsular region. As such, these areas need to be studied in very high temporal resolution (24X365). Hence, the scientific programme of CREM envisages establishment of two baseline stations with continuous monitoring of GHGs at Ranichauri (in the Central Himalayas) and Kodaikanal in the peninsula with having emphasis on long term trends. Both being high altitude stations, are suitable for sampling of free well mixed air over the respective region.

GHGs data from different regions of the country are essential to extrapolate the flux values obtained from Inverse C – Cycle models for different parts of the country in a broad manner. It requires characterizing the zonal variability of GHGs across east-west India and to bring out characteristic features of contrasting areas viz. arid and non-vegetated areas in the west, sub-
humid and deciduous forests of Central India bearing a strong seasonal signature, the humid tropical areas of the NE with dense vegetation and a island station representing maritime climate. Location of planned sites is depicted in Figure 1.

Figure 1. Climate related environment monitoring in India.

7.1.3 Methodology
Monitoring will be carried out using both continuous (baseline) and grab sampling strategies. NDIR, CRDS and Gas chromatography techniques will be used to measure concentration of GHGs under on-line and off-line strategies respectively following WMO/GAW protocols and QA/QC. Collecting discrete samples in specialized flasks at frequency of 3 – 5 per day and analyzing the contents at a Central lab in New Delhi will help supplement the information from the continuous monitoring sites. IMD is being equipped to take apart in inter-calibration activities of GAW/WMO to maintain proper calibration standards and precision requirements.

7.1.4 Greenhouse gas inventories
A greenhouse gas inventory is an accounting of the amount of greenhouse gases emitted to or removed from the atmosphere over a specific period of time (e.g., one year). It also provides information on the activities that cause emissions and removals, as well as background on the methods used to make the calculations. Policy makers use greenhouse gas inventories to track emission trends, develop strategies and policies and assess progress. Scientists use greenhouse gas inventories as inputs to atmospheric and economic models.

In 1994, the aggregate emissions from the anthropogenic activities in India amounted to 7,93,490 Gg of CO₂; 18,083 Gg of CH₄; and 178 Gg of N₂O. In terms of CO₂ equivalent2 (Tg- CO₂ eq.), these emissions amounted to 12,28,540 Gg. The per capita CO₂ emissions were 0.87 t-CO₂ in 1994, 4 percent of the US per capita CO₂ emissions in 1994, 8 percent of Germany, 9 percent of UK, 10 percent of Japan and 23 percent of the global average. CO₂ emissions contributed, 65 per cent of total GHGs; CH₄ contributed 31 per cent and four per cent of emissions were contributed by N₂O (Figure 2.1). On a sectoral basis, 7,43,820 Gg CO₂-equ. of GHGs were emitted from energy sector (61 per cent); 3,44,485 Gg of CO₂-equ. emissions came from the agriculture sector (28 per cent); 1,02,710 Gg of CO₂-equ. were contributed by the industrial processes (8 per cent); 23,233
Gg from waste disposal (2 per cent) activities and 14,292 Gg were generated from land use, land-use change and forestry sector (1 per cent) \((NACOM 2004)\).

7.1.5 INDOFLUX

Another programme “INDOFLUX” has also been planned to integrate terrestrial, coastal and oceanic environment to refine the Global Carbon Cycle model by using the gridded inventory of regional fluxes and confirming the ambient concentrations from the baseline data of the Indian region. The programme envisages to monitor different parameters like biogenic gas flux \((\text{CO}_2, \text{CH}_4 \text{ and } \text{N}_2\text{O})\), net radiation balance, PAR, aerosol optical thickness, fluxes of \text{CO}_2, heat, energy and momentum, evapotranspiration, air temperature, wind, land use changes, precipitation, soil moisture, soil temperature, sea surface temperature, light attenuation, soil nutrients, salinity, total suspended solids, primary production, soil respiration, aquatic respiration leaf area index, aerosol deposition etc. the data will support economic and strategic co-operation and collective actions internationally (Figure 2).

Figure 2. Proposed INDOFLUX network in India.

Acknowledgements

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References


7.2 Greenhouse Gas and Trace Gas Measurements Programme in New Zealand

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7.2.1 Introduction

New Zealand is located in the mid latitudes of the South Pacific, where the atmosphere is heavily influenced by the Southern Ocean and is therefore ideal for observations of atmospheric carbon dioxide relatively unaltered by local sources. Since 1970 observations of CO₂ have been made at Wellington, and from 1973 at Baring Head (41.41 °S, 174.87 °E). This coastal site is a GAW regional station and is located at the top of an 80m cliff. The site is exposed with either strong northerly or southerly winds dominating the meteorology; air arriving at the site approximately 30 % of the time is from a baseline southern oceanic sector.

![Figure 1. Cluster analysis of 4 day back trajectories for Baring Head. Trajectories with similar features are grouped into clusters providing a mean trajectory for each cluster.](image)

7.2.2 Baring Head clean air station

Measurements of greenhouse gas species are either continuous observations in the case of CO₂ and O₂, or discrete samples in the case of the other species. These discrete samples are collected either on demand remotely or when the CO₂ concentration has been stable to within 0.2 ppm for the last four hours. The ^14CO₂ observations are made by integrating the air over a 10 day period.

Calibration to the appropriate scale is maintained through regular re-calibration of primary gases and the use of IAEA reference materials.

Intercomparison programmes are maintained with other labs for concentration and archive tanks are used to maintain isotope record integrity over length of the time series. Data are
available through WDCGG and NIWA ftp.

Table 1. Measurements of greenhouse gases and related species made at Baring Head Clean Air Station by NIWA

<table>
<thead>
<tr>
<th>Species</th>
<th>Started</th>
<th>Method</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1970</td>
<td>NDIR</td>
<td>NOAA04</td>
</tr>
<tr>
<td>^13CO₂</td>
<td>1996</td>
<td>GC-IRMS</td>
<td>V-PDB (NBS19)</td>
</tr>
<tr>
<td>^14CO₂</td>
<td>1954</td>
<td>AMS</td>
<td>NBS oxalic acid</td>
</tr>
<tr>
<td>CH₄</td>
<td>1989</td>
<td>GC FID</td>
<td>NIST moving to NOAA05</td>
</tr>
<tr>
<td>^13CH₄</td>
<td>1987</td>
<td>IRMS</td>
<td>V-PDB (NBS19)</td>
</tr>
<tr>
<td>N₂O</td>
<td>1996</td>
<td>GC ECD</td>
<td>SIO moving to NOAA</td>
</tr>
<tr>
<td>CO</td>
<td>1989</td>
<td>GC RGA</td>
<td>NOAA</td>
</tr>
<tr>
<td>^13CO</td>
<td>1989</td>
<td>IRMS</td>
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<tr>
<td>^14CO</td>
<td>1989</td>
<td>AMS</td>
<td>NBS oxalic acid</td>
</tr>
<tr>
<td>O₂</td>
<td>1999</td>
<td>Paramagnetic</td>
<td>SIO</td>
</tr>
</tbody>
</table>

7.2.3 Carbon dioxide

![Figure 2](image_url)

Figure 2. The CO₂ concentration in stable clean air conditions for Baring Head. Air is considered clean when the concentration is within 0.2 ppm for 4 hours.

Since measurements began the concentration of atmospheric CO₂ has risen by over 50 ppm, from 324 ppm to a mean annual concentration of 378 ppm in 2006. During the decade of the 1970's the average growth rate was 1.2 ppm/yr, and through the 1980's and 1990's the rate was 1.5 ppm/yr. From 2000 the mean annual growth rate has increased to 1.9 ppm/yr.

![Figure 3](image_url)

Figure 3. The growth rate of atmospheric CO₂ in clean air at Baring Head, calculated as a 12 month running mean.
7.2.4 **Methane**
Observations at both Baring Head and Arrival Heights, Antarctica of CH₄ concentration and δ¹³CH₄ have enabled us to model chlorine sink processes (Allan 2005, Allan 2007) for CH₄. The apparent kinetic isotope effect (KIE) variability and magnitude cannot be explained by OH sink processes alone. A mean atomic Chlorine sink for atmospheric methane of 25 Tg y⁻¹, would enrich the δ¹³C by 2.6 ‰ and help explain the observed KIE.

7.2.5 **Carbon monoxide**
The variability of hydroxyl radical concentrations on time scales of months and years have been assessed through interpretation of a 13 year time series of atmospheric ¹⁴CO (Manning 2005). This species is oxidized by hydroxyl radicals and analysis suggests that although there have been short periods where reductions of the order of 10% in OH concentrations have occurred, there is no evidence for long term changes in OH concentrations.

7.2.6 **Other activities**
NIWA also runs a flask and cylinder collection programme at Arrival Heights Antarctica (77.80°S, 166.67°E, 184m) where air samples are collected monthly for later analysis. In collaboration with NIES Japan and GCOS transects across the Pacific collect air-samples several times a year. pCO₂ measurements over ten years from New Zealand subtropical waters to subantarctic surface water.

7.2.7 **Future plans**
Continuous measurements of CO₂ aboard the NIWA vessel the RV Tangaroa. This ship operates from North of New Zealand to the Ross Sea in Antarctica and operates a full meteorological station. Implementation of a CO₂ measurement system at Lauder which will act as a ground truth station for the Orbiting Carbon Observatory. Collaboration on methane inter-comparisons with University of the South Pacific in Fiji.

**Acknowledgements**
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**References**


7.3 Recent Changes in Trace Gas Levels at Cape Point, South Africa

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7.3.1 Introduction
Measurements of the environmentally important trace gases CO₂, CH₄, N₂O, CO and O₃ have been made at Cape Point (34 °S, 18 °E) spanning differing time periods. Observations range from 14 complete years for CO₂ to 28 years in the case of CO. With respect to N₂O, the first seven years (1989 – 1995) have been excluded from current analyses because of lower data quality. Here the latest trend and growth rate estimates for these five gases, based on data filtered with respect to background concentrations, are presented. It should be noted that the temporal variability of trend curves and growth rates is highly dependent on the degree of smoothing chosen for the calculations. In addition, trends of CO₂ and CH₄ have been determined for non-background conditions covering the past ten years.

7.3.2 Results and discussion
CO₂ levels at Cape Point have increased from 354.6 ppm, when measurements commenced in 1993, to 379.4 ppm at the end of 2006 (Figure 1a). Growth rates, calculated as derivatives of the trend curve, fluctuated between 1.5 and 2.2 ppm yr⁻¹ (as obtained with 5-year smoothing) and displayed an overall increase. Linear regression performed on the growth rates indicates an increase of the fit from 1.6 ppm yr⁻¹ in early 1993 to 2.1 ppm yr⁻¹ at the end of 2006 (Figure 1b).
For CH₄, an overall decrease in growth-rates, fluctuating markedly over the years, has been observed since 1983 (Figure 2, top). Methane levels have stabilized since 2003, and during 2006 the CH₄ growth rate even dropped to about -1 ppb yr⁻¹. A linear fit of the growth rates yields values of 13 ppb yr⁻¹ for the beginning of 1983 and zero growth for mid-2005 (Figure 2, bottom).

From 1982 till the mid-1990s the non-background CH₄ trend has closely matched that of the background data. However, thereafter non-background levels have continued their upward trend till present (Figure 2, top). There is evidence (see below) that this is probably related to growing local sources to the north of the station.

![Cape Point: CH₄ (1983-2006)](image)

**Figure 2. CH₄ time series (top) and CH₄ growth rates (bottom).**

![Cape Point: CH₄ growth rates (1983-2006)](image)

Wind sector-dependent growth rates for CO₂ and CH₄ have been determined on the basis of monthly averages and medians. The rates reveal an enhanced long-term increase for both gases within the northerly sector (Figure 3). For CO₂, the ppm-per-year increase was 3.2 % higher
than for background conditions (1.94 vs. 1.88 ppm yr\(^{-1}\)). Similar calculations for CH\(_4\) yielded a 55 \% higher rate relative to background (3.74 vs. 2.41 ppb yr\(^{-1}\)). Due to the underlying CH\(_4\) concentration distribution, the medians yielded a smaller difference between the rates. The increased trends as associated with air advected from the north of Cape Point most probably reflect the recent expansion of the greater Cape Town area.

The N\(_2\)O mole fractions as measured at Cape Point have increased from 311 ppb in 1996 to 319 ppb in 2006. The data display a nearly constant growth rate, yielding an average of 0.72 ppb yr\(^{-1}\).

Over most of its 28-year measuring period, the CO time series has not displayed any significant long-term trend, although some inter-annual variability is evident (Figure 5). However, since 2003 an overall decline has been observed in the CO mole fractions, which culminated in an abnormally low annual minimum during February 2006 as well as a lower than usual annual maximum in October 2006. Reduced 2006 CO levels have also been observed at other SH sites. The underlying causes are still being investigated.

For O\(_3\) a positive trend was recorded between 1990 and 2002, accompanied by an increase in seasonal peak-to-peak amplitudes. Since 2003 the increase has levelled off again.

![Figure 4. CO time series with regression curve and trend.](image)

![Figure 5. Time series of surface ozone at Cape Point.](image)

**Acknowledgements**

We are indebted to our colleagues, D. van der Spuy for instrumental maintenance and for having processed the raw data as well as to B. Parker for his IT support and administrative management.
7.4. Carbon Dioxide and Methane Concentration and Flux Measurements at the GAW station of Pallas-Sodankylä

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7.4.1 Introduction

The Pallas-Sodankylä GAW station consists of two nodes. The in-situ trace gas and aerosol observations are made at Pallas in western part of Lapland (Figure 1). At Sodankylä, located 125 km to the east, there is the Arctic Research Centre of FMI. There we measure many kinds of advanced observations, for example ozone soundings, total ozone, and Aerosol Optical Depth, in addition to routine meteorological and sounding observations. Sodankylä has also a micrometeorological CO₂ flux site in a Scots pine forest, which is the most widespread forest type in Lapland. At Sodankylä, column CO₂ and CH₄ measurements will start using very high-resolution Fourier Transform Infra Red spectroscopy of solar radiances. It is planned that the site will join Total Carbon Column Observing Network (TCCON).

This short report will, however, describe the activities at Pallas which is a complex of sites for observations of GHG concentrations, aerosols and ecosystem fluxes. Trace gas concentrations, calibrated according to GAW-standards, are measured at main site, Sammaltunturi. Two ecosystem flux sites Kenttärova (micrometeorological CO₂ flux measurements above a spruce forest) and Lompolojänkkä (CO₂ and CH₄ flux measurements in a wetland) observe fluxes year round. In addition the area has two other stations, Matorova (filter and wet deposition sample collection) and Laukukero (automatic weather station). More detailed description of the stations and overview of the results, except for Lompolojänkkä, can be found in Hatakka et.al. (2003).

![Figure 1. Locations of FMI's measuring stations at Pallas.](image)

7.4.2 Sammaltunturi

Sammaltunturi is the main site at Pallas measuring continuously ozone, SO₂, NOₓ, CO₂, CO, CH₄, N₂O, SF₆, H₂, aerosol size distribution, scattering, absorption and number concentrations, radon, and different meteorological parameters. In addition canister samples are collected twice weekly for volatile organic compound analysis at FMI. NOAA cooperative sampling
network flasks have been collected weekly. Auditing was performed in 2007 by WCC-Empa laboratory for selected measurements and for the infrastructure of the station. Methane results were in good agreement with Empa and no further recommendations were made. The infrastructure was found to be state-of-the-art.

For the CO₂ measurements, which are measured by LI-7000, a new set of six WMO/CCL CO₂ standards was acquired in 2007. A GC with FID and μECD detectors with external interface and a custom made programme is used for measuring CH₄, CO, N₂O and SF₆. Carbon monoxide is measured with FID after converting it to methane with a Nickel catalyst. Working standards are calibrated against 3 CH₄/CO, and 5 N₂O/SF₆ standards from WMO/CCL (NOAA) a few times a year. These cylinders were recalibrated by NOAA in 2007. Measurements of H₂ and CO started in 2007 using Peak Performance 1 RCP instrument. Presently, we have four Exeter cylinders for calibration, filled and measured in Max Planck In, Jena. We have participated in intercomparisons organized by CARBOEUROPE and EUROHYDROS projects to follow the quality of the measurements. Back trajectories are calculated routinely for the station, 8 trajectories a day with 120 hour length. These trajectories have been used to classify transport of methane to the station (Aalto et al., 2007). The CO₂ concentrations show seasonal cycle typical for northern boreal regions (Figure 2).

Figure 2. Daily average CO₂ concentrations at Sammaltunturi.

7.4.3 Kenttärova

Kenttärova lies on a hill top plateau ca. 60 m above the surrounding plains. A 20 m high measurement tower is situated in a Norway spruce forest aged between 70 and 170 years. At the station CO₂ and sensible and latent heat fluxes are measured using eddy covariance technique at the height of 23 m (Aurela et al, 2005). The high-frequency (10 Hz) instruments for flux measurements are Metek USA-1 sonic anemometer and LiCor-7000 CO₂/H₂O analyzer. Fluxes are calculated as 30 min average covariances and appropriate corrections for the fluxes are made by software made at FMI. Calibrated CO₂ concentrations are measured at three different heights (gradient), and during summer also automated respiration chamber measurements are conducted at the site. In addition, the station has extensive set of meteorological measurements, including
temperature and humidity profiles in air and soil, global and reflected solar radiation, long-wave radiation upwards and downwards, photosynthetic photon flux density (PPFD), net radiation, snow cover depth and cloud layer height.

![Figure 3. Daily average CO2 concentrations from Sammaltunturi mountain top station together with daily average net CO2 fluxes at Kenttärova spruce forest both showing the signal from the boreal vegetation.](image)

An example of CO2 fluxes and concentrations for year 2003 is given in Figure 3. Half hourly CO2 fluxes are processed to daily averages. We observe net respiration (positive fluxes upward) during winter, from September to April. Commencement of photosynthesis occurs in April and net daily fluxes turn downwards in May. Often there is still some snow on the ground then. The net uptake has its maximum in July when in full daylight conditions flux is around 0.4 mg CO2 m^-2 s^-1. Daily net uptake starts to decrease in August when days get shorter and ecosystem respiration is still relatively high. The forest turns to net CO2 source in the end of August – early September. Seasonal trend of atmospheric concentrations at Sammaltunturi, located at 200 m higher elevation, follow the forcing of the net fluxes by the forest (Thum et al., 2008). Obviously it is not only the local forests which affect atmospheric concentrations at Sammaltunturi but the source area is much larger. However, we can say that the flux observations catch the main features of the ecosystem CO2 exchange in the boreal region.

### 7.4.4 Lompolojänkkä

Lompolojänkkä is a subarctic aapa mire (wetland). The measurement site was established to quantify the local source because of observed elevated CH4 concentrations at Sammaltunturi. Measurements at the station include CO2 and CH4 fluxes by eddy covariance technique, and CO2 and CH4 concentrations at two heights. The CO2 flux measurement system at Lompolojänkkä is similar to that at Kenttärova, except for measurement height, 2.5 m. For the CH4 fluxes, we use a high flow TDLaser. Calibrated ambient air CH4 and N2O concentrations are measured chromatographically by FID and ECD. This system has four minute cycle period and uses one working standard of dried natural air. During growing season emissions are measured also by two automated chambers.
This *aapa* mire is a net source (positive fluxes upwards in Figure 4.) of CO$_2$ to the atmosphere except during the growing season, June – August, when negative daily average net balances show that it is a sink. Typical noontime net uptake rates of about 0.3 mg CO$_2$ m$^{-2}$ s$^{-1}$ in midsummer (Aurela et al., submitted). It is relatively high uptake rate because this is a nutrient rich fen. Over the year it is a net CO$_2$ sink. Methane emissions are high due to the minerotrophy and sedge dominated vegetation. These plants have internal conduits which provide oxygen to the roots and at same time transfer methane directly from the root zone to the atmosphere. Micrometeorological observations show that methane emissions continue through winter because only very top layers of the mire are frozen. Emissions are elevated during the period of snowmelt in May, possibly causing higher atmospheric concentrations at Sammaltunturi site. During the growing season emissions are high and depend mostly on temperature and phenology of the vegetation. In September, emissions decline and after that wetland emissions have only minor effects on the concentrations at Sammaltunturi.

![Graph](image)

*Figure 4. Daily average methane and carbon dioxide fluxes at the mire site (upper panel) and hourly methane and carbon dioxide concentrations at the main GAW-site in 2007 (lower panel). The wetland emission of methane are clearly visible in the Sammaltunturi arctic mountain top site ambient air concentrations in June – early September period.*

**7.4.5 Conclusions**

The flux and concentration measurements at the forest and wetland sites, 200-300 m below the hilltop site, help us to quantify the effect of surrounding vegetation and changing weather on the concentrations at the GAW main site. Concentration and flow field in the area have been
simulated using a fluid dynamics model to further understand modifications of the concentrations at the GAW site by the local terrain and natural sources (Aalto et al., 2006). Further developments at Pallas include starting of continuous VOC concentration measurements during 2009 at Sammaltunturi.

References
7.5 Set-Up of a New Continuous Greenhouse Gas Monitoring Station for CO₂, CH₄, N₂O, SF₆, and CO in Northern Italy
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7.5.1 Introduction
The Institute for Environment and Sustainability of European Union Joint Research Centre in Ispra, Italy (JRC-Ispra) is currently setting up a new continuous long-term greenhouse gas (GHG) monitoring station for CO₂, CH₄, N₂O, SF₆, and CO in Northern Italy. The rational behind this project is 1) to contribute to the sparse near-ground continuous GHG monitoring network in Southern Europe, 2) to support inverse modelling “top-down” emission estimates for Northern Italy (notably the Po Valley area) using the new TM5 4DVAR modelling technique (Bergamaschi et al., 2007; Meirink et al., 2007), and 3) to follow and verify the development of GHG trends in Southern Europe in relation to emission reduction measures under the Kyoto protocol (and further emission reduction programmes).

From the end of September 2007 onwards we started the quasi-continuous monitoring of CO₂, CH₄, N₂O, and SF₆ at the JRC-Ispra site (215 m ASL) with a gas chromatography (GC) system based on the set-up by Worthy et al. (1998) utilising a 15 m mast (to be extended in the near future to 32 m). Carbon monoxide and other air quality data are available from the co-located Ispra EMEP/GAW station. Beside measurements from a small tower at the JRC site we plan to set-up a second GHG monitoring site at the meteorological station of the “Centro Geofisico Prealpino” of Varese on top of the nearby “Campo dei Fiori” mountain (1200 m ASL, 10 km north of the institute) to be in operation by autumn 2008. Ultimately, the dual valley-and-mountain station allows us to study and compare GHG observations at the bottom and the top of the boundary layer. In addition, we intend to include a direct ²²²Rn monitor (ANSTO) to complement the Ispra monitoring site (Zahorowski et al., 2004). The location of Ispra and nearby mountain station site is shown in Figure 1.

Figure 1. Overview of JRC Ispra area GHG monitoring sites (left panel) and the present high altitude GHG sites around the Po valley (right panel).
7.5.2 System set-up and performance

The GHG GC-system runs at a time resolution of 6 minutes. An hourly sequence of measurements starts with a working high and working low standard followed by six ambient samples and is completed with a working high and working low standard (making 10 measurements per hour). The instrument precision, based on the measurement of a target gas cylinder replacing two ambient samples every 6 hours, is typically 0.08 ppmv for CO₂, 1 ppbv for CH₄, 0.4 ppbv for N₂O and 0.18 pptv for SF₆ (for 10 days of continuous sampling). The working standards themselves are calibrated against 3 high precision primary standards provided by NOAA/ESRL. A schematic of the JRC Ispra GHG GC system and typical chromatograms for the FID and ECD are shown in Figure 2.

![Schematic of the JRC Ispra GHG GC system (left panel) and typical chromatograms for the FID and ECD channel (right panel).](image)

7.5.3 Meteorology and air quality in the Ispra area

Precipitation in the area is mainly in the form of short periods of intense rain by synoptic disturbances during winter and early spring, as well as thunderstorms during the summertime and early fall. In general, the relative humidity (RH) in the Ispra area is moderate to high (60-80%) throughout the summer and occasionally high during winter, but the air can also be very dry especially during Föhn episodes were RHs can drop to <20%. These Föhn episodes (lasting typically for a few days up to a week) bring relative clean northwesterly air masses from the Alps to the region and can be accompanied with strong gusty winds.

Based on meteorological observations from the meteorological station on top of the Campo dei Fiori for the year 2006 (data by courtesy of Prof. Salvatore Furia, Centro Geofisico Prealpino, Varese, Italy) as well as back-trajectory analysis based on ECMWF wind fields (not shown here), we find that for the whole year the wind direction is roughly equally dominated by a northwesterly and southeasterly flow. However, on a seasonal time scale, shown in Figure 3 (left panel), the predominant wind direction appears to be southeasterly during summer and northwesterly during winter.

Daily mean CO and O₃ concentrations for the Ispra area (EMEP/GAW site data for the year 2002) shown in Figure 3 (right panel) indicate that CO concentrations are lowest during late spring to early autumn and can be by a factor of 10 higher during winter. This is mainly related to emissions from local domestic wood burning for residential heating that get trapped in the shallow winter inversion layer, especially during low-wind high-pressure episodes. The ozone concentrations are highest during summer when photochemical production conditions are optimal and a southerly flow is moving highly polluted humid air masses from the Po valley to the area. Preliminary results from our GHG monitoring system show strong accumulation of GHG in the
winter night-time inversion layer with concentrations up to 500 ppmv of CO₂, 2400 ppbv of CH₄, 330 ppbv of N₂O, and 8 pptv of SF₆, together with strongly elevated CO, black carbon and particulate matter concentrations (detected at the nearby EMEP/GAW station). On the contrary, relatively clean air masses can be brought to the Ispra area by a northwesterly flow over the Alps containing near continental background GHG concentrations levels.

![Campo dei Fiori daily mean wind direction year 2006](image)

**Figure 3.** Air mass origin for the Campo dei Fiori for the year 2006 based on daily mean wind direction for the year 2006 (left panel) and daily mean CO and O₃ concentrations for the from the Ispra EMEP/GAW site data for the year 2002 (right panel).

### 7.5.4 Summary and outlook
A quasi-continuous high precision GHG monitoring system for CO₂, CH₄, N₂O, and SF₆ has been set-up successfully at the JRC Ispra and is in operation since end of September 2007. The set-up of complementary GHG monitoring system on top of the nearby 1200 m Campo dei Fiori mountain is in preparation to be in operation by Autumn 2008. In addition, a direct ²²²Radon monitor will be included at the JRC-Ispra site to allow for regional radon calibrated “top-down” GHG emission estimates and to support the TM5 model transport scheme evaluation. Wind direction as well as back-trajectory analysis indicates that the Campo dei Fiori mountain station has good potential for becoming an important continuous monitoring station representative for northern Italy (notably the Po Valley). The station data will allow us to optimize inverse modelling “top-down” greenhouse gas emission estimates for these regions with the new TM5 4DVAR inverse modelling system (Bergamaschi et al., 2007).

### Acknowledgements
We kindly acknowledge the constructive advice and input of Martina Schmidt and colleagues (LSCE Paris), Ingeborg Levin and colleagues (University Heidelberg), Rolf Neubert and colleagues (CIO Groningen), Alex Vermeulen (ECN Petten), and Doug Worthy (Environment Canada).

### References


7.6 Non-CO₂ Greenhouse Gas Mixing Ratios at Jungfraujoch, Switzerland
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Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Air Pollution/Environmental Technology, Ueberlandstrasse 129, CH – 8600 Duebendorf, Switzerland.

7.6.1 Introduction
The Swiss high-Alpine site Jungfraujoch is the highest worldwide station providing a comprehensive measurement programme of essential climate variables of atmospheric composition in full compliance with the Global Climate Observing System (GCOS) implementation plan. Continuous observations of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and halons by Empa started in 2000, measurements of methane, nitrous oxide, and sulphur hexafluoride were commenced in February 2005. Concentrations of molecular hydrogen are continuously recorded since summer 2005. Continuous observations of CO₂ by the University of Berne (Leuenberger et al., 2005; Uglietti et al., 2007) and of aerosol properties by the Paul Scherrer Institute (Cozic et al., 2007) complete the measurement programme. These long-term in-situ observations are used for trend analyses, investigations of transport processes, as well as the allocation and quantification of emissions and their trends, e.g. for an independent verification of compliances with the Kyoto- and Montreal Protocol.

7.6.2 Sampling site
The high altitude research station Jungfraujoch (JFJ, 7° 59' E, 46° 32' N, 3580 m a.s.l.) is situated on a mountain saddle in the central Swiss Alps between the Jungfrau mountain (4158 m a.s.l.) in the West and the Moench mountain (4099 m a.s.l.) in the East. Due to its unique place, the year-round accessibility, and the excellent infrastructure, the Jungfraujoch research station is well suited for long-term ground-based monitoring of trace gas mixing ratio trends in the free troposphere. It is also an appropriate study site for European regional source allocations during pollution events due to its location in central Europe and its proximity to anthropogenic greenhouse gas source regions (Reimann et al., 2004; Reimann et al., 2005b).

7.6.3 Experimental
23 individual halocarbons are automatically analyzed by gas chromatography-mass spectrometry (Agilent 5793N). The individual compounds are quantified by single ion mass spectrometry of selected characteristic ions and their specific chromatographic retention times. The measurements are part of the SOGE network (System for Observation of Halogenated Greenhouse Gases in Europe), where halogenated organic compounds are measured continuously at 3 additional background sites in Europe (Mace Head, Ireland; Ny-Alesund, Spitsbergen and Monte Cimone, Italy). SOGE is related to the world-wide AGAGE programme (Advanced Global Atmospheric Gases Experiment) in terms of measurement techniques, standard propagation and quality assurance. The experimental aspects of the halocarbons are described in detail in numerous publications (Simmonds et al., 1995; Reimann et al., 2004; Reimann et al., 2005b; Vollmer et al., 2006; Stemmler et al., 2007; Reimann et al., 2007).

CH₄, CO, N₂O, and SF₆ are quasi-continuously measured using an Agilent 6890N gas chromatograph equipped with a flame ionization detector (FID) for CH₄ and an electron capture detector (ECD) for N₂O and SF₆. Each ambient air sample is bracketed with calibration runs using real-air standards (working standards) with concentrations representative for Northern Hemisphere tropospheric concentrations. The real-air standards are analysed for CH₄ by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane based on NOAA ESRL certified gas cylinders. A comparison with AGAGE standards showed an agreement well within the precision of the measurement. N₂O and SF₆ concentrations in the working standards were determined by cross-calibration with AGAGE standards. These results are currently reported on the SIO-98 (for N₂O) and SIO-2005 (for SF₆) calibration scales (Prinn et al., 2000, Vollmer and Weiss, 2002).
A commercial gas chromatograph (Reduction Gas Analyzer (RGA-3), Trace Analytical, Inc. California, USA) is used to measure H$_2$ and CO via reduction of mercuric oxide and detection of mercury by UV absorption.

Besides the greenhouse gas and related tracer measurements the measurement programme of Empa at Jungfraujoch also includes continuous in-situ analyses of ozone (O$_3$), carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO$_2$), the sum of nitrogen oxides (NO$_y$), and sulphur dioxide (SO$_2$). Daily samples are taken for the determination of particulate sulphur. The concentrations of PM10 are continuously observed as well as measured as 24-hour bulk samples.

7.6.4 Results

Figure 1 shows the time series of the cooling agent HFC-134a from 2000 to 2007 for the 4 SOGE stations. The observed concentrations at JFJ compare very well with other background stations when sampling unpolluted air masses. In contrast to the more remote sites in Ny-Alesund and Mace Head, JFJ is also occasionally under the influence of polluted air masses due to its location in central Europe and its proximity to anthropogenic source regions. When combining measurements and trajectory statistics such events can be used to allocate source regions in Europe (see Figure 2). Whereas HFC emissions are mainly originated from the highly industrialized Po Basin in Northern Italy only little emissions can be still observed for the Montreal Protocol restricted CFCs and HCFCs. This approach was also already applied for less reactive oxygenated volatile organic compounds at JFJ (Legreid et al., 2007).

Nevertheless, background concentrations that correspond very well with the data from more remote sites can be determined when extracting conditions using appropriate statistical (see e.g. Reimann et al., 2005b) or meteorological filters (Forrer et al., 2000) when JFJ is under the influence of pristine air masses.

Besides the rather qualitative approach of determination of European source regions, pollution events are also used for quantitative emission estimates. Figure 3 illustrates estimates of the Swiss emissions of the Kyoto Protocol targeted greenhouse gases CH$_4$ and N$_2$O. The estimates in blue are based on measured trace gas ratios to carbon monoxide during pollution events at JFJ. These ratios allow - under the assumption of known CO emission sources for Switzerland – an independent experimental verification of other reported emissions. Our results for 2005 agree well with the Swiss greenhouse gas inventory based on economic data that is provided by the Swiss Federal Office for the Environment according to UNFCC and IPCC guidelines (see www.climatereporting.ch).

Figure 1. Mixing ratios of the cooling agent HFC-134a at the 4 SOGE stations (Reimann et al., 2005a, updated).
Figure 2. Potential European source regions of several anthropogenic halocarbons in the year 2005, by combining measurements and trajectory statistics at Jungfraujoch. Units indicate averaged relative excursions above the baseline, linked to trajectories that passed over the respective grid cell (Reimann et al., 2007).

Figure 3. Comparison of Swiss CH$_4$ and N$_2$O emissions from the Swiss greenhouse gas inventory and observation derived estimates.

Long-term measurements of halocarbons are also used to assess the consequences of international treaties regulating their emissions. For this purpose recent quasi-continuous observations of non-CO$_2$ greenhouse gases at the high-Alpine site Jungfraujoch were combined with reconstructed histories and other long-term time series. This combination allows assessing the current global radiative forcing budget of non-CO$_2$ greenhouse gases at JFJ and the influence of regulations due to the Montreal Protocol on Substances that Deplete the Ozone Layer in terms of climate change. Extrapolated atmospheric greenhouse gases trends from 1989 assuming a business-as-usual scenario, i.e. no Montreal Protocol restriction, were used and compared to the observations (see Figure 4).
The observed trends and the prevented increases were subsequently multiplied with the radiative efficiencies of the respective gases. This approach showed that the Montreal Protocol did not only succeed to reduce the ozone depletion but also contributed to alleviate the increasing atmospheric greenhouse effect already before the Kyoto Protocol came into force (Steinbacher et al., 2007). Thus, measures taken to protect stratospheric ozone are also beneficial in terms of global warming.

7.6.5 Conclusions and outlook

The Empa activities at the high-Alpine site Jungfraujoch comprise perennial long-term measurements of trace gases in line with GCOS recommendations, trajectory analyses and the consideration of existing emission inventories. The combination of these approaches allows:

- To identify trends of GHGs by applying appropriate background filters.
- To independently verify emission inventories based on economic data.
- To allocate potential source regions for various trace gases.

These 3 techniques enable an independent verification of compliances of the Kyoto- and Montreal Protocol.

Future improvements are planned to achieve by activities that include:

- The application of more advanced background/pollution event determination approaches.
- The extension of the analysis to longer time series.
- The integration of other sampling sites in Europe to get more reliable source apportionments.

Acknowledgements

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References


7.7 Progress on the Background Greenhouse Gases and Related Tracers Measurement Programme in China
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7.7.1 Introduction
Since 1990, CMA has been participating actively in the GAW supporting global networks for greenhouse gases and other atmospheric components. Scientific aim is to obtain observational constraints on the global and regional budget, including global and regional burden, long-term trend, and annual variations in trend, seasonal cycles, and spatial variations, and use the observations to quantify sources and sinks.

7.7.2 Site and in-situ measurement programme
Mt. Waliguan is located in a drought temperate climatic zone surrounded primarily with low grasslands and mountainous regions. Atmospheric CO2 has been measured using a Licor6251 non-dispersive infrared (NDIR) analyzer since 1994. Atmospheric CH4 has been measured quasi-continuously by using a Hewlett Packard (HP) 5890 Series II gas chromatograph (GC) equipped with a flame ionization detector (FID) since 1994. Ambient air is supplied via 3/8 o.d. Dekobon tubing extending 80 m up the tower, approximately 5 m away from the laboratory.

7.7.3 Measurement scale and calibration (traceability)
In-situ atmospheric CO2 and CH4 measurements at Mt. Waliguan are indirectly traceable to the international absolute WMO mole fraction scale maintained by the WMO Central Calibration Laboratory (hosted by NOAA ESRL). Two sets of six secondary tanks are run against each other periodically to check internal consistency. Working standard gases are filled at WLG and calibrated by the secondary standard gases before and after use. The CO2 data from 1994 to 2007 has been adjusted to be consistent with the WMO X2007 scale. The CH4 standard scale at Waliguan is relative to a CH4 measurement scale maintained by the Meteorological Service of Canada (MSC). The MSC CH4 scale has been compared with the NOAA ESRL CH4 scale through several inter-comparison experiments. The CH4 data at Waliguan from 1994 to 2007 has been adjusted to NOAA-2004 CH4 scale.

7.7.4 Data Processing and time series
Hourly averaged CO2 data is computed from valid minute data for one hour measurements. Hourly averaged data are selected using “R” based on an algorithm “robust local regression” to distinguish samples of regionally representative air (background) from samples influenced by local sources and sinks (non-background). Using this statistical method, the acquired rate of the valid data which were categorized as background CO2 values are about 70%. Daily averages are based on those background hourly averages only. Monthly averages are computed from the daily averages. Hourly CH4 data are generated by arithmetic means from the valid raw data (typically 6-7 injections per hour). Valid hourly data are selected using “R” based on an algorithm “robust local regression” to distinguish samples of regionally representative air (background) from samples influenced by local sources and sinks (non-background). About 50% of the data were categorized as selected background CH4 values. The arithmetic means of selected hourly data has been used to generate daily and monthly data. Figure 1 showed atmospheric CO2 and CH4 hourly average data from July 1994 to December 2007 at Mt. Waliguan.
Figure 1. Atmospheric CO$_2$ and CH$_4$ hourly average data from July 1994 to December 2007 at Mt. Waliguan (WLG, 36°17'N, 100°54'E, 3816m asl), western China.

7.7.5 Contribution and near future plan of CMA

Sixteen years of flask sampling data from the cooperative China-U.S. greenhouse gases measurements programme at Mt. Waliguan (36°17'N, 100°54'E, 3816m asl) in Western China are used effectively to help produce 3D annual global carbon cycle greenhouse gases pictures and to contribute the GlobalView-CO$_2$ and GlobalView-CH$_4$ data products. Figure 2 showed seven GAW stations in China and the 3D annual global carbon cycle greenhouse gases pictures with red lines indicate measurement data from Mt. Waliguan. The CMA is going to highlight and enhance collaboration with advanced/experienced international organizations and institutions to set-up an integrated greenhouse gases and related tracers observational system, to make in-situ and discrete measurements (including atmospheric CO$_2$, CH$_4$, N$_2$O, SF$_6$, CO, H$_2$, halogenated compounds, $\delta^{13}$C & $\delta^{18}$O in CO$_2$) from the GAW stations in China under the GAW framework. The measurements will be carefully calibrated on internationally agreed reference gas scales, and quality controlled, so that the measurements in China are an integral part of the global international effort to make continuous measurements of greenhouse gases. The results will be studied for trends in space and time, and for relationships between trace gases and with environmental variables. The objectives is to provide high quality data from a number of typical background regions of China to permit climate and carbon cycle modellers to improve our understanding of the carbon cycle and predict how the atmosphere and climate will evolve in the future as a result of human's activities.
Figure 2. The seven GAW stations in China (left figure) and the 3D annual global carbon cycle greenhouse gases pictures (right figure) showing atmospheric CO$_2$, $\delta^{13}$C & $\delta^{18}$O in CO$_2$, and CH$_4$, CO, N$_2$O, SF$_6$. Red lines indicate measurement data from Mt. Waliguan (WLG, 36°17'N, 100°54'E, 3816m asl), western China.

References


7.8 Results from the Tall Tower Measurement Station for Atmospheric Greenhouse Gases at Bialystok, Poland

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3 University of Leeds, Leeds, UK
4 University of East Anglia, Norwich, UK

7.8.1 The Bialystok station

The tall tower measurement station near Bialystok, Poland (53°13ʹN, 23°01ʹE, 183 masl) was set up in 2005 as part of the tall tower atmospheric measurement network formed under the EU project CHIOTTO (Continuous High precisioOn Tall Tower Observations of greenhouse gases) (Vermeulen et al., 2004), and it is presently being operated under the EU project CarboEurope IP. The area within a few hundred kilometers around the tower is flat, with a maximal elevation of 250 m above sea level. The land is covered by crops (about 60%), pastures and forest; there is no significant local industry. The nearest town, Bialystok, with ~300000 inhabitants, is situated about 20 km SE of the tower.

Figure 1. (left) Footprint area of the Bialystok (BIK) tall tower station (level 300 m agl) estimated with the COMET model, for the year 2005 (pers. comm., A. Vermeulen, ECN Netherlands); (right) photo of the BIK tower.

7.8.2 Technical setup

Mole fractions of CO2, CH4, CO, N2O and SF6 and the O2/N2 ratio are measured in-situ, quasi-continuously. The system is designed to measure alternately air sampled from five heights of the tower: 5 m, 30 m, 90 m, 180 m and 300 m. Before being analyzed, the air is first cryogenically dried to a dewpoint of about -80°C. The measurement system is installed inside a temperature controlled laboratory container (±2°C).

CO2 and O2 mole fractions are measured successively from the same air sample with a LiCor 7000 non-dispersive infrared (NDIR) CO2 analyzer and a Sable Systems “Oxzilla” oxygen fuel cell analyzer. The O2/N2 ratio is calculated using the measured O2 mole fraction, taking into account the CO2 dilution effect. The analyzers are calibrated every 40 hours using air from a set of four high pressure cylinders with concentrations spanning the atmospheric range. Air from a “Target” cylinder is analyzed every few hours to check the stability of the system. The O2 and CO2 analyzers are installed inside a thermostated chamber (± 0.1°C) to avoid temperature variations influencing the measurement.

CH4 and CO mole fractions are measured with an Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID) and a Ni catalyst methanizer, using Molsieve-5A
and Unibeads-1S packed columns. The same chromatograph is equipped with an electron capture detector (ECD) and Haysep Q columns for the analysis of N\textsubscript{2}O and SF\textsubscript{6}. The sample air is measured alternately with a reference gas from a high pressure cylinder, and the ratio between sample and reference peaks is used to compute the sample mole fraction. A calibration takes place every five days using air from a set of four high pressure cylinders, and a "Target" cylinder is analyzed every few hours to check the stability.

Meteorological parameters are measured at different heights on the tower and the data are transmitted to a computer via a CAN-BUS.

Besides quasi-continuous measurement, flask samples are filled regularly and sent for analysis at the Max Planck Institute for Biogeochemistry (MPI-BGC) laboratory in Jena, Germany. These provide the possibility to measure additional species (H\textsubscript{2}, Ar/N\textsubscript{2}, \textsuperscript{18}O and \textsuperscript{13}C in CO\textsubscript{2}), and constitute at the same time an important means for quality checking the in-situ measurement.

The measurement system operates unassisted, controlled by a custom written Labview™ program. A computer connection made by Symantec pcAnywhere™ software via ISDN allows remote control of the system and data transfer to MPI-BGC.

7.8.3 Data quality

A detailed evaluation of the measurement performance, including estimation of precision and accuracy, was performed after the first 18 months of operation. We provide here two diagnostics of system performance.

The long-term standard deviation of the Target cylinder measurement is assigned as an average measurement precision of the data covering this time period (Figure 2). The precision results, shown in the Figure 2 as standard deviations, and summarized in Table 1, are comparable (for CO\textsubscript{2}, O\textsubscript{2}/N\textsubscript{2} and N\textsubscript{2}O) or better (for CH\textsubscript{4}, CO and SF\textsubscript{6}) than the precision goals of the CHIOTTO project, which have been established taking into account the WMO recommendations (WMO – GAW 161, 2005).

![Figure 2. Time series of the Target cylinder measurement at Bialystok tall tower, used as a quality control check on the data.](image)

The comparison between the in-situ measurement and the results of the flask samples analyzed at MPI-BGC GasLab is one of the means employed to verify the accuracy of the in-situ measurement. A significant systematic difference of about 10 ppb has been found between the CO mole fraction measured in-situ and the flask sample results, which can be only partly explained by changes in the flask samples during storage. The reason is not a calibration scale difference, since the comparisons with MPI-BGC using high pressure cylinders did not show a similar shift. The suspected reason for the observed difference is a contamination source in the flask sampler,
where the samples are stored with open valves before and after filling, for a significant period of time. For all the other species, no statistically significant differences have been found between the in-situ measurement and the results of flask samples.

Table 1. Average precision of the measurement at Bialystok station, and the precision targets of CHIOTTO project.

<table>
<thead>
<tr>
<th>Species</th>
<th>BIK average precision (stdev)</th>
<th>CHIOTTO precision goals</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.095 ppm</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>O₂/N₂</td>
<td>4.81 permeg</td>
<td>5 permeg</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.82 ppb</td>
<td>2 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>0.40 ppb</td>
<td>1 ppb</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.18 ppb</td>
<td>0.1 ppb</td>
</tr>
<tr>
<td>SF₆</td>
<td>0.043 ppt</td>
<td>0.1 ppt</td>
</tr>
</tbody>
</table>

7.8.4 Selected results

In order to illustrate the nature of the station we discuss some main features of the data, like diurnal and seasonal variation of the signals.

7.8.4.1 Diurnal variations of CO₂ and O₂/N₂

A particularity of atmospheric oxygen measurements is that the O₂ variations are usually reported as O₂/N₂ ratio and not as mole fraction. The O₂/N₂ ratio is expressed in “per meg”, a relative unit defined by comparison with an arbitrary standard (Keeling & Shertz, 1992).

\[
\delta \frac{O_2}{N_2} \text{ (permeg)} = \left( \frac{O_2/N_2}_{\text{sample}} \right) - 1 \times 10^6
\]

The reason for this convention is the “dilution” effect: the mixing ratio of oxygen in air can be altered by variations of other air components (for example CO₂), without the oxygen quantity actually changing. In contrast, the changes in O₂/N₂ ratio can only be due to changes in number of moles of oxygen or nitrogen. In many cases the fluxes of nitrogen in and out of the atmosphere can be neglected, and then the variations of O₂/N₂ ratio represent the changes in the number of moles of oxygen.

During the warm season and under fair weather conditions, the thermally induced atmospheric vertical mixing follows a diurnal periodicity which overlaps with the diurnal cycle of release and uptake of CO₂ due to respiration and photosynthesis of the land biosphere, and with the diurnal cycle of human activity. These effects combine to result in a diurnal evolution of the CO₂ mole fraction and of its vertical gradient.

During night-time, CO₂ released (mainly by land biosphere respiration) accumulates near ground, in the absence of strong vertical mixing. Accordingly, large increases are observed in CO₂ mole fraction near the ground and a build-up of large vertical gradients. During the day, when the net exchange between the biosphere and atmosphere is dominated by photosynthesis, the air is well mixed up to typically 1-3 km. Thus the observed decrease of the CO₂ mole fraction due to photosynthesis is much smaller compared to the night-time increase, due to dilution over the mixed layer of the air column.

The short term variations of atmospheric O₂ are typically linked to the variations of CO₂, because during the processes of respiration, photosynthesis and fossil fuel combustion, O₂ is consumed when CO₂ is produced and vice versa. The diurnal cycle of O₂/N₂ ratio is therefore largely anti-correlated with the diurnal cycle of CO₂.
The dissimilarity in the diurnal signals between the warm and the cold season reflects both differences in sources and sinks and the seasonality of the atmospheric circulation. During the cold season, respiration is reduced and photosynthesis declines to a very low level. According to model simulations (C. Rödenbeck, MPI-BGC Jena, pers. comm.), the anthropogenic emissions and the land biosphere respiration are on the same order of magnitude. Also, the diurnal periodicity of vertical mixing disappears; the air column of a few hundred meters above ground is most of the time well mixed, and temperature inversions appear at non-regular time intervals. As can be observed in Figure 3, the average diurnal variation decreases in amplitude or even becomes indiscernible and independent of height in the cold months.

Figure 3. Monthly averaged diurnal cycles of CO₂ and O₂/N₂. The upper panels show CO₂ (ppm) and the lower panels O₂/N₂ (per meg). The colours represent different sampling heights. The x-axis of each plot covers a 24 hours interval, centred on midnight.

7.8.4.2 Observed O₂:CO₂ ratios for the diurnal signals

The correlation between the variations of atmospheric oxygen and carbon dioxide is currently used to distinguish ocean and land uptake of CO₂ on global and regional scales. This utilization relies on the fact that, for land sources and sinks (fossil fuel and land biosphere), the gas exchange of the two species is linked by stoichiometric factors. For the exchange between land biosphere and atmosphere, the presently assumed O₂:CO₂ molar ratio is -1.1±0.05 (Severinghaus, 1995). The global average ratio for fossil fuel burning was estimated to be about 1.4 moles of O₂ consumed per mole of CO₂ produced (Keeling, 1988).

Based on the assumed O₂:CO₂ ratio specific to CO₂ exchange with the land biosphere, a tracer APO has been defined (Stephens et al., 1998), which is essentially unchanged during gas exchange between the land biosphere and atmosphere:

\[
APO \text{ (per meg)} = \frac{O₂}{N₂} \text{ (per meg)} + 1.1 \times 4.8 \times (CO₂ \text{ (ppm)} – 350);
\]

where:

- 4.8 is the conversion factor from ppm to per meg-equivalent units for CO₂;
- -1.1 is the stoichiometric ratio for the land biosphere — atmosphere exchange

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APO is by definition invariant to land biosphere – atmosphere exchange of CO₂ and O₂, as long as such exchanges occur in the proportion of -1.1 between O₂ and CO₂. Thus variations in APO should be only due to air-sea gas exchange of O₂ in the absence of fossil fuel emissions. Therefore APO can give information on the proportion of the oceanic influence in an air parcel. This is only approximately true, as the stoichiometric O₂:CO₂ ratio during fossil burning is somewhat more negative than the coefficient for land biosphere CO₂ exchange.

We calculated daily O₂:CO₂ ratios (for each height of the tower separately) for each 24-hours interval of the vegetation period between 12:00 GMT and the same hour the following day, as illustrated in Figure 4. The ratios were computed as slopes of a MODEL-2 least squares fit, minimizing the residuals on both x and y axes and taking into account the estimated uncertainties for both x (CO₂) and y (O₂/N₂) (York et al., 2004).

Figure 4. Illustration of CO₂ and O₂/N₂ variations over a 24-hour period (sampling height 30 m) and the corresponding O₂:CO₂ ratio calculated as slope of a linear fit. The apparent “gaps” are because of sampling from different heights of the tower.

Figure 5 shows the daily O₂:CO₂ ratio estimates for the signal at 30 m above ground, during the interval Apr – Oct-2006. Each data point represents the ratio calculated for one 24-hour interval (starting at 12:00 GMT) and the error bars represent the estimated error of the slopes.

Figure 5. Diurnal O₂:CO₂ ratio at 30 m height during the vegetation period in 2006. Each point represents the O₂:CO₂ ratio for one 24-hour interval. The error bars represent the error of the O₂:CO₂ slopes. The value of -1.1 is marked as a reference.

The largest part of the night-time CO₂ increase observed at Bialystok at 30 m is due to land biospheric respiration. According to model simulations (e.g. Geels et al., 2007) and to estimations based on the CO: CO₂ ratio, the fossil fuel contribution can be considered smaller than 10% of the
total CO₂ signal. The ocean influence does not significantly contribute to the periodical variations on diurnal time scale. The night-time variations of CO₂ and oxygen represent therefore mainly gas exchange between the local to regional land biosphere and atmosphere. It is thus expected that the O₂:CO₂ ratios should be close to the value of -1.1, slightly more negative due to the contribution of fossil fuel combustion. This is obviously not directly observed (Figure 5), the resultant O₂:CO₂ ratios being significantly less negative than the expected range.

It must be noted, however, that the calculated ratios are mainly those associated with respiration and not the total gas exchange between the land biosphere and atmosphere. This is because, as discussed in the previous section, the atmospheric signature of the gas exchange between the land biosphere and atmosphere (in terms of mole fraction variations) is dominated by respiration, since the photosynthesis signal is strongly diluted by vertical mixing.

We can thus conclude that the variations of atmospheric mole fractions induced by the gas exchange between land biosphere and atmosphere at this particular location and for this particular time interval are not well represented by the generally accepted O₂:CO₂ molar ratio of -1.1.

This result does not necessarily imply that the oxidative ratio of the local land biosphere is lower (in absolute value) than the assumed average, although this is one of the possible causes (e.g. Randerson et al., 2006). Another explanation could be related to the differential transport and storage of CO₂ and O₂ in the forest canopy and in soil.

It is not clear how important this result is for the longer term signals, used to separate air-sea and air-land gas exchange. However it has important implications for the interpretation of short-term APO signals, since APO is defined assuming that there is a constant factor of -1.1 for the O₂ and CO₂ exchange between the land biosphere and atmosphere.

7.8.4.3 Seasonal cycles of CO₂, O₂/N₂ and APO at Shetland Island (SIS) and Bialystok (BIK)

Shetland Island, Scotland (SIS) is a marine flask sampling station (60°10’N, 01°10’E, 30 masl) managed by MPI-BGC. The calculated seasonal cycles of CO₂, O₂/N₂, APO and the residual terrestrial component of the oxygen seasonal cycle (O₂/N₂ (land bio)) at BIK and SIS are shown in Figure 6. The data used to compute the seasonal cycles are weekly flask samples for SIS and robust weekly averages of afternoon values for BIK.

Figure 6. a) Location of sampling stations BIK and SIS; b) Seasonal cycles of CO₂, O₂/N₂, APO and the land biosphere component of O₂/N₂ at BIK (300 m sampling height) and SIS. The 4-harmonic curves are detrended and centred to zero mean. Dataset: Jul-05 to Jan-07.
The CO₂ seasonal cycle, which is mainly due to the land biosphere activity, has smaller amplitude at SIS, and it is delayed compared to BIK by about six weeks, which is on the order of hemispheric mixing time.

In contrast to CO₂, the O₂/N₂ seasonal cycle includes a significant oceanic component. Assuming that APO is conservative to the gas exchange with the land biosphere and it is little influenced by fossil fuel emissions on seasonal time scale, its seasonal cycle can be considered as representing the oceanic contribution to the oxygen seasonal cycle. Consequently, the difference between the O₂/N₂ and APO seasonal cycles represents the land biosphere component of the O₂/N₂ seasonal cycle. By comparing the seasonal cycles of O₂/N₂ and APO at marine and continental stations it is thus possible to estimate the attenuation of oceanic influence over the continent, and to constrain the longitudinal atmospheric transport.

The ocean and the land biosphere have approximately equal contributions to the total O₂/N₂ seasonal cycle at SIS. At BIK the oceanic contribution accounts for about 32% of the total O₂/N₂ seasonal cycle when the 300 m sampling height is considered, and this proportion decreases to about 23% for the 30 m sampling height (not shown). This difference between the sampling heights is consistent with the fact that the higher sampling level has a wider influence area, while the air sampled closer to the ground is more locally influenced. The calculation of these proportions is based on the peak to peak amplitude of the seasonal cycles.

The observed O₂:CO₂ ratio for the seasonal cycle at BIK (Figure 7) does not reproduce the results based on diurnal data in the previous section. An essential difference is the significant contribution of ocean influence in the seasonal variations, which is not present in the daily signal. The O₂:CO₂ ratio of the seasonal variations changes from -1.65 at the SIS marine station to -1.39 at BIK.

In light of the previous section, we can examine how this result changes if we assume that the O₂:CO₂ ratio specific to gas exchange with the land biosphere is different from the generally used -1.1. Supposing that this O₂:CO₂ factor was -1.0 instead of -1.1, we recalculate APO with this revised ratio. Repeating the seasonal cycle calculation using the new APO definition, the proportion of APO from the total O₂/N₂ seasonal cycle becomes about 39% at BIK at 300 m above ground, compared to the previously calculated 32%. It can be observed that the result differs considerably from the previous calculation. This comparison shows the necessity of expanding the knowledge on the atmospheric O₂:CO₂ signature of the land biosphere – atmosphere gas exchange, and its variability on different spatial and temporal scales.
References
ANNEX A

14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracer Measurement Techniques

(September 10–13, 2007, Helsinki, Finland)

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Monday, September 10

8:00–9:00 Registration

9:00–9:10 Organizers Information on organization of the meeting
9:10–9:20 P. Plathan Welcome to Helsinki

WMO/IAEA

9:20–9:40 L. Barrie The WMO GAW Programme

General presentations

9:40–10:00 Y. Viisanen GAW research in the Finnish Meteorological Institute
10:00–10:20 P. Ciais Autumn warming implies a shorter seasonal carbon uptake

10:20-10:50 Break

Standards and calibration (Chair: T. Machida)

10:50–11:10 P. P. Tans The WMO-X2007 mole fraction scale for CO₂-in-air
11:10–11:30 B. Hall Improvements in the WMO/GAW nitrous oxide mole fraction scale
11:30–11:50 A. Jordan The EUROHYDROS calibration scale for hydrogen
11:50–12:10 Y. Tohjima Evaluation of carbon isotope effect on CO₂ measurements by NDIR analyzer

12:10–13:10 Lunch

13:10–14:20 Discussion concerning standards and handling of calibration gases (P. P. Tans)

14:20–14:40 Break

14:40–15:10 Recommendations concerning standards and handling of calibration gases

15:10–18:00 Poster session with refreshments
Tuesday, September 11

Intercomparison activities (Chair: G. Brailsford)

8:30–8:50 R. Neubert A long-term intercomparison experiment of two frequently-used atmospheric $^{222}$Radon monitors
8:50–9:10 I. Levin Five years of international flask intercomparison (SAUSAGE flask ICP)
9:10–9:30 Y. Tsutsumi Activities in QA/SAC and WCC in Japan
9:30–9:50 K. Masarie NOAA comparison activities: Are we closer to the required measurement accuracy?
9:50–10:30 Break
10:50–12:00 Discussion and recommendations concerning intercomparison activities (M. Schmidt)
12:00–13:00 Lunch

Isotope calibration and measurements (Chair: S. Aoki)

13:00–13:20 H. D. Graven Measurements of $^{14}$CO$_2$ from the Scripps CO$_2$
13:40–14:00 L. Huang Challenges and recommendations of traceability maintenance of high precision isotope measurements in atmospheric CO$_2$
14:00–14:20 W. A. Brand Variability of $\delta^{13}$C and $\delta^{18}$O in CO$_2$ generated from NBS19 calcite and implications for the VPDB scale in air CO$_2$ records
14:20–14:50 Break
14:50–15:10 B. H. Vaughn High precision calibration instrumentation for $\delta^{13}$C of atmospheric CO$_2$, carbonates, pure CO$_2$, and CO$_2$/H$_2$O equilibration with waters
15:10–15:30 J. W. C. White Stable isotopes of CO$_2$ and CH$_4$ in the NOAA network
15:30–17:00 Discussion and recommendations concerning isotope calibration and measurements (W. A. Brand, H. D. Graven)
Wednesday, September 12

Measurement techniques (Chair: M. Leuenberger)

8:30–8:50  A. J. Gomez-Pelaez  Installation of a new gas chromatograph at Izana GAW station (Spain) to measure CH₄, N₂O, and SF₆
8:50–9:10  E. R. Crosson  Ultra-sensitive measurements of methane, carbon dioxide and water vapor for atmospheric monitoring
9:10–9:30  L. P. Steele (presented by M. van der Schoot)  Measuring selected atmospheric trace gases using gas chromatography and a Valco pulsed discharge ionization detector
9:30–9:50  H. Yamagishi  In-situ measurements of atmospheric oxygen/nitrogen ratio at Ochi-Ishii by using GC/TCD technique
9:50–10:10  S. Morimoto (presented by S. Ishidoya)  Development of high precision continuous measurement system of the atmospheric O₂/N₂ ratio using a fuel cell oxygen analyzer
10:10–10:30  Break
10:30–10:50  P. Ciais  ICOS, building a new European research infrastructure to measure the carbon cycle
10:50–12:00  Discussion and recommendations concerning GHG and O₂/N₂ measurement techniques (E. Dlugokencky)
12:00–13:00  Lunch

Data management and quality assurance (Chair: D. Worthy)

13:00–13:20  H. E. Scheel  Report of the WCC-N₂O
13:20–13:40  J. Klausen  A screening analysis of ozone, carbon monoxide and methane data at WDCGG
13:40–14:00  M. V. van der Schoot  Calibration and network monitoring performance of LoFlo continuous CO₂ analysers
14:00–14:20  Y. Tsutsumi  The publication of WDCGG data submission and dissemination guide
14:20–14:40  Break
14:40–15:40  Discussion and recommendations concerning data management and quality assurance (H.-E. Scheel)
15:40–17:00  Draft of recommendations (I. Levin)
19:00  Dinner at the restaurant Uunisaari (http://www.uunisaari.com/, click “kartta” for the location)
Thursday, September 13

Measurement networks (Chair E. Brunke)

9:00–9:20 T. Vesala Absolute CO₂ measurements at European flux towers
9:20–9:40 L. Haszpra Quarter century of atmospheric CO₂ monitoring and research in Hungary
9:40–10:00 A. Vermeulen The CHIOTTO project: Results and where to go now
10:00–10:20 M. Schmidt Atmospheric greenhouse gas measurements in France
10:20–10:40 Break
10:40–11:00 S. S. Assonov CO₂ isotopic composition in the upper troposphere: The project CARIBIC
11:00–11:20 T. Machida Measurements of atmospheric CO₂ using commercial airliners
11:20–11:40 P. P. Tans Requirements for global observing systems for carbon dioxide and other greenhouse gases
11:40–12:20 Discussion concerning measurement networks and strategies (M. Heimann)
12:20–13:20 Lunch
13:20–14:00 Recommendations concerning measurement networks and strategies
14:00–14:20 Break
14:20–16:00 Discussion and approval of the draft recommendations (I. Levin)
16:00 End of the meeting
Posters

Standards and calibration

K. Katsumata  Development of carbon monoxide standard in background atmospheric level by dynamic dilution method
T. Machida  Preparing and maintaining of CO₂ calibration scale in National Institute for Environmental Studies

Intercomparison

A. M. Crotwell  Evaluation of the internal agreement of NOAA/ESRL flask analysis systems

Isotopes

C. Allison  Improved traceability for measurements of the stable isotopic composition of atmospheric CO₂
S. S. Assonov  N₂O correction used for isotopic analysis of atmospheric CO₂
S. Aoki  Development of high-precision measurement system for δ¹³C and δD of atmospheric methane
H. Mukai  Preliminary experiment for change in oxygen isotope ratio of CO₂ in a glass bottle

Measurement techniques

A. J. Gomez-Pelaez  A brief overview of the theory of flow along GC packed columns and some practical consequences for measuring atmospheric CH₄, N₂O, and SF₆
M. Laakso  Performance, applications and field experiences for a compact carbon dioxide measurement probe for outdoor use

Data management and QC/QA

Y. Tsutsumi  The global analysis method by the WDCGG using the archived data
B. Wastine  CO₂ measurement techniques and calibration strategy in the RAMCES network

Observations of greenhouse gases and national programmes

S. D. Attri  Greenhouse gas monitoring in India
G. W. Brailsford  Greenhouse gas and trace gas measurements programme in New Zealand
E.-G. Brunke  Recent changes in trace gas levels at Cape Point, South Africa
A. Francesco  Greenhouse gas measurements in Italy
S. Hammer  Lessons from a continuous molecular hydrogen record in Heidelberg on continental hydrogen sources and sinks
N. K. Indira  First analysis of the atmospheric CO₂ measurements at Hanle Observatory, Northern India
H. T. Koponen  Monitoring forest soil respiration using stable isotope techniques
S. van der Laan  A new set-up for semi-continuous measurements of CO₂, CH₄, N₂O, SF₆ and CO using gas chromatography
T. Laurila  Carbon dioxide and methane concentrations and flux measurements at the GAW station of Pallas-Sodankylä
M. C. Leuenberger  CO₂ and O₂ trends at three sites in Europe
I. T. Luijkx Continuous atmospheric CO₂ and O₂ measurements on the F3 North Sea gas and oil platform

I. Mammarella On exchange processes of CO₂ between vegetation and atmosphere during stable night-time conditions

F. Meinhardt Monitoring of greenhouse gases in the air monitoring network of the Federal Environment Agency (UBA) in Germany

R. Neubert Soil air and soil flux measurements of ²²²Radon and CO₂ – CO₂ soil flux parameterization at Lutjewad (NL)


N. N. Paramonova Greenhouse gas monitoring, performed by Main Geophysical Observatory at Russian Federation

E. Popa Results from the tall tower measurement station for atmospheric greenhouse gases at Bialystok, Poland

J. Pumpanen CO₂ budget of Scots pine and silver birch seedlings determined with CO₂ exchange measurements and ¹⁴C pulse labeling under controlled laboratory conditions

H. Scheeren Set-up of a new continuous greenhouse gas monitoring station for CO₂, CH₄, N₂O, SF₆, and CO in Northern Italy

M. Steinbacher In-situ measurements of non-CO₂ greenhouse gases at Jungfraujoch, Switzerland

N. Valkov Bulgarian contribution to the WMO WDCGG

A. Vermeulen Methane and ²²²Radon vertical gradient measurements at Cabauw tall tower

D. Worthy The Canadian GHG observational programme – summary of progress to 2007

L. X. Zhou Progress on the background greenhouse gases and related tracers measurements programme in China
PREVIOUS MEETINGS OF THE WMO EXPERTS IN CO₂ MEASUREMENT

The first meeting of the Experts on Carbon Dioxide Measurement was held in La Jolla, California, United States of America, and sponsored by the World Meteorological Organization (WMO). WMO has sponsored all subsequent meetings. These meetings have provided a quasi-regular communication among all national CO₂ monitoring programmes, which has ensured that CO₂ is monitored with the best current techniques available, that advantage is taken of new methodologies as they become available, and that all programmes are intercalibrated by accepted international standards.

The following is a list of meetings in this series:

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<td>3-7 March 1975</td>
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<td>2. Geneva, Switzerland</td>
<td>8-11 September 1981</td>
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<td>3. Lake Arrowhead, California, USA</td>
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<td>7. Rome, Italy</td>
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* Number of reports in the WMO Executive Panel-I/Document 5, 13.3.1975.
† Number of reports in the WMO Research Department/GAW Report Series.


8. Review of the Chemical Composition of Precipitation as Measured by the WMO BAPMoN by Prof. Dr. Hans-Walter Georgii, February 1982.


14. Effects of Sulphur Compounds and Other Pollutants on Visibility by Dr. R.F. Pueschel, April 1983.


19. Forecasting of Air Pollution with Emphasis on Research in the USSR by M.E. Berlyand, August 1983.


26. Sulphur and Nitrogen in Precipitation: An Attempt to Use BAPMoN and Other Data to Show Regional and Global Distribution by Dr. C.C. Wallén. April 1986 (WMO TD No. 103).


29. Recommendations on Sunphotometer Measurements in BAPMoN Based on the Experience of a Dust Transport Study in Africa by Dr. Guillaume A. d'Almeida. September 1985 (WMO TD No. 67).


43. Recent progress in sunphotometry (determination of the aerosol optical depth). November 1986.


58. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at BAPMoN sites for the years 1986 and 1987 (WMO TD No. 306).
62. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at BAPMoN sites for the year 1988 (WMO TD No. 355).


69. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at Global Atmosphere Watch (GAW)-BAPMoN sites for the year 1989 (WMO TD No. 400).


72. Integrated Background Monitoring of Environmental Pollution in Mid-Latitude Eurasia by Yu.A. Izrael and F.Ya. Rovinsky, USSR (WMO TD No. 434).


75. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at Global Atmosphere Watch (GAW)-BAPMoN sites for the year 1990 (WMO TD No. 447).


77. Report of the WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques, Lake Arrowhead, California, 14-19 October 1990.


84. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at GAW-BAPMoN sites for the year 1991 (WMO TD No. 543).

85. Chemical Analysis of Precipitation for GAW: Laboratory Analytical Methods and Sample Collection Standards by Dr Jaroslav Santroch (WMO TD No. 550).


89. 4th International Conference on CO₂ (Carqueiranne, France, 13-17 September 1993) (WMO TD No. 561).

91. Extended Abstracts of Papers Presented at the WMO Region VI Conference on the Measurement and Modelling of Atmospheric Composition Changes Including Pollution Transport, Sofia, 4 to 8 October 1993 (WMO TD No. 563).


97. Quality Assurance Project Plan (QAPjP) for Continuous Ground Based Ozone Measurements (WMO TD No. 634).


104. Report of the Fourth WMO Meeting of Experts on the Quality Assurance/Science Activity Centres (QA/SACs) of the Global Atmosphere Watch, jointly held with the First Meeting of the Coordinating Committees of IGAC-GLONET and IGAC-ACE, Garmisch-Partenkirchen, Germany, 13 to 17 March 1995 (WMO TD No. 689).


113. The Strategic Plan of the Global Atmosphere Watch (GAW) (WMO TD No. 802).


120. WMO-UMAP Workshop on Broad-Band UV Radiometers (Garmisch-Partenkirchen, Germany, 22 to 23 April 1996) (WMO TD No. 894).


126. Guidelines for Site Quality Control of UV Monitoring (lead author A.R. Webb) (WMO TD No. 884).


129. Guidelines for Atmospheric Trace Gas Data Management (Ken Masarie and Pieter Tans), 1998 (WMO TD No. 907).


131. WMO Workshop on Regional Transboundary Smoke and Haze in Southeast Asia (Singapore, 2 to 5 June 1998) (Gregory R. Carmichael). Two volumes.

133. Workshop on Advanced Statistical Methods and their Application to Air Quality Data Sets (Helsinki, 14-18 September 1998) (WMO TD No. 956).


135. Sixth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Zurich, Switzerland, 8-11 March 1999) (WMO TD No.1002).


139. The Fifth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Halkidiki, Greece, September 1998)(WMO TD No. 1019).


146. Quality Assurance in monitoring solar ultraviolet radiation: the state of the art. (WMO TD No. 1180).


149. Comparison of Total Ozone Measurements of Dobson and Brewer Spectrophotometers and Recommended Transfer Functions (prepared by J. Staehelin, J. Kerr, R. Evans and K. Vanicek) (WMO TD No. 1147).

150. Updated Guidelines for Atmospheric Trace Gas Data Management (Prepared by Ken Maserie and Pieter Tans (WMO TD No. 1149).


154. WMO/IMEP-15 Trace Elements in Water Laboratory Intercomparison. (WMO TD No. 1195).


159. IGOS-IGACO Report - September 2004 (WMO TD No. 1235).


167. The German Contribution to the WMO Global Atmospheric Watch Programme upon the 225th Anniversary of GAW Hohenpeissensberg Observatory (edited by L.A. Barrie, W. Fricke and R. Schleyer (WMO TD No. 1336).


170. WMO/GAW Expert Workshop on the Quality and Applications of European GAW Measurements (Tutzing, Germany, 2-5 November 2004) (WMO TD No. 1367).


174. World Data Centre for Greenhouse Gases Data Submission and Dissemination Guide (WMO TD No. 1416).

176. The Tenth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Northwich, United Kingdom, 4-8 June 2007) (WMO TD No. 1420).


178. Plan for the implementation of the GAW Aerosol Lidar Observation Network GALION, (Hamburg, Germany, 27 - 29 March 2007) (WMO TD No. 1443).


180. Towards a Better Knowledge of Umkehr Measurements: A Detailed Study of Data from Thirteen Dobson Intercomparisons (WMO TD No. 1456).


182. IGACO-Ozone and UV Radiation Implementation Plan (WMO TD No. 1465).

