WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

No. 161

12th WMO/IAEA MEETING OF EXPERTS ON CARBON DIOXIDE CONCENTRATION AND RELATED TRACERS MEASUREMENT TECHNIQUES

(Toronto, Canada, 15-18 September 2003)

May 2005

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hosted by the Meteorological Service of Canada

edited by Doug Worthy and Lin Huang

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DEDICATION

Neil Bruce Albert Trivett: 1943 - 2002

This WMO Report is dedicated to our esteemed friend Neil Trivett. The WMO's Global Atmospheric Watch (GAW) community has strongly benefited from Neil's integrative attitude and long-term experience in atmospheric monitoring. His profound understanding of experimental techniques, his open-minded character, and innovative spirit greatly contributed to the development and success of the GAW programme. Neil was born in 1943 in North Bay, Ontario in Canada. He studied under John Monteith and received his PhD from the University of Nottingham, U.K., in 1972. In his early career, Neil taught and guest lectured at Indiana University in Bloomington in the US, at the University of Queensland in Brisbane, Australia, and at the University of Guelph in Canada. He began his scientific career at the Meteorological Service of Canada (MSC) in 1975 as a research scientist for the Hydrometeorological Research Division. In 1984, Neil accepted a position as head of MSC's Canadian Baseline Programme. He led the Baseline Programme for 14 years and expanded it from a grab-sampling network of two stations to a national network with 4 stations across Canada, including two continuous measurement sites. Neil deserves much of the credit for the establishment of the internationally renowned GAW observatory at Alert in the Canadian High Arctic. He retired from MSC in 1998. During his career, he fostered numerous international partnerships, and, in his kind and gentle way, helped many colleagues assemble their national monitoring programmes. Neil was one of the leading scientists in the WMO GAW community, and a very good friend to many of us. He was elected "Social Director" during many Experts Meetings and CO_2 Conferences: We do sorely miss him.

GROUP PICTURE

ABBREVIATIONS AND ACRONYMS USED IN THIS REPORT

AVD	Absolute Volumetric Determination
CARBOEUROPE	Programme regrouping ecosystem and atmospheric research on the carbon balance of Europe (EU funded project)
CARIBIC	Civil Aircraft for Regular Investigation of the atmosphere Based on an Instrument Container
CCL	Central Calibration Laboratory
CDIAC	Carbon Dioxide Information Analysis Centre
CLASSIC	Circulation of Laboratory Air Standards for Stable Isotope inter Comparisons
CMDL	Climate Monitoring and Diagnostics Laboratory, Boulder, CO, U.S.A.
CSIRO	Commonwealth Scientific & Industrial Research Organisation
DBMS	Data Base Management Strategy
ECD	Electron Capture Detector
EMPA	Eidgenössische MaterialPrüfungsAnstalt
FID	Flame Ionisation Detector
GAW	Global Atmosphere Watch (WMO Programme)
GCP	Global Carbon Project
GG	Greenhouse Gases
GLOBALVIEW	Co-operative Atmospheric Data Integration Project
GOOS	Global Ocean Observing System
GTOS	Global Terrestrial Observing System
IAEA	International Atomic Energy Agency
ICP	InterComparison Project
IGACO	Integrated Global Atmospheric Chemistry Observations
IGBP	International Geosphere-Biosphere Programme
IGCO	Integrated Global Carbon Observation
IHALICE	International HALocarbon in Air Comparison Experiment
IHDP	International Human Dimensions Programme
MOPITT-TERRA	Measurements Of Pollution In The Troposphere
MOZAIC	Measurement of ozone, water vapour, carbon monoxide and nitrogen oxides aboard Airbus in-service aircraft
MPI-BGC	Max-Planck Institut für Biogeochemie, Jena, Germany
MSC	Meteorological Service of Canada
NACP	The North American Carbon Programme
NCAR C-DAS	National Center for Atmospheric Research Carbon Data-Model Assimilation
NIES	National Institute for Environmental Studies, Tsukuba, Japan
NIST	National Institute of Standards and Technology
OCO	Orbital Carbon Observatory
OSSE	Observing System Simulation Experiment
QA/SAC	Quality Assurance/Science Activity Centre
RGD	Reduction Gas Detector
SAG	Scientific Advisory Group
SCIAMACHY	SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY
SIO	Scripps Institution of Oceanography
SRM	Standard Reference Material
TACOS	Terrestrial and Atmospheric Carbon Observing System -Infrastructure (EU funded project)
TCO	Terrestrial Carbon Observations
TDLAS	Tunable Diode Laser Absorption Spectroscopy
UNFCCC	United Nations Framework Convention on Climate Change
VPDB	Vienna Pee Dee Belemnite (Isotope Standard)

VSMOW	Vienna Standard Mean Ocean Water (Isotope Standard)
VUV	Vacuum UltraViolet (Fluorescence)
WCC	World Calibration Centre
WCRP	World Climate Research Programme
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization

EXPERT GROUP RECOMMENDATIONS

The scientists present at the 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, September 15-18, 2003 in Toronto, recommend the following procedures and actions, in order to achieve the adopted WMO goals for global network comparability among different laboratories and various components as summarised in Table 1. The term “network precision” used in earlier recommendations has been replaced by the term “network comparability”. Definitions of terms concerning precision, accuracy etc. are given in Table 2.

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

Component	**Inter-laboratory comparability**
CO_2	± 0.1 ppm (± 0.05 ppm in the southern hemisphere)
$\delta^{13}C\text{-}CO_2$	± 0.01 ‰
$\delta^{18}O\text{-}CO_2$	± 0.05 ‰
$\Delta^{14}C\text{-}CO2$	± 2 ‰
O_2/N_2	± 1 per meg
CH_4	± 2 ppb
CO	± 2 ppb
N_2O	± 0.2 ppb

Table 2: Definitions of terms related to data quality.

Term	**Definition**	**Ref.**
Accuracy (of a test method)	The closeness of agreement between a test result and the accepted reference value.(a)	[1]
Comparability	Mean difference between two sets of measurements, which should be within given limits.(b)	
Bias	The difference between the expectation of the test results and an accepted reference value.	[2]
Precision	Degree of internal agreement among independent measurements made under specific conditions.(c)	[2]
Repeatability (of results of measurements)	Closeness of the agreement between the results of successive measurements of the same measure and carried out under the same conditions of measurement.(d)	[2]
Reproducibility (of results of measurements)	Closeness of the agreement between results of measurements of the same measure and carried out under changed conditions of measurement.(d)	[2]
Uncertainty (Standard uncertainty)	A parameter associated with the result of a measurement that characterises the dispersion of values that could reasonably be attributed to the measure and.(e,f) (Uncertainty of the result of a measurement expressed as a standard deviation)	[2] [3]

(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 Ref. (3).*
[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 (3). As further stated in Ref. (3), "error" is an idealised concept and errors cannot be known exactly. "Error" and "uncertainty" are not synonyms, but represent completely different concepts.*

1. CO_2 CALIBRATION

1.1 Background

Round-robin comparisons 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 (see Table 1). These systematic differences contribute to uncertainties in the location and magnitude of surface fluxes derived from atmospheric composition measurements. A CO_2 Central Calibration Laboratory (CCL) remains one of the fundamental components of the WMO strategy for addressing these problems.

1.2 The CO_2 Central Calibration Laboratory requirements

a) The CCL maintains the WMO Mole Fraction Scale for Carbon Dioxide in Air by carrying out regular calibrations of this primary scale with an absolute method at approximately annual intervals. The primary scale shall range from approximately 180 ppm (covering atmospheric values in ice cores) to over 500 ppm (expected atmospheric background values in the latter part of the 21st century). The scale is currently embodied in a set of 15 CO_2-in-air mixtures 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. This includes an ongoing collaboration with the Scripps Institution of Oceanography (SIO) aimed at quantifying a potential shift of the WMO scale that may have occurred when the responsibility for maintenance of the scale was transferred from SIO to the Climate Monitoring and Diagnostics Laboratory (CMDL).
c) The CCL provides complete and prompt disclosure of all data pertaining to the maintenance and transfer of the primary scale to the measurement laboratories participating in the WMO Global Atmosphere Watch (GAW) Programme.
d) The CCL will update that scale when warranted, as the CO_2 mole fractions of the WMO Primary Standards become better known over time through repeated absolute measurements and comparisons. Revisions of the WMO Scale by the CCL must be distinguished by name, such as WMO X2003.
e) The CCL provides calibrated reference gas mixtures of CO_2-in-air (called “transfer standards”) at the lowest possible cost.
f) The CCL provides for a backup in case a catastrophic event occurs.
g) In order to make possible a level of consistency among the CO_2 calibration scales of laboratories participating in the WMO GAW programme of ± 0.03 ppm or less, the CCL shall aim to provide the calibrated standards for transfer of the primary scale to secondary and tertiary standards at that level of consistency.

Recommendations

1.3 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 Carbon Dioxide in Air. Each GAW measurement laboratory must actively maintain its link to the WMO Scale by having its primary laboratory standards re-calibrated by the CCL every three years. 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) Each GAW measurement laboratory should maintain a strictly hierarchical scheme of transferring the calibration of its laboratory primary gases 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 retroactive changes) in the assigned values of higher level reference gases 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 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 primary standards to lower level standards, which could be beyond the precision with which laboratory primary 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.

1.4 Improving links to WMO Primary Standards

e) CMDL organises 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 redefining laboratory calibration scales. We recommend 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 8 on Quality Control).

f) While scales can only be 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.

g) In such cases, the WMO and IAEA Expert committees undertake the responsibility for the evaluation of the effectiveness of such measures and for recommending modifications to existing protocols.

2. CO_2 STABLE ISOTOPE CALIBRATION

Since the 11th CO_2 experts meeting 2001 in Tokyo, considerable progress has been made towards a tighter connection of the CO_2-in-air standards/references to the VPDB scale, which is one of the important activities initiated or endorsed by the Tokyo meeting. However, a consensus has not been achieved, regarding how to establish and maintain the traceability for isotope measurements of atmospheric CO_2 within the network comparability target (see Table 1) **via only one primary standard** (i.e. NBS19) on VPDB scale. There are a number of points in regard to this issue.

Recommendations

a) The VPDB-CO_2 scale should remain the primary scale for expressing stable isotope ratio measurements of atmospheric CO_2, which is the link to the measurements involving major carbon reservoirs on the Earth surface (atmosphere, ocean, and terrestrial ecosystems).

b) Results of CO_2-in-air samples with the CO_2 originating from NBS19, NBS18 and other widely recognized carbonate materials as new references have been presented by MPI-BGC Jena (work performed within the European TACOS Project). Measurement precision of ± 0.015 permil (δ^{13}C) and ± 0.03 per mill (δ^{18}O) respectively has been achieved. With a carbonate material close to NBS19 in most properties (‘Mar-J1’) the link to VPDB is considered appropriate. In order to prove that the CO_2 has not been changed by the mixing process, the NBS19-CO_2 in air should be measured against the pure CO_2 from NBS19, and the difference in δ^{13}C and δ^{18}O should be close to or within the assigned network comparability (i.e. ± 0.01 permil for carbon and ± 0.05 permil for oxygen).

c) CO_2 from carbonate materials other than NBS19 (e.g. IAEA-CO1, CO8 and CO9) as well as laboratory standards in greater supply such as CAL1 and CAL2 (MSC) should also be mixed into CO_2-free air in order to span a large range of isotopic compositions and provide a means for monitoring the stability and behaviour of laboratory working standards/references~~.~~

d) NIES has prepared two large sets of CO_2 samples flame sealed in glass tubes with isotopic values close to air-CO_2 and to NBS19. Provided these samples can be measured with the required high precision of ± 0.015 and ± 0.03 permil in δ^{13}C and δ^{18}O, respectively, they can serve as a medium term anchor of the difference between NBS19 and air-CO_2. For fulfilling such role, it should be proved that the values are well calibrated on the VPDB-CO_2 scale.

e) It has been demonstrated that a reproducibility of about ± 0.015 permil in δ^{13}C and about ± 0.05 permil in δ^{18}O of carbonates can be consistently achieved over a period of several years. These values are close to the assigned network comparability requirement. Direct calibrations of air CO_2 lab standards on VPDB scale via the primary standard NBS19 and other IAEA recommended international standards (e.g. NBS18) should be encouraged since it is the shortest and most independent way to link lab-standards to the primary standard.

f) The CSIRO/IAEA CLASSIC cylinders continue to be a valuable resource in particular to link past measurements to future CO_2-in-air reference materials which are expected to be better linked to VPDB and VSMOW scales.

g) A version number with detailed documentation (i.e. including constants and equations used) should always accompany the assignment of in-house working standards/references to the VPDB scale, or changes to the assignment. The documentation should be available in the literature or public domain.

h) New data on the N_2O correction suggest that more frequent checks should be made on the ionisation efficiency ratio of N_2O and CO_2. The finding requires further experiments. The adoption of a CO_2-in-air reference will render this correction less critical.

i) Groups measuring absolute isotopic ratios in pure gases (e.g., the Institute for Reference Materials and Methods, Geel, Belgium) should be encouraged to work alongside the TACOS and similar programmes to improve links between CO_2-in-air and carbonate standards, with the eventual aim of supplementing primary links of the CO_2-in-air measurements.

j) A carbonate material in sufficient supply with isotopic values close to air-CO_2 is required as a long-term anchor of air-CO_2 measurements. The search for such material, as recommended by the 11th WMO/IAEA CO_2 experts meeting, is considered urgent. IAEA will enhance its efforts to locate and characterize such material.

k) Due to the influence of plant and surface water on atmospheric CO_2 it is suggested to directly link ^{18}O of CO_2-in-air references to VSMOW instead of VPDB. This would eliminate the ambiguity of the VPDB scale resulting from the less precisely known fractionation factor of ^{18}O in CO_2-H_2O equilibrium. Activities to equilibrate CO_2-in-air with well-characterized water under tightly controlled conditions are endorsed and welcome to be presented at the 13th CO_2 experts meeting.

3. RADIOCARBON IN CO_2 CALIBRATION

Radiocarbon (^{14}C) observations in atmospheric CO_2 are gaining increased interest in carbon cycle research, in particular for budgeting regional fossil fuel CO_2 contributions/emissions. Standardisation of Radiocarbon analysis is well established in the Radiocarbon Dating Community since many years, and the New Oxalic Acid Standard (NIST SRM 4990C) has been agreed upon as the main Standard Reference Material. Other reference material of various origin and ^{14}C activity is available and distributed by e.g. IAEA.

In the atmosphere, recent $\Delta^{14}C$ gradients (north versus south in the free troposphere and marine vs. continental within hemispheres) are very small and on the order of general measurement precision, i.e. only several permil up to very few percent. The “detection limit” to derive regional fossil fuel contributions even with the highest measurement precision is thus only about 1 ppm at best. An intercomparison activity dedicated to ^{14}C laboratories participating in atmospheric $^{14}CO_2$ monitoring is, therefore, strongly recommended.

4. O_2/N_2 CALIBRATION

Twelve laboratories worldwide have been identified which make high-quality atmospheric O_2/N_2 measurements (see Annex 2). Currently there exists no common calibration scale, and small-scale intercomparison efforts have been undertaken by only a few laboratories. Participants were unanimous that significant efforts should now be taken to improve community-wide intercomparison.

In considering an ideal calibration and intercomparison programme, the following points were considered:

a) Ultimately there is a need for a globally standardised calibration scale which all labs/field sites are linked to.
b) One or more mechanisms are needed which provide quality assurance that data derived from flask measurements from one lab are comparable to data derived from flask measurements from a second lab.
c) One or more mechanisms are needed which provide quality assurance that data derived from continuous measurements from one lab/field site are comparable to data derived from continuous measurements from a second lab/field site.
d) Any calibration or intercomparison programme must take into account the fact that many different analyser techniques are currently used within the community to achieve high-precision O_2/N_2 measurements (e.g. interferometric, mass spectrometric, paramagnetic, VUV absorption, gas chromatographic, and electrochemical fuel cell).

Ten of the twelve O_2/N_2 labs (of Annex 1) were represented at this meeting, and the following recommendations were agreed upon by all participants:

a) A “Round-Robin Cylinder” intercomparison programme will be initiated. This will consist of two sets of three high pressure cylinders to be analysed by all participating labs, with the two sets to rotate in opposite direction. At this stage we do not recommend that this programme should result in a common calibration scale, instead it should be used to establish and maintain a link between existing calibration scales. This decision should be reassessed at the 13th WMO/IAEA Experts Meeting in 2005.
b) For those laboratories which make flask measurements, we will initiate a “Sausage Flasks Matrix” intercomparison programme. This will involve a primary laboratory simultaneously filling a pair of flasks from each participating laboratory from a high pressure cylinder and distributing to all labs for analysis.

c) Although we did not formalise a programme, we strongly encourage all flask measurement laboratories to initiate or continue “Shared Flasks” intercomparison programmes. That is, programmes whereby two (or more) laboratories analyse sample air from a station site, either from exactly the same flasks, or from flasks filled simultaneously at a given site. The wider community at this meeting discussed the possibility of a “Super-Site”, where a single field station is used to link all flask analysis laboratories in such intercomparison programmes. If such a Super-Site is adopted, it would be wise for the O_2/N_2 community to adopt the same site.
d) Ralph Keeling (SIO) agreed to be the “Primary Lab”, supplying all high pressure gas cylinders for the round-robin cylinder programme, and filling all flasks for the sausage flasks matrix programme.
e) Andrew Manning (MPI-BGC) agreed to collate all data resulting from the two programmes.

5. CH_4 CALIBRATION

5.1 Background

There is currently no internationally-accepted standard scale for measurements of atmospheric methane. To make optimal use of existing measurements in studies of the global CH_4 budget, either all measurements must be on the same standard scale, or conversion factors must be determined to convert from one scale to another. Fortunately, many members of the CH_4 measurement community have compared their standard scales, and multiplicative factors have been determined that allow us to put many measurements on a common scale. This approach has been effectively used in the Co-operative Atmospheric Data Integration Project to produce GLOBALVIEW-CH_4. Despite this, the community would benefit from an internationally-accepted scale that is transferred to laboratories participating in the GAW network by a Central Calibration Laboratory.

5.2 Proposal for a CH_4 Central Calibration Laboratory (CCL)

NOAA CMDL has developed a gravimetrically-based CH_4 standard scale that covers the nominal range of 300-2600 nmole/mole CH_4, so it is suitable for measurements of CH_4 in glacial and interglacial ice cores, and at GAW background sites. At the 12th WMO/IAEA CO_2 Experts Meeting, there was general agreement that this new CMDL scale should define the WMO CH_4 mole fraction scale, and that CMDL should take on the role of CCL for CH_4; CMDL is also CCL for CO_2, CO, and N_2O. The estimated time frame for CMDL to assume the role of CH_4 CCL is mid-2004, after the details of the new gravimetric scale have been published. As with the other species, CMDL will transfer the CH_4 scale to GAW participants as well as to the WCCs at the lowest possible cost and with the smallest possible uncertainty. WCCs and QA/SACs undertake tasks and procedures for carrying out station system and performance audits and intercomparison in co-operation with the GAW Central Calibration Laboratory in the GAW network. EMPA is the designated World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA). Travelling standards used for methane audits at global GAW sites refer to the new CMDL scale. CMDL will continue CH_4 intercomparison as part of the CO_2 round-robin experiments.

6. CO CALIBRATION

6.1 Background

Being the major chemically active trace gas resulting from large scale natural and non-natural phenomena like biomass burning and fossil fuel combustion, and being a precursor gas for global background tropospheric ozone, CO is frequently measured. Most measurements are based on in situ analyses and the analysis of collected air samples. NOAA/CMDL provide a large and systematic set of observations at the surface, which forms by far the most important source of experimental information. Observations made during aircraft campaigns form the second most important database. At some sites, spectroscopic data allow, or have allowed, retrieval of information about the vertical distribution. Presently also satellite data are becoming available (MOPITT-TERRA, SCIAMACHY-ENVISAT, TESS-AURA), and the wide geographical coverage combined with a (be it limited) vertical resolution, at times combined with data assimilation models, enables for the first time 3D information about major pollution plumes to be constructed. In-situ, ground based measurements are important as they provide the high temporal resolution that cannot be achieved through either satellite or flask measurements.

6.2 Analytical

The present recommendations solely pertain to the calibration of non-remote sensing methods. The validation of remote sensing data is a complicated separate issue not treated here. Experience has shown, however, that even the accurate calibration of CO measurements based on chemical/physical methods is far from trivial. Basically, mixing ratios of 40 to 250 nmole/mole have to be determined with a standard uncertainty of ± 1 ppb.

Unlike CO_2, for CO there is a low degree of standardisation in analytical techniques deployed. There are in fact at least six analytical techniques in use. In (estimated) order of frequency of usage: (1-RGD) gas chromatography using a reduction gas detector, (2-GFC) gas filter correlation, (3-VUV) vacuum ultraviolet fluorescence, (4-FID) gas chromatography using methanization and a flame ionisation detector (FID), (5-TDLAS) Tunable Diode Laser Absorption Spectroscopy, and sporadically (6-AVD) absolute volumetric determination. For the last 2 methods no instruments are commercially available.

The specific calibration problems for CO are that a) gravimetric mixtures have to be diluted to environmental levels, which introduces errors, and b) that at these levels CO mixing ratios in storage containers are not stable over time periods of years or longer. NOAA/CMDL's Carbon Cycle Group has on two occasions organised round-robin tests involving 5 to 10 laboratories. This has helped "the international CO community" enormously, but also exposed some drift and inconsistency in the NOAA/CMDL calibration scale.

It is noted that like for CO_2, CO mixing ratios in gas storage cylinders may change with time. The preparation of a gravimetric standard, does not *a priori* guarantee that the actual CO mixing ratio corresponds to the assumed one. There are two ways around this problem, namely either more extensive research in understanding the problems of stability of CO in storage cylinders, or volumetric measurements. Presently, only the Max-Planck-Institute for Chemistry, Mainz, Germany, carries out volumetric measurements of CO.

Recommendations

WMO has endeavoured to improve the international situation by starting to implement an audit system for CO measurements at 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 based on the mixing and dilution of CO in air, and that is occasionally verified independently by the absolute volumetric determination procedure used by the Max-Planck-Institute for Chemistry in Mainz, Germany. A realistic target for the standard uncertainty of measurements is at the 1% level. For establishing global trends, and to get a sufficiently accurate estimate of the tropospheric burden, it seems that 1% is both analytically attainable, and scientifically sufficient.

6.3 Recommendations

NOAA/CMDL is the CCL for carbon monoxide. In this capacity, they provide calibrated reference gas mixtures ('transfer standards') to laboratories participating in the GAW CO programme at the lowest possible cost. CO calibrations should be traced back to the scale maintained by NOAA/CMDL. This scale was revised in 2000, and all measurements at GAW stations should refer to the new scale. 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 inter-comparisons at global GAW stations. Travelling standards used for audits at global GAW sites refer to the new CMDL scale. Round robins (organised by CMDL) showed some inconsistencies and/or drift in the CO scale. The Scientific Advisory Group (SAG) Reactive Gases is now being established, and is scheduled to meet in fall 2004. Further steps and recommendations will be co-ordinated by the SAG members.

7. N_2O CALIBRATION

7.1 Summary of the NOAA N_2O calibration scale

The NOAA 2000 N_2O scale was developed in 2000 from 17 gravimetric standards. Prior to 2000 the scale was based on six gravimetric standards prepared in 1993. Two of these were dropped from the 2000 set, as the cylinders were low in pressure. The set of 17 ppb-level standards contains four in the year 1993 gravimetrically prepared standards (in 29-L Aculife-treated aluminium cylinders) and 13 in the year 2000 gravimetrically prepared standards (in 5.9-L untreated aluminium cylinders obtained from Scott-Marrin Inc.). The set was derived from three different ppm-level standards, all of which were prepared from 99.9% N_2O (Scott Specialty Gases). The 1993 standards were prepared with Air Products zero air, scrubbed with 1-L traps of molecular sieve and Ambersorb. The 2000 standards were prepared using Linweld ultra high purity zero air scrubbed with molecular sieve and Ambersorb, plus two additional 150 cc traps of molecular sieve and activated charcoal chilled to 0ºC. All gravimetrically prepared standards in 2000 contain CO_2 (330-380 ppm) and SF_6 (1-6 ppt). The 1993 standards contain CO_2 (350–400 ppm) and highly variable SF_6 (0-40 ppt).

In 2002, an Agilent 6890 gas chromatograph was configured for N_2O/SF_6 analysis.

Column:	3/16", Porapak Q, 3m main, 2m backflush
ECD:	Agilent, 340 deg C
Oven:	56 deg C
Carrier:	N_2 (45 cc/min main, 45 cc/min backflush), doped with 0.05 cc/min CO_2
Sample loop:	9 cc
GSV:	Valco 12-port
Typical repeatability	0.1-0.2 ppb (1 s.d.)

Recommendations

The precision of the Agilent/N_2 system has proved to be better than that of the previously used Valco/P5 system (operated with 95% Ar/ 5% CH_4 as carrier gas). More importantly, this instrument has proved to be more stable over changes in operating conditions and carrier gas.

At NOAA, primary standards are prepared gravimetrically as described above. Secondary standards are dilutions of free tropospheric air obtained from Niwot Ridge, Colorado, USA, for which concentrations are determined by reference to the primary standard curve. Secondary Standards are used to calibrate Tertiary Standards for distribution to NOAA sites and laboratories. It is the NOAA Tertiary Standards that are used as Laboratory Standards by the World Calibration Centre (WCC) and any participating laboratories.

A set of laboratory standards with five different N_2O mole fractions calibrated by NOAA should be obtained by each GAW station and should serve as the station's highest-level standards. These are to be safeguarded, used only for infrequent calibrations of working standards or reference gas, and they should be recalibrated by NOAA every 5 years. Working standards at each laboratory can be either appropriately prepared synthetic gas mixtures or dried ambient air compressed into high-pressure aluminium cylinders. Besides N_2O, synthetic mixtures should contain atmospheric levels of N_2, O_2, and CO_2 as a minimum. For the use at a GAW station these have to be calibrated by comparison with the station's set of primary laboratory standards or an equivalent set of standards traceable to the NOAA CMDL scale.

The mean interhemispheric difference in N_2O 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 N_2O in the atmosphere, which requires not only high precision of measurements, but also high consistency among assigned values for standards. Ideally, the expanded uncertainty would be ± 0.1 ppb or better, but this may prove too difficult a goal to meet in the short term.

Currently, NOAA maintains its scale by analysing 17 primary standards annually, and five secondary standards over the 280-350 ppb range weekly. A second working standard (310 ppb) is run weekly as a secondary check on uncertainties. Precision (1 standard deviation) normally varies between ± 0.02 and ± 0.1%. An analytical precision of ± 0.02% produces an uncertainty in predicting an unknown from a 5-standard curve of ca. ± 0.1 ppb near ambient values and ± 0.13 resp. ± 0.15 ppb at 250 and 350 ppb. However, at present, the precision does not hold at 0.02% over the long term. At this time, consistency for assigning values to standards can be guaranteed at ± 0.3 ppb, although ± 0.2 ppb is a realistic short-term goal. Consistency of ± 0.1 ppb among standards should be attainable in the long term.

7.2 Participating Laboratories and Field Sites

For most N_2O systems, the repeatability (2 standard deviations) of the gas chromatographic method under ambient sampling is expected to be better than ± 1% (± 3 ppb). A value of at least ± 0.2% (± 0.6 ppb) should be aimed at for all GAW stations. With high-quality equipment and maintenance, a precision of ± 0.08% (± 0.3 ppb) can be achieved. Precision should be determined from multiple, interspersed analyses of a gas of constant N_2O mole fraction (e.g. working standard) during routine operation.

For basic calibration of the analytical system and for intercomparison, five different N_2O mole fractions ranging between 290 and 350 ppb should be used. This will determine the response curve of the ECD. Working standards should be compared with laboratory standards at least twice a year. It is recommended to run analyses of samples of assigned N_2O mole fraction from a "target cylinder" once per day or more frequently. This will enable early detection of minor malfunctions of the analytical system. These and other analytical and quality control procedures are discussed in detail in the Measurement Guidelines / Data Quality Objectives for N_2O, which are currently being edited by the SAG GG (Report in preparation).

8. GENERAL RECOMMENDATIONS FOR QUALITY CONTROL OF ATMOSPHERIC MEASUREMENTS

a) Besides round-robin comparisons, more frequent intercomparison activities between pairs of laboratories, which for example also more closely simulate the analyses of actual air samples, such as flask air intercomparison (ICP) experiments are strongly recommended. The tremendous benefit of routine intercomparison has been demonstrated (ref. 4) and is reinforced. Mutual exchange of air in glass flasks is encouraged as a means to detect experimental deficiencies at an early stage and remove discrepancies in the results fast.
b) 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 (ref. 5) are able to increase the benefit of mutual flask exchange.
c) Another possibility to link several laboratories in one single intercomparison exercise is the establishment of “Super Sites”, field stations which could take on the task to fill a larger number of flasks regularly and simultaneously with ambient air and distribute them to participating laboratories.
d) Clear protocols and reports of experience gained in intercomparison projects should be provided. Results should be published in the peer-reviewed literature. 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.
e) The participants of the WMO/IAEA Experts meeting strongly support the IHALICE intercomparison initiative which also includes CO_2, CH_4, CO, N_2O and SF_6.

9. GENERAL RECOMMENDATIONS FOR DATA MANAGEMENT AND ARCHIVING

9.1 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) Demonstrates that mixing/isotope ratios can be unambiguously and automatically reproduced from raw data at any time in the future
b) Demonstrates that revisions to a laboratory’s internal calibration scale can be efficiently and unambiguously propagated throughout the database
c) Supports routine and automatic database updates of all measurement and meta data
d) Ensures that all data reside locally, in a single location, and are centrally accessible to internal users
e) Ensures fast and efficient retrieval of all data
f) Maximises users’ ability to assess data quality
g) Facilitates data exploration
h) Minimises the risk of data loss or corruption due to theft, misuse, or hardware/software failure
i) Maximises security to primary data (e.g., data from which all processed data is derived)
j) Supports routine and automatic backup of all data
k) Supports complete data recovery in the event of catastrophic data loss

GAW measurement laboratories are encouraged to use WMO document #150 as a guideline in developing and implementing an atmospheric data management strategy.

9.2 Data Archiving

Laboratories participating in the WMO-GAW programme must submit their data regularly to the World Data Centre for Greenhouse Gases (WDCGG). A co-ordinated annual submission of data, with clearly identified version number and 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).

9.3 Co-operative Data Products

All laboratories making high-quality atmospheric carbon dioxide and methane 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.

10. 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 quantify the present state of the fluxes of greenhouse gases and better understand the controlling processes.

2. 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.

International scientific planning 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 feedback, 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 Integrated Global Carbon Observing Strategy Partnership (IGOS-P) has formed a Theme Team called IGCO (Integrated Global Carbon Observation) to report on those systematic global carbon observational networks that can form the backbone of a future monitoring system, building 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 IGCO Theme Team task is 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.

In both GCP and IGCO documents, 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 of local flux information. 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“).

Recommendations

There are two major novel developments in the planning of atmospheric trace gas measurement strategies since the former WMO meeting in Tokyo in 2001

The Orbital Carbon Observatory (OCO) satellite mission from NASA is scheduled for launch in 2007 and expected to deliver the first global coverage of column integrated CO_2 measurements using differential absorption in the short wave infrared region of the spectrum. The target precision of OCO measurements is ±1 ppm but there are a number of potential sources of bias in the remotely sensed CO_2 data that call for specific in situ validation measurements, in particular high-quality vertical profiles.

New major regional programmes have received funding to increase the density of atmospheric trace gas observations and terrestrial carbon observations over North America (NACP; http://www.esig.ucar.edu/nacp/) and Western Europe (CARBOEUROPE ; http://www.bgc-jena.mpg.de/public/carboeur/). It is important that those regional programmes remain tightly linked to the international 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 development of 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.

Plans for future carbon observing networks are to a large extent based on anticipated advances in modelling, inversion, and data assimilation techniques to make use of higher resolution and higher variability data. Because these analytical tools are still in development it is difficult to quantitatively assess the success of various planned observing system enhancements. Nevertheless, existing and prototype modelling systems can be used for guidance on where we should be concentrating our precious resources. Critical questions to address include the relative benefit of a few very high accuracy measurements versus many somewhat lower accuracy measurements, the trade-off between low cost flask measurements and more expensive continuous measurements, the value of high-variability and high-signal continental boundary-layer data relative to lower-variability but lower-signal marine boundary layer and free troposphere data, the importance of vertical profile data for constraining CO_2 fluxes and testing boundary-layer parameterizations in comparison to striving for denser surface coverage, and the benefits of including measurements of other species. Thus we should continue to support efforts at quantitative network optimisation, such as the NCAR C-DAS (National Centre of Atmospheric Research Carbon Data-Model Assimilation, http://www.cdas.ucar.edu/) and observing system simulation experiments (OSSE).

Ideally we would have these questions answered before we committed significant resources to a particular strategy, but we only get one chance to sample the atmosphere so it is well justified to expand the observations before the analytical tools are mature. While we must presently rely on less sophisticated network design exercises, calculations, and reasoning, we have reasonable confidence in a number of basic parameters describing the optimal future carbon observing system.

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, 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) 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 CO_2 mixing ratio observations (ref. 6). These observations will enable us to quantify regional sources and sinks by means of inverse modelling.

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

d) Develop high-quality measurements of carbon cycle tracers that can be used to attribute natural fluxes to their controlling processes ($^{13}CO_2$, O_2/N_2, ^{18}OCO) and separate fossil fuel emissions ($^{14}CO_2$, CO…)

e) Develop high-quality measurements of transport tracers (SF_6, ^{222}Rn, C_2Cl_4…) in order to validate numerical models of atmospheric transport, in particular their vertical mixing.

f) Report actual uncertainties on individual data where available. In particular, pursue the development of data products for modellers (e.g. GLOBALVIEW) that can include wherever possible information on representativeness, calibration offsets, etc…

g) 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 ΔpCO_2 surveys programmes to make atmospheric measurements.

h) 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 resolution to better account for sources and sinks heterogeneity. 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.

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(3) *ISO Publications, Guide to the expression of uncertainty in measurement, International Organization for Standardization (Geneva, Switzerland), ISBN 92-67-10188-9, 110 p. (1995). The abbreviation of this title is GUM. Equivalent guide: American National Standard for Calibration - U.S. Guide to the Expression of Uncertainty in Measurement, ANSI/INCSL Z540-2-1997, NCSL International, Boulder, USA, 101 p. (1997).*

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ANNEX 1

INSTITUTES CARRYING OUT HIGH-QUALITY ATMOSPHERIC O_2/N_2 MEASUREMENTS

1. Bowdoin College, USA
   Lead Scientist: Mark Battle

2. CSIRO-Atmospheric Research, Melbourne, Australia
   Lead Scientist: Ray Langenfelds

3. Institute of Ocean Sciences, Vancouver, Canada
   Lead Scientist: C.S. Wong

4. Max-Planck-Institute for Biogeochemistry, Jena, Germany
   Lead Scientists: Willi Brand, Andrew Manning

5. National Centre for Atmospheric Research, Boulder, USA
   Lead Scientist: Britt Stephens

6. National Institute for Environmental Studies, Japan
   Lead Scientist: Yasunori Tohjima

7. National Institute for Water and Atmospheric Research, Wellington, New Zealand
   Lead Scientists: Gordon Brailsford, Rona Thompson

8. Princeton University, USA
   Lead Scientist: Michael Bender

9. Scripps Institution of Oceanography, USA
   Lead Scientist: Ralph Keeling

10. Tohoku University, Japan
    Lead Scientist: Takakiyo Nakazawa

11. University of Bern, Switzerland
    Lead Scientist: Marcus Leuenberger

12. University of Groningen, The Netherlands
    Lead Scientists: Harro Meijer, Rolf Neubert

WORKSHOP PROCEEDINGS

1. OPENING OF THE MEETING

The Twelfth Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques was held in Toronto, Canada, from September 15th to 18th, 2003. The meeting was hosted by the Meteorological Service of Canada (MSC) and co-sponsored by the World Meteorological Organization (WMO) and International Atomic Energy Agency (IAEA).

Dr Douglas M Whelpdale, Director of Environment Canada's Climate Research Branch opened the meeting by welcoming all participants and recognizing the truly multinational attendance with participants coming from 16 different countries. He noted that MSC was honoured to host this meeting and provided a summary of recent developments at MSC in carbon cycle research and Global Atmospheric Watch (GAW) activities. He also noted that MSC recognized the importance of accurate and precise measurements of greenhouse gases and related tracer measurements, specifically within a strategically designed long-term global atmospheric observational system. He concluded by expressing hope for a successful meeting and wished every one a pleasant stay in Toronto.

2. SPONSORS REPORTS

2.1 The WMO Global Atmosphere Watch (GAW) Programme

L. A. Barrie, WMO

2.1.1 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, 2001; Strategic Plan Addendum, 2004). 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 12th 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 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 was recently 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. It will do this through the ongoing activities of the cientific Advisory Group (SAG) for Greenhouse Gases that met after this expert meeting and this global community representing carbon cycle research and measurments.

The focus, goals and structure of GAW are outlined in detail in the Strategic Implementation Plan (GAW Report 142) and its addendum (GAW Report 156). Recognizing the need to bring scientific data and information to bear in the formulation of national and international policy, the GAW mission is threefold:

a. Systematic monitoring of atmospheric chemical composition and related physical parameters on a global to regional scale
b. Analysis and Assessment in support of environmental conventions and future policy development
c. Development of a predictive capability for future atmospheric states.

2.1.2 GAW Monitoring

The components of the GAW monitoring programme are summarized in Figure 1. Global GAW networks focus on six measurement groups: greenhouse gases, UV radiation, ozone, aerosols, major reactive gases (CO, VOCs, NO_y and SO_2), 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 23 Global, 640 Regional and 73 Contributing stations are operating or have 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 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. Table 1 summarizes the facilities related to quality assurance and archiving in GAW for the GAW target variables as well as some critical ancillary variables. Over 80% of these facilties have been established under GAW since 1989 while the rest that preceded GAW have been strengthened through membership in the programme. In addition to these facilities, 7 regional calibration centres for total ozone are in operation.

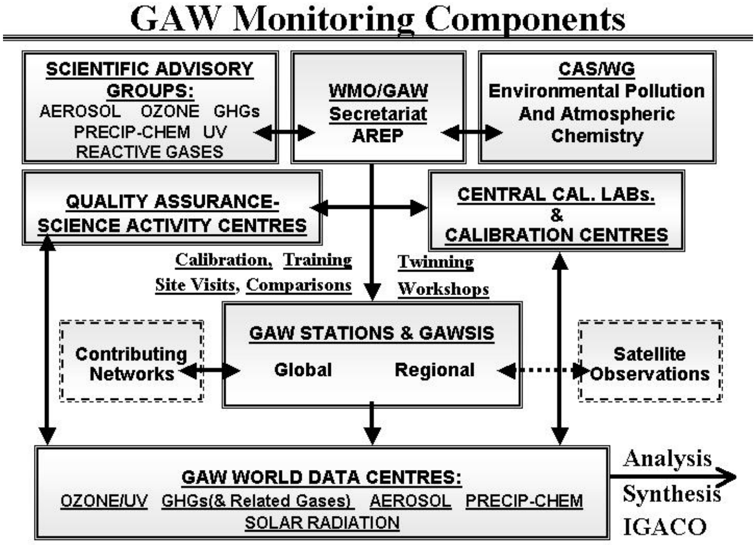


Figure 1: Components of the WMO/GAW Global Monitoring Programme.

Table 1: ***Summary of GAW calibration, quality assurance and data archiving facilities (as of December 2003). The world central facilities have assumed global responsibilities, unless indicated (am: americas; e/a: europe and africa; a/o: asia and the south-west pacific). From the addendum to the gaw strategic implementation plan (strategic plan addendum, 2004).***

Species	QA/SAC	World Calibration Centre	Central Calibration Laboratory (CCL, Reference Standard)	World Data Centre
CO_2	JMA (A/O)	CMDL	CMDL	JMA
CH_4	EMPA (Am, E/A) JMA (A/O)	EMPA (Am, E/A) JMA (A/O)	CMDL	JMA
N_2O	UBA	IMK-IFU	CMDL	JMA
CFCs				JMA
Total Ozone	JMA (A/O)	CMDL[1], MSC[2], MGO[3]	CMDL[1], MSC[2]	MSC
Ozone Sondes	FZ-Jülich	FZ-Jülich	FZ-Jülich	MSC
Surface Ozone	EMPA	EMPA	NIST	JMA
Precipitation Chemistry	ASRC-SUNY	ASRC-SUNY	ISWS	ASRC-SUNY
CO	EMPA	EMPA	CMDL	JMA
VOC	UBA	IMK-IFU		JMA
SO_2				JMA
NO_x				JMA
Aerosol		IfT (Phys. Properties)		JRC
Optical Depth		PMOD/WRC	PMOD/WRC[4]	JRC
UV Radiation	ASRC-SUNY (Am)	SRRB (Am)		MSC
Solar Radiation		PMOD/WRC	PMOD/WRC	MGO
^{85}Kr, ^{222}Rn		EML		JMA
^{7}Be, ^{210}Pb		EML		EML

ASRC-SUNY	Atmospheric Sciences Research Centre, State University of New York (SUNY), Albany NY, USA, hosting the World Data Centre for Precipitation Chemistry (WDCPC)
BSRN	Baseline Surface Radiation Network, Federal Institute of Technology (ETH), Zürich, Switzerland
CMDL	Climate Monitoring and Diagnostic Laboratory, National Oceanographic and Atmospheric Agency (NOAA), Boulder CO, USA
EML	Environmental Measurements Laboratory, Department of Energy (DoE), New York City NY, USA
EMPA	Swiss Federal Laboratories for Materials Testing Research and ResearchTesting, Dübendorf, Switzerland
FZ-Jülich	Forschungszentrum Jülich, Jülich, Germany
IMK-IFU	Institut für Meteorologie und Klimatologie Atmosphärische Umweltforschung, Forschungs-zentrum Karlsruhe in der Helmholtz-Gemein-schaft, Garmisch-Partenkirchen, Germany
ISWS	Illinois State Water Survey, Champaign IL, USA
IfT	Institute for Tropospheric Research, Leipzig, Germany
JMA	Japan Meteorological Agency, Tokyo, Japan, hosting the World Data Centre for Greenhouse Gases (WDCGG) and the Quality Assurance/Science Activity Centre for Asia and the South-West Pacific
JRC	Environment Institute, Ispra, Italy, hosting the World Data Centre for Aerosols (WDCA)
MGO	A.I. Voeikov Main Geophysical Observatory, Russian Federal Service for Hydrometeorology and Environmental, St. Petersburg, Russia, hosting the World Radiation Data Centre (WRDC)
MSC	Meteorological Service of Canada – formerly Atmospheric Services (AES), Environment Canada, Toronto, Canada, hosting the World Ozone and UV Data Centre (WOUDC)
NIST	National Institute for Standards and Testing, Gaithersburg MD, USA
PMOD/WRC	Physikalisch-Meteorologisches Observatorium Davos/World Radiation Centre, Davos, Switzerland
SRRB	Surface Radiation Research Branch of NOAA's Air Resources Laboratory, Boulder CO, USA
UBA	German Environmental Protection Agency, Berlin, Germany

[1] Dobson only

[2] Brewer only

[3] Filter instruments

[4] Precision Filter Radiometers (PFR)

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 Implementation Plan (Strategic Plan, 2001; Strategic Plan Addendum, 2004). 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 23 GAW Global stations is shown in Figure 2.

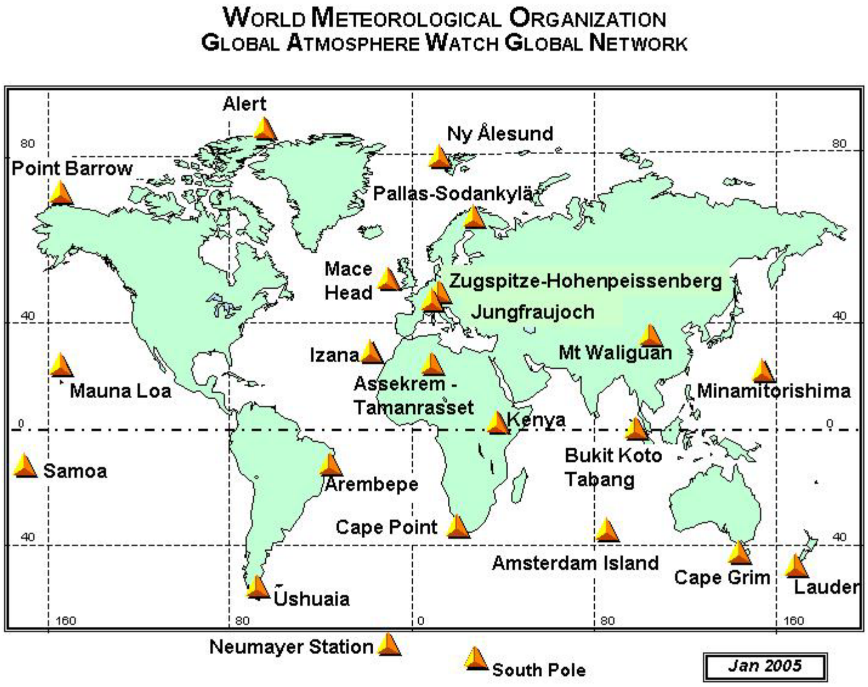


Figure 2: Global stations in the GAW network.

To monitor global distributions and trends of a particular variable with sufficient resolution to answer outstanding gaps in understanding of environmental issues related to global warming due to greenhouse gases requires not only Global but also Regional and Contributing stations. The GAW global network for surface based carbon dioxide observations is shown in Figure 3. There are also global networks for other variables such as methane, nitrous oxide, aerosol variables, balloon sonde ozone, total column ozone, surface ozone, reactive gases and precipitation chemistry that involve different combinations of the three types of stations and network configurations (e.g. GAW Report #152, 2003).

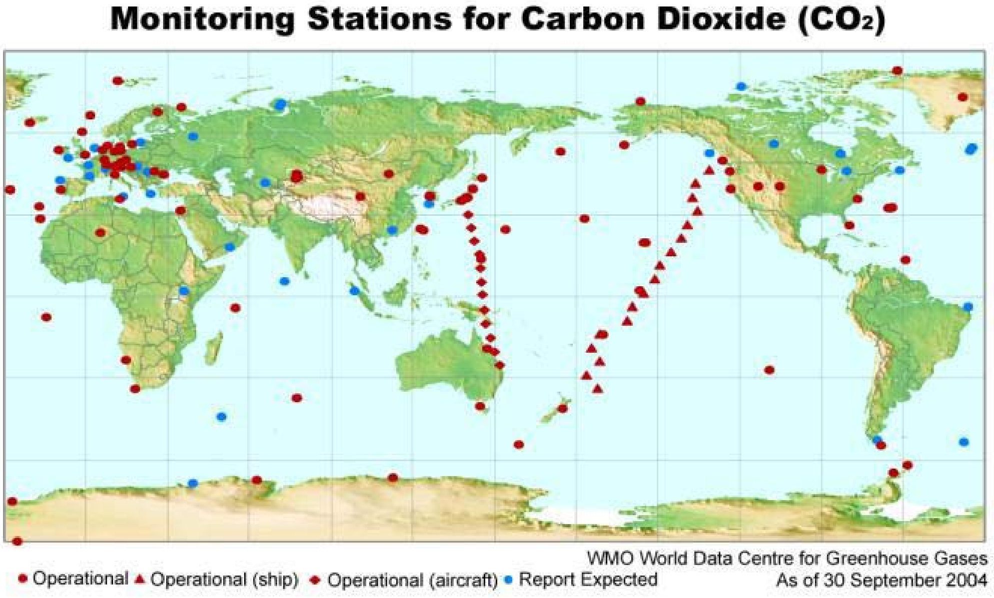
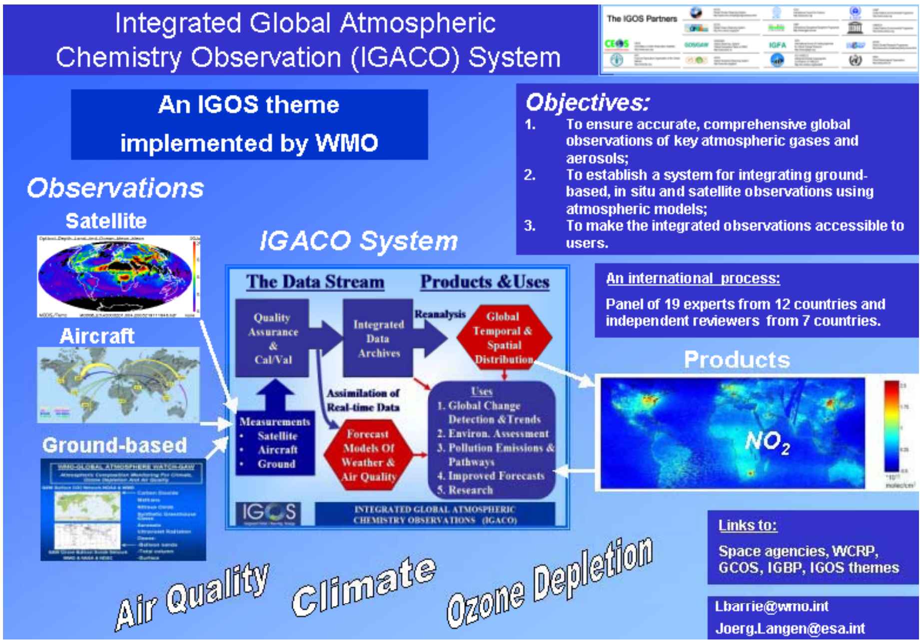


Figure 3: The GAW surface carbon dioxide network. Support for calibration, audits and maintenance advice are provided by the GAW facilities listed in Table 1.

2.1.3 The Future of GAW Global Atmospheric Chemistry Monitoring

Recently, WMO/GAW has taken the lead in co-chairing with the European Space Agency a scientific assessment of the past, present and future state of global atmospheric composition observations, the measurement requirements and priorities in the next 15 years for Integrated Global Atmospheric Chemistry Observations (IGACO). The IGACO Atmospheric Chemistry Theme Report (IGACO, 2004) produced for the partners of the Integrated Global Observing Strategy (IGOS) recommends an approach for integration of ground-based, aircraft and satellite observations of 13 chemical groups in the atmosphere using atmospheric models that assimilate not only meteorological observations but also chemical constituents. The IGACO objectives and components are summarized in Figure 4. Socio-economic issues related to climate change, ozone depletion/ UV increase and air quality benefit by having such a system in place. IGACO is a blueprint for the next generation GAW activities. WMO/GAW is the designated lead in the implementation.

Within the framework of IGACO, the next generation GAW will evolve to meet the observational needs and challenges of climate change, ozone depletion, air quality and long range transport of air pollution. It is essential that the groundwork laid in the past 16 years for global surface-based and aircraft monitoring systems is maintained and strengthened. Technological advances in measurement methodology and data exchange will shape the next generation GAW monitoring programme. The merging of ground-based in situ and remote sensing observations with routine aircraft and satellite measurements through the use of "smart interpolators" that are under development by the research and modelling community is at once a daunting and exciting challenge. The expert measurement and modelling community that meets every two years in this forum will play a key role in implementing an integrated global atmospheric carbon dioxide and methane gas measurement system.



Objectives:

1. To ensure accurate, comprehensive global observations of key atmospheric gases and aerosols;
2. To establish a system for integrating ground-based, in situ and satellite observations using atmospheric models;
3. To make the integrated observations accessible to users.

An international process:

Panel of 19 experts from 12 countries and independent reviewers from 7 countries.

Links to:

Space agencies, WCRP, GCOS, IGBP, IGOS themes

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Figure 4: A schematic of the Integrated Global Atmospheric Chemistry Observations (IGACO) system and its partners, links to societal needs and driving environmental issues.

References

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2001	*GAW: 2001, Strategic Plan, Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007), A Contribution to the Implementation of the Long-Term Plan, GAW Report 142.*
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2004	*GAW: Strategic Plan Addendum for the period 2005-2007 to the Strategy for the implementation of the Global Atmosphere Watch Programme (2001-2007), GAW Report 142.*
2004	*IGACO: 2004, The Integrated Global Atmospheric Chemistry Observations (IGACO) Report of IGOS-WMO-ESA, GAW Report 159, 53 pp.*

2.2 Carbon Stable Isotope Programmes and Activities at IAEA

Manfred Gröning (IAEA)

For more than 40 years the IAEA has actively been involved in the standardization of stable isotope measurements for light elements. Recent activities in the field of stable isotope reference materials increased the number of available materials to a total of 56. Of these, twenty are carbon stable isotope reference materials, including carbonates, CO_2 gases and organic compounds, which are distributed worldwide as part of IAEA's Analytical Quality Control Services. IAEA supports continuously the production of further reference materials. A re-calibration of virtually all these carbon reference materials was initiated in cooperation with four experienced laboratories. Preliminary results show a considerable improvement in uncertainties for recommended carbon isotope values, and suggest the necessity for a stretching of the carbon scale. His effort should result in an improved consistency for reporting carbon stable isotope data.

Carbon dioxide plays a very significant role in these standardization efforts, as it is still the major gas used for mass spectrometric isotope measurements for the elements carbon and oxygen. While stringent calibration schemes linking to a primary reference material are absolutely essential for isotopic measurements on solid materials and water, atmospheric carbon dioxide isotope measurements are not in all cases traceable back to primary reference materials. This poses severe problems for the intercomparability and traceability of isotope scales used in different laboratories to the primary VPDB scale. This problem is being tackled in the frame of ongoing international activities, just to mention the TACOS CO_2 from carbonates into air project, the NARCIS II CO_2 flame sealed glass tube samples and the use of CSIRO/IAEA CLASSIC cylinders. The IAEA has identified a carbonate material with a carbon isotope composition close to that of air CO_2. Its intrinsic isotopic variability as stalagmite material needs further investigation on best milling and processing methods to prepare a sufficiently homogeneous material for its desired use for calibration purposes.

In the IAEA programme for 2004/2005 and beyond, a new project is aimed at studying water and carbon cycle dynamics in the biosphere and atmosphere and the impact of climate change on those. This includes investigations of isotope methodologies for improved characterization of CO_2-H_2O exchange processes.

In this respect, it is interesting to continue the discussion started during the 12th WMO/IAEA CO_2 Experts Meeting on potentially linking $\delta^{18}O$ data of the CO_2-in-air scale to VSMOW instead of VPDB.

The WMO/IAEA CO_2 Experts Meetings provide very efficient means to facilitate discussions and to decide on the most urgent future steps for improvements in analyses and quality of measurements. The participation of scientists and institutions from the developing world in the worldwide atmospheric trace gas monitoring programmes is an essential requirement to improve the worldwide coverage of sampling stations and for efficient dissemination of the analytical know-how to further countries.

3. CARBON DIOXIDE MEASUREMENTS

3.1 Consistency of the CO_2 primary standards in JMA

Yukitomo Tsutsumi, Hidekazu Matsueda and Sakiko Nisioka

Abstract

Since 1980's, the Japan Meteorological Agency (JMA) and the Meteorological Research Institute in JMA have conducted long-term monitoring programmes of atmospheric and oceanic CO_2 in Japan Meteorological Agency (JMA). In 1986, JMA established a calibration system with the primary standard gases to propagate a CO_2 scale to secondary and working standards that were used for the monitoring programmes of JMA and MRI. The JMA primary standards were calibrated on the basis of the WMO mole fraction scale maintained at the World Calibration Centre (WCC) in CMDL/NOAA to keep traceability with other GAW stations.

A long-term record of calibration data for the standard gases is useful to evaluate the quality of CO_2 measurements in the JMA/GAW project. In the present paper, we report results of investigations of the standard gases using remaining calibration data, correction methods for inconsistency of the primary standards, and preliminary results of the correction.

3.1.1 Introduction

JMA has carried out an atmospheric CO_2 monitoring at Ryori since 1987, at Minamitorishima global station since 1994, and in Yonagunijima since 1997. The network covers a large part of the western Pacific region (Watanabe et al., 2000). On the other hand, a research vessel, Ryofu-Maru, has observed CO_2 in seawater and the air over the ocean in the western North Pacific since 1981. Furthermore, another research vessel, Keifu-Maru, has also observed CO_2 in seawater since 2000.

MRI had studied to observe CO_2 in seawater and the air over the ocean using a ship since early 1980's (Inoue et al., 1995). This observation study in the western Pacific was succeeded to the monitoring by the JMA. MRI also made several ship observations and an aircraft observation as campaigns (Inoue et al., 1991; Matsueda and Inoue, 1991). To study an exchange between the atmosphere and vegetation, CO_2 monitoring in MRI has conducted at the surface since 1986 (Inoue and Matsueda, 1996) and at the top of a 200m tower in Tsukuba, Japan since 1992 (Inoue and Matsueda, 2001). The CO_2 concentration at the upper troposphere has been observed using regular commercial flights between Japan and Australia in April 1993 (Matsueda and Inoue, 1996), and the trend and latitudinal distributions were analyzed in Matsueda et al. (2002a; 2002b).

3.1.2 Hierarchy of CO_2 standards gases in JMA

Regional distributions and variations of CO_2 concentration are important for understanding the global carbon cycles. Spatial and temporal comparisons of CO_2 mixing ratio among observation sites are essential to reveal the regional variations. Traceability of standard gases is essential to make these comparisons. To achieve this consistency of scale, the WMO/GAW establishes the measurement guide for CO_2 quality management and calibrations (WMO, 2000). The maintenance of standard gases plays an important role to keep the traceability of CO_2 measurements. JMA adopts three ranks of hierarchy for standard gases (Figure 1) according to the guide for CO_2 measurement (WMO, 2000).

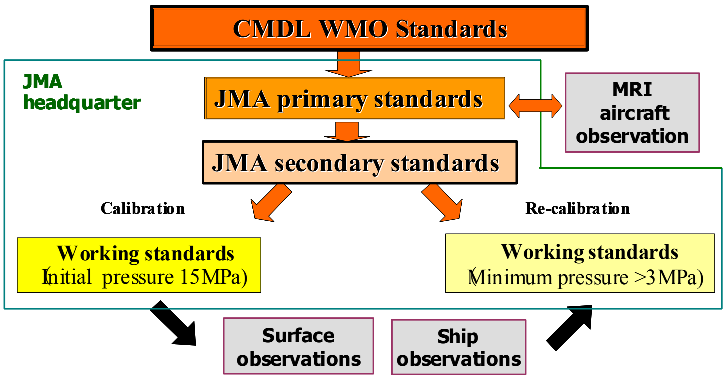

Figure 1: Hierarchy of JMA standards gases. The JMA primary standards are regularly compared with the MRI standards.

3.1.3 History of the primary standards in JMA

JMA primary standard is the highest rank of standard gases in JMA, and all of CO_2 measurements in JMA are standardized by this primary standard. The JMA primary standard is calibrated by the WMO/WCC before the use. We have four generations of the primary standards as listed in Table 1. First generation of primary standards was filled in cylinders made by nickel-molybdenum steel and calibrated at the Scripps Institute of Oceanography, University of California (SIO). After the 1st generation, the primary standards were filled in Aluminium cylinders at Nippon Sanso Corp. in Japan according to the method from Tohoku University, and were calibrated at SIO (at CMDL after the 3rd generation). JMA secondary standards are used for determination of mixing ratios of working standards that are used in the observations at the sites and vessels. The secondary standards are used for saving the consuming of the primary standard, enabling long-term use of the identical primary standard. All of the secondary standards are filled in Aluminium cylinders by the method from Tohoku University.

The most important point to notice for maintain standard gases is a verification of a concentration drift during the use. The JMA primary standards are regularly calibrated one another among the same generation, and checked drifts of the concentrations (Figure 2). We call this method as “self-calibration”. The self-calibration is one of effective ways to estimate the drift of standard gases. The JMA primary standards are also compared with the MRI standards. However, we had not systematically checked the data before. In this work we investigated these data, and found some issues.

Table 1: Historical record of JMA primary standard gases. Calibration values were labelled by the WCC. Re-calibration values were determined using the next generation primary standards.

Gene-ration	WCC	Cylinder Number	calibration	date	re-calibratio	date	duration	difference
First	SIO	134160	321.16	1986/09.25	323.370	1991/7/3	1986/11/21 ~	2.21
		134150	330.19	～	331.290	1991/7/3	1991/12/2	1.10
		134151	340.53	1986/10/13	341.540	1991/7/3		1.01
		134163	348.92		349.840	1991/7/2		0.92
		134164	362.14		363.450	1991/7/2		1.31
		134127	368.57		369.380	1991/7/2		0.81
Second	SIO	CQA00207	271.04	1991.04	270.620	1996/4/19	1990/7/31 ~	-0.42
		CQA00211	290.49	ditto	290.310	1996/4/19	1996/4/26	-0.18
		CQA00208	313.07	ditto	313.100	1996/4/19		0.03
		CQA00210	329.71	ditto	329.880	1996/4/17		0.17
		CQA00209	342.55	ditto	342.780	1996/4/17		0.23
		CQA00212	354.16	ditto	354.500	1996/4/16		0.34
		CQA00204	365.86	ditto	366.240	1996/4/16		0.38
		CQA00213	378.41	ditto	378.820	1996/4/16		0.41
		CQA00205	390.47	ditto	391.110	1996/4/12		0.64
		CQA00206	410.08	ditto	410.800	1996/4/12		0.72
Third	SIO	CQB08401	249.26	1997/9/29	249.521	2000/9/9	1995/1/25 ~	0.26
		CQB05944	269.87	1995/10/10	269.977	2000/9/9		0.11
		CQB05943	289.71	1995/10/8	289.733	2000/9/9		0.02
		CQB05939	308.51	1995/10/5	308.455	2000/9/10		-0.06
		CQB05946	329.80	1995/10/5	329.711	2000/9/10		-0.09
		CQB05942	340.39	1995/10/5	340.216	2000/9/10		-0.17
		CQB05949	352.49	199510/05	352.373	2000/9/11		-0.12
		CQB05950	364.42	1995/10/5	364.250	2000/9/11		-0.17
		CQB05951	378.15	1995/10/6	377.976	2000/9/11		-0.17
		CQB05952	389.63	1995/10/6	389.407	2000/9/12		-0.22
		CQB05954	407.71	1995/10/6	407.484	2000/9/12		-0.23
		CQB08402	430.42	1997/10/14	429.811	2000/9/13		-0.61
		CQB08403	450.88	1997/10/14	449.988	2000/9/13		-0.89
Fourth	CMDL	CQB09465	209.33	1999/1/25	209.485	2002/6/26	1998/9/29 ~	0.16
		CQB09466	239.55	1999/1/18	239.671	2002/6/26		0.12
		CQB09468	272.08	1999/1/18	272.199	2002/6/26		0.12
		CQB09469	289.57	1999/1/11	289.623	2002/6/27		0.05
		CQB09471	309.39	1999/1/11	309.477	2002/6/27		0.09
		CQB09295	330.18	1998/12/8	330.266	2002/6/27		0.09
		CQB09296	343.95	1998/12/8	344.013	2002/6/28		0.06
		CQB09297	353.88	1999/1/4	353.887	2002/6/28		0.01
		CQB09298	363.80	1999/1/4	363.815	2002/6/28		0.01
		CQB09299	379.26	1998/12/14	379.403	2002/6/29		0.14
		CQB09300	389.36	1998/12/14	389.440	2002/6/30		0.08
		CQB09472	409.13	1998/12/18	409.199	2002/6/30		0.07
		CQB09467	439.47	1998/12/18	439.494	2002/7/2		0.02

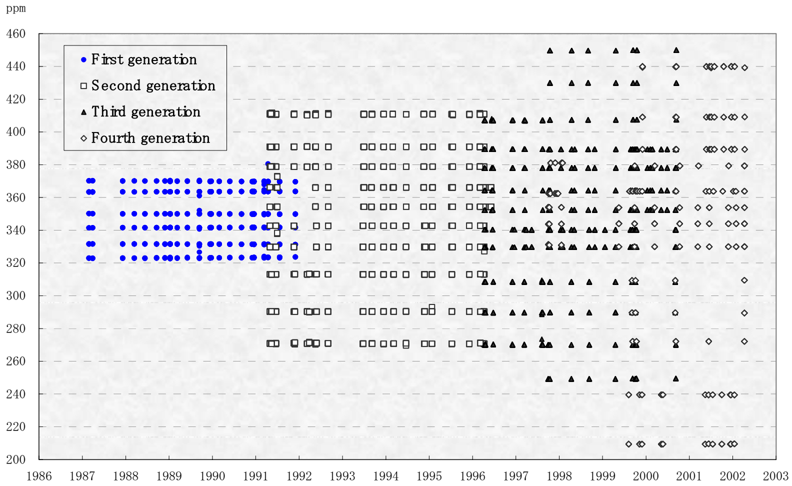

Figure 2: The self-calibration results over the four-generations of JMA primary standards.

3.1.4 The results of investigations

We precisely checked the self-calibration data from the 4th generation of primary standards that are currently used into the 1st generation of primary standards in turn. As a result, we found that the maximum drift of 4th generation primary standards was 0.066 ppm/year, and the maximum drift of 3rd and 2nd generations primary standards were 0.025 ppm/year and 0.024 ppm/year, respectively. While it is difficult to estimate a drift accurately by self-calibration, these facts indicate that no typical drift occurred in the 2nd, 3rd, and 4th generations primary standards during the use. However, the maximum drift of the 1st generation of primary standards was 0.140 ppm/year (Figure 3). This suggests that some cylinders in the 1st generation primary standards seem to have typical drifts.

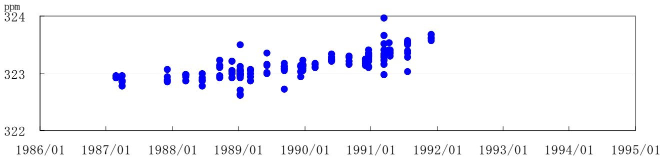

Figure 3: The self-calibration result of the 1st generation of primary standard that showed the maximum drift (cylinder number 13416).

The MRI established their own primary standard for their observational studies as described Section 0 The MRI keeps a mono-generation primary standard, and they have been regularly compared with the JMA multi-generation primary standards since 1993.

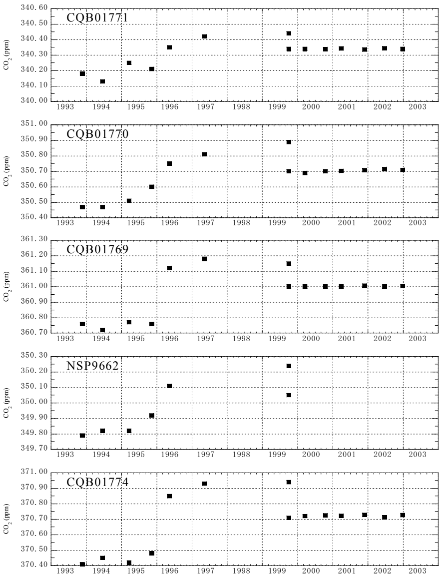

Figure 4: The concentrations of MRI primary standards that were determined by the JMA primary standards. There are concentration gaps around 1996 and 1999.

Figure 4 shows examples of the concentrations of MRI primary standards that were determined by the JMA primary standards. The precision of JMA calibration system is less than 0.02 ppm, indicating that the significant dispersion of the concentrations in Figure 4 is found beyond the precision of the instrument. The two different concentrations in 1999 are due to the difference of standard gases used in this calibration. The periods of time when the concentration gaps occurred in 1996 and 1999 coincide with the periods of the replace of the JMA primary standards. On the other hand, the MRI has regularly made self-calibrations of their primary standards since 1993. Their results showed that the estimated drifts of the standard gases ranged between -0.02 and +0.02 ppm/year during 1993-1997, and ranged between -0.04 and 0.03

ppm/year during 1997-1999. From these facts, the obvious generation gaps (~0.4ppm) of the MRI standards against the JMA standards in 1996 and 1999 suggest that there are concentration gaps among the four-generations in the JMA primary standards. Here, the concentration gap means the difference between a labelled concentration by the WCC and an estimated concentration.
From the investigations, we can conclude as follows:

- The 1st generation of JMA primary standards have drifted;
- Besides the 1st generation of primary standards, the primary standards have not typically drifted;
- There are concentration gaps among generations of the JMA primary standards.

3.1.5 How to cope with these issues

a. The drift of the 1st generation of JMA primary standards

First, we must estimate the magnitudes of drifts of the 1st generation of JMA primary standards. And then, we can correct the concentrations (including the drift) of the 1st generation of primary standards.

We used the same-generation secondary standards to probe the magnitudes of drifts of the 1st generation of primary standards — the concentrations of the 1st generation of primary standards were reversely determined by initial calibration data that had been used to determine the secondary standards by the primary standards. The 1st generation of JMA secondary standards (6 Aluminium cylinders) was filled at Nippon Sanso Corp. in 1986 as described in Section 0and they were refilled in Nov. 1989. As shown in Figure 5, all cylinders of the primary standard show drifts of upward tendency. Furthermore, gaps before and after the refilling support the drifts of the primary standards. However, the JMA secondary standards may also drift.

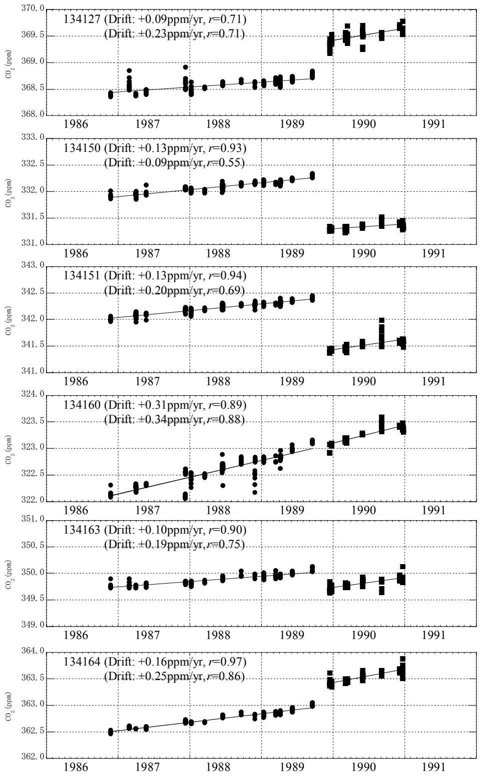

Figure 5: The concentrations of the 1st generation of primary standards that were determined by the 1st generation of secondary standards.

To estimate drifts of the secondary standard, the secondary standards were divided into two groups, and self-calibrations were conducted within the same groups. The drift velocities of first group (PLG74051A, PLG74038A, PLG74041A) ranged from -0.013 to +0.015 ppm/year, and cylinders in the first group were not seemed to have typical drifts. However, the drift velocities of second group (PLG74047B, PLG74044B, PLG74054B) ranged from -0.109 to +0.038 ppm/year, indicating that one or two cylinders in the second group seemed to have some drifts.

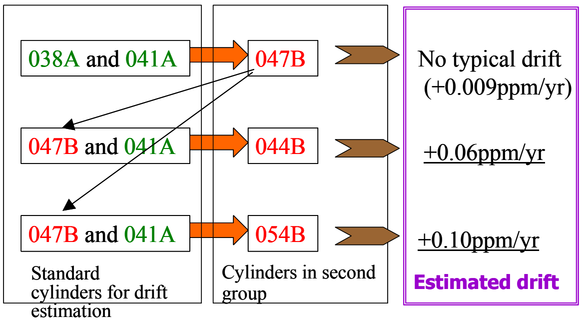

Figure 6: Schematic diagram of estimations of drift on the secondary standards. The first 5-digits of the cylinder number ("PLG74") are omitted.

Magnitude of the drifts of the second group of JMA secondary standards were estimated by the ways as follows (Figure 6):

1. A concentration of a cylinder, No. PLG74047B was determined by cylinders Nos. PLG74038 and PLG74041A, and the estimated drift of PLG74047B was negligible (+0.009 ppm/year);
2. A concentration of cylinder, No. PLG74044B was determined by cylinders Nos. PLG74047B and PLG74041A that were estimated to have no typical drift, and the estimated drift of PLG74044B was +0.06 ppm/year;
3. A concentration of cylinder No. PLG74054B was determined by the same cylinders as case of Nos. PLG74044B, and the estimated drift was +0.10 ppm/year.

We determined the concentrations of 1st generation of secondary standards using the above results during the period of time from November 1986 to September 1989. Using these secondary standards, we corrected the 1st generation of primary standards. After the re-filling of the secondary standards, they were estimated to have no typical drift. Moreover, the concentration of each 1st generation of primary standard was adjusted to fill the gaps that were seen in Figure 5. Figure 7 shows the concentrations of the 1st generation of JMA primary standards (including drift) that were determined by the above ways.

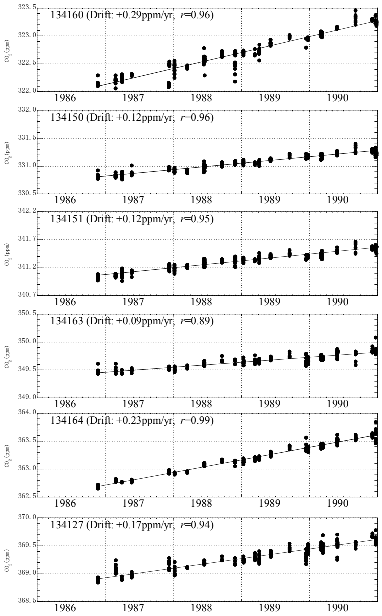

Figure 7: The concentrations of the 1st generation of JMA primary standards that were determined by the secondary standards.

b. Corrections of the generation gaps of the primary standards in JMA

Before JMA terminated the use of each-generation primary standards, they were re-calibrated by the next generation (Table 1). JMA used to employ the labelled value by the WCC in spite of the comparison results before this correction. Using the comparison results between the generations, the concentrations were corrected to fill the gaps. First, concentrations of the 4th generation primary standards were fixed, and the correction of standards in each generation was traced back to the 1st generation in turn. The schematic diagram of the correction concept for the JMA standards is illustrated in Figure 8. Before the concentration gap of the primary standard between the 1st generation and 2nd generation was filled, the drifts of the 1st generation of primary standards were corrected as described in Section 0.

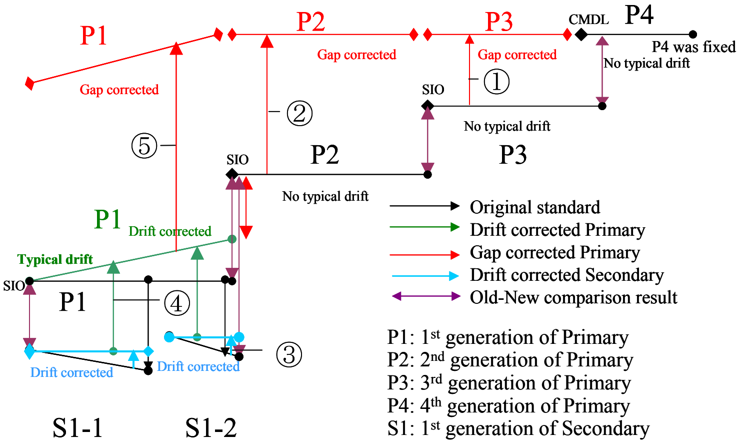

Figure 8: Schematic diagram of the correction concept for the JMA standards. The circled numbers in the diagram are the order traced back for correction.

3.1.6 *The preliminary results of corrections of the JMA primary standards*

While all of the CO_2 observation data have not corrected yet, we made preliminary corrections for an intercomparison with MRI and for the WMO CO_2 Intercomparison in 1996-1997. Figure 9 shows preliminary results of concentrations of the MRI standards that were determined by the corrected JMA primary standards from 1993 to 2002. Since MRI standards are comprised of a mono-generation, the results are fairly improved. Figure 10 shows the results of the CO_2 Intercomparison conducted by the WMO during 1996-1997. The closed circles in the figure are re-calculated results by the corrected JMA primary standards. The results show that the corrected concentrations are very closed to those of the CMDL.

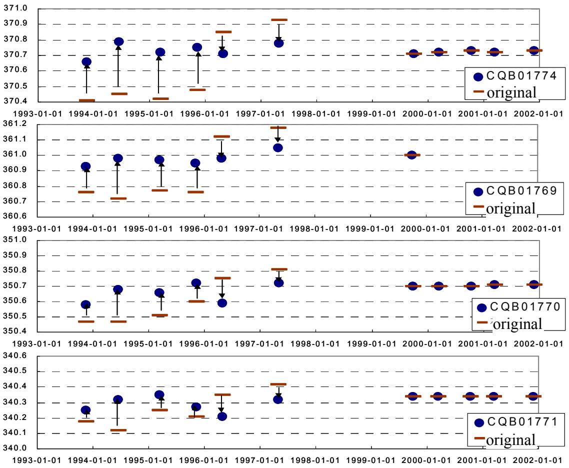

Figure 9: The MRI standards against the corrected primary standards in JMA. Bas are original concentrations and circles are corrected values.

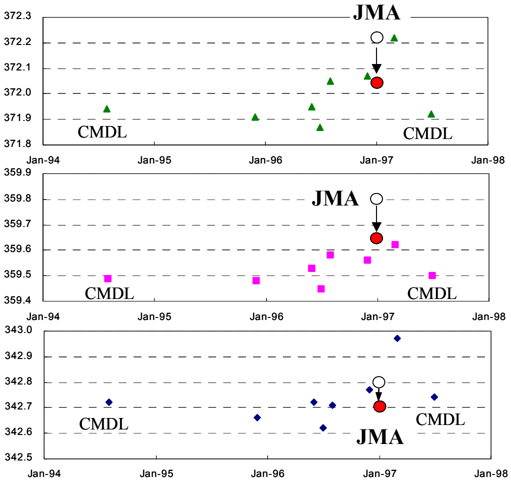

Figure 10: Preliminary results of the WMO CO_2 Intercomparison in 1996-1997. Open circles are original values, and closed circles are corrected values.

3.1.7 *Summaries and future plans*

We investigated the stability of our multi-generation primary standards, and devised the way to correct the drift and the generation gaps. The preliminary re-calculation of CO_2 concentration using these corrected primary standards showed reasonable results. We are going to re-determine the 2nd and 3rd generations of the secondary standards. The 1st generation of secondary standards will not be re-determined because they were used for the drift-correction of the primary standards. All working standards will be re-calculated by the corrected secondary standards. Afterwards, all observational values will be re-calculated using these corrected working standards. In this process, all of fitting curves that were calculated every 2 hours in 3 observation sites are needed to be re-calculated for the correction of observational concentration during the periods of time when the re-calibrated working standards were used. Since we have already established a relational database for CO_2 observation and all observational outputs from the instruments are systematically saved in the database, we will be able to perform these re-calibrations and re-calculations systematically.

3.1.8 Acknowledgments

We would like to thank K. Suda, R. Hirano, Y. Sawa, T. Tsuboi, H. Kamiya, K. Nemoto, H. Nagai, M. Yoshida, S. Iwano, O. Yamamoto, H. Morishita, K. Kamada, and A. Wada who are the members of a task force for the investigation and discussion.

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3.2 Maintenance and Propagation of the WMO Mole Fraction Scale for Carbon Dioxide in Air

Pieter Tans and Conglong Zhao

3.2.1 Manometric measurements through 2003

The fifth set of manometric calibrations of the 15 WMO Primary reference gas mixtures of CO_2-in-air was completed by CMDL in April 2003. The calibration system and measurement procedure is described by Zhao et al. (1997). A total of 62 measurements were performed, with each of the Primaries receiving at least three calibrations on different days. The results, including those of all previous calibration episodes, are shown in Figure 1. No measurement has been omitted. Also shown are the infrared measurements performed by the Scripps Institution of Oceanography (SIO). They incorporate the revisions received by CMDL in early 2002. The values assigned to the 15 WMO Primaries were fully determined by the SIO data from 1992 to mid-1996, jointly based on the SIO and CMDL measurements from mid-1996 to early 2001, and completely on the CMDL measurements alone from 2001 to the present. It is important to note that, when the WMO CO_2 Experts Meeting transferred responsibility for maintaining the WMO Scale from SIO to CMDL in 1995, the assignment of values to the new WMO Primaries was still based entirely on the calibrations by Scripps, and furthermore that those values were somewhat different from what they are now, after the revisions received in early 2002.

Within each group of CMDL calibrations (called a “calibration episode”, of which we now have had five) the standard deviation of all calibrations with respect to the mean for each Primary cylinder can be calculated. Table 1 shows that the scatter of individual calibrations has decreased significantly over time.

Table 1: Scatter of individual CMDL calibrations.

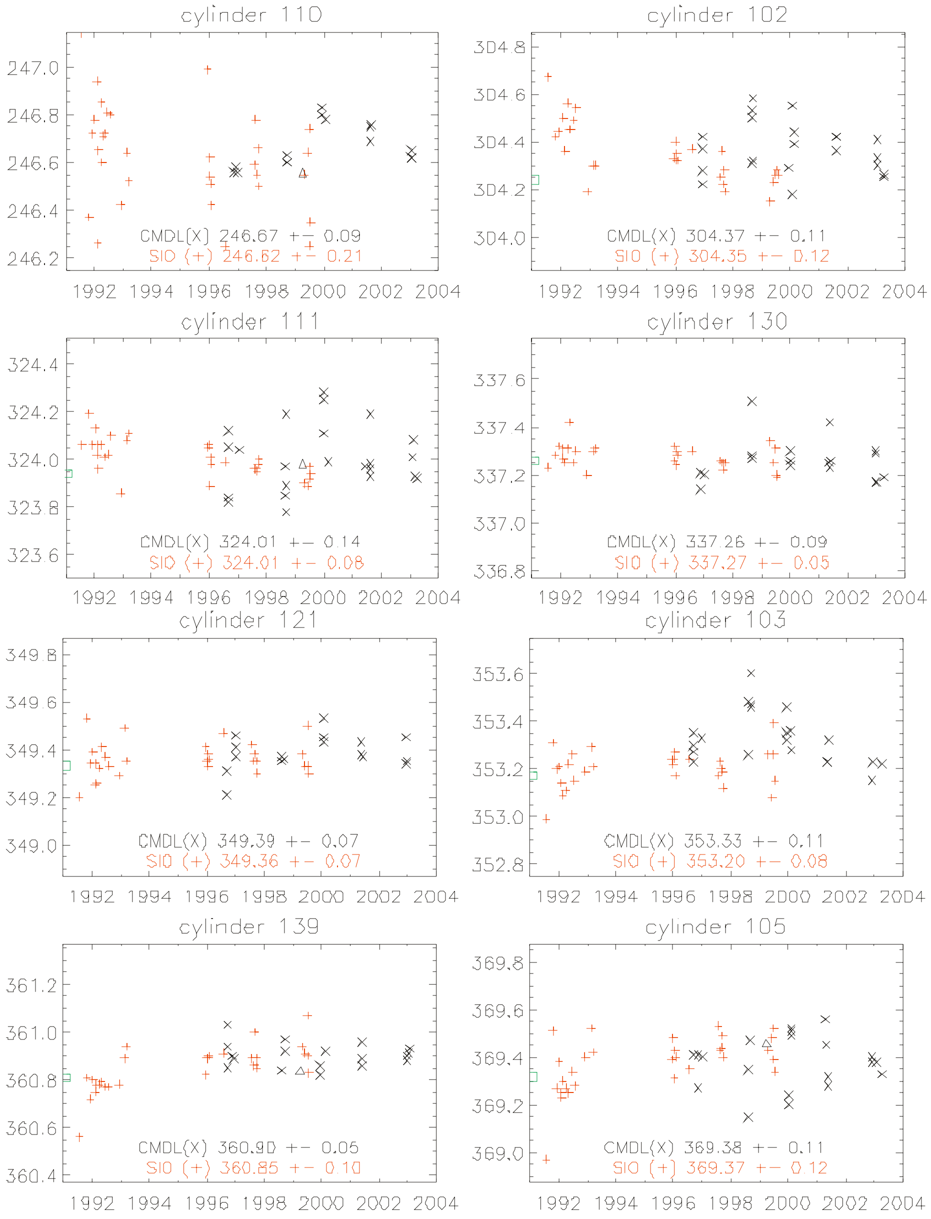
Mean date of episode	Overall st. dev.
November 1996	0.12
August 1998	0.14
January 2000	0.12
July 2001	0.08
January 2003	0.06

When the averages of each cylinder for each calibration episode are calculated, it is seen that those averages differ from one another by more than what would be expected by calculating the standard error of the mean of each cylinder for each calibration episode. (The standard error of the mean is simply the standard deviation of the individual measurements of each Primary divided by the square root of the number of measurements during one episode). The larger than expected differences imply that there are slight variations in calibrations of pressure, volume ratio, and temperature, or variations in procedure between episodes, and that the best statistic to characterize variance of the measurements over many years is probably obtained by using the averages of each Primary for each episode. Slight variations in conditions or in procedure are also suggested by calculating how the average of all 15 cylinders differs between episodes, as shown in Table 2. There is no evidence of overall drift of the WMO Primaries or of the system from 1996 to 2003.

Table 2: Difference of the mean of 15 Primaries in each episode from the average of all episodes.

Mean date	
November 1996	−0.058
August 1998	0.030
January 2000	0.060
July 2001	0.005
January 2003	−0.038

The current WMO Scale is defined by the average of all five CMDL calibration episodes for all Primary gas mixtures. We will next compare the differences of every CMDL calibration episode to the current scale, which are plotted in Figure 2, together with curve fits through the differences. The curve fits are quadratic and cubic polynomials, which are typically used to define the scale once values have been assigned to the individual cylinders. Figure 2 gives an impression of the “random” component of the calibrations, as well as of the more systematic differences between episodes.



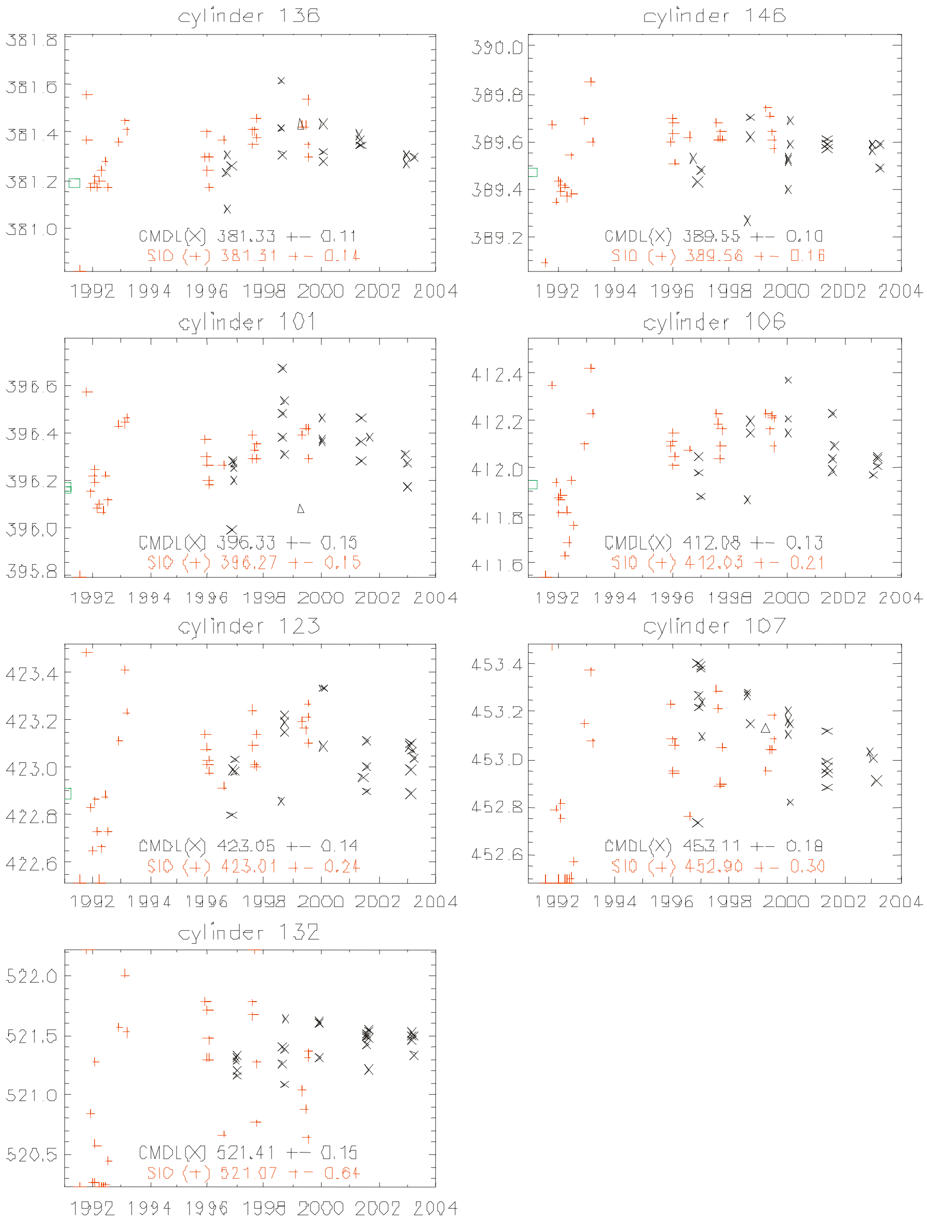


Figure 1: All calibrations performed on the WMO Primary reference gas mixtures of CO_2-in-air through 2003. Crosses: CMDL manometric measurements; Red "plus" symbols: infrared measurements at the Scripps Institution of Oceanography (SIO) relative to the previous set of WMO Primaries maintained by David Keeling at SIO; Green squares: infrared measurements by CMDL relative to the secondary standards maintained by CMDL until 1993 that were based on the previous WMO Primaries at SIO; Triangles: manometric measurements by SIO. Values that fall outside the plotted ranges are depicted on the upper or lower axes. The averages and one-sigma standard deviations of individual measurements are written on the plots. The vertical range of all plots is 1 ppm except for the highest level standard.

3.2.2 Recent Development of the WMO Scale

We can also compare all previous actual assignments of the WMO Primaries to the current WMO Scale. This is shown in Figure 3. As noted above, the past assignments of the Primaries were based on the original values received from Scripps, not on the revisions (called the X99A scale by Scripps) received in 2002. Therefore, the differences shown in Figure 3 do not correspond with what is plotted in Figure 1. CMDL defined the WMO Scale as the average of all calibrations available until that time, shown as WMO 1993.2 etc. in Figure 3. In late 2001 we decided to base the WMO Scale entirely on the CMDL manometric calibrations alone, of which we had completed four episodes at the time. The Scripps calibrations exhibited considerable inconsistency among themselves, especially at the low and high ends of the scale. The difference with CMDL increased significantly at higher concentrations. The X99A revision did not eliminate the internal inconsistencies between successive Scripps calibrations, but the overall average difference from CMDL became much smaller, and is only 0.02 ppm lower than CMDL in the ambient range of 345-415 ppm. The WMO Scale based on CMDL data alone is shown in Figure 3 as WMO 2001.8 and later. Note that the scatter of the individual assignments before 2001.8 is smaller because the Scripps measurements were done with an NDIR analyzer, whereas the

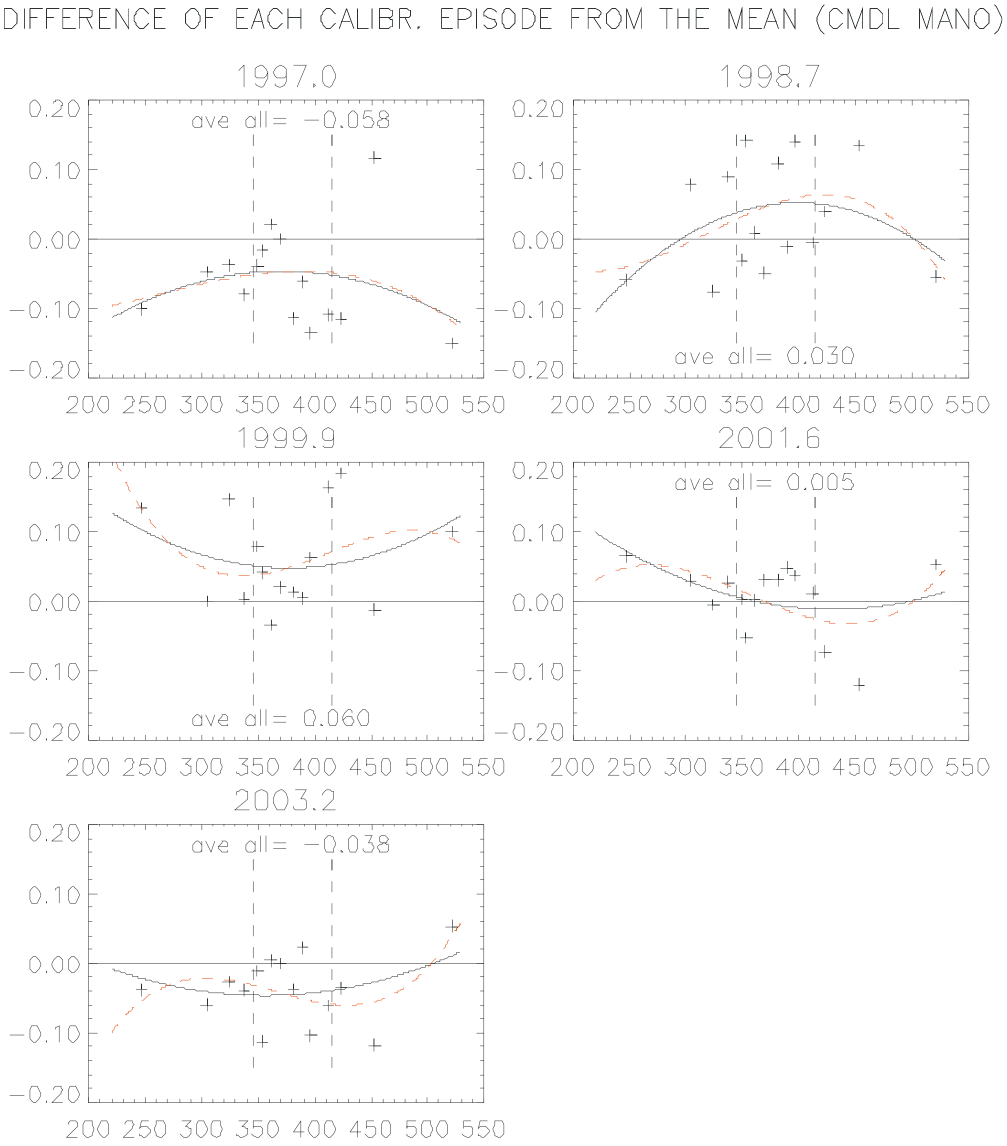


Figure 2: Differences of each CMDL calibration episode from the mean of five calibration episodes. Assigned values for each cylinder along the x-axis (ppm); Differences along the y-axis (ppm); Solid curve: quadratic polynomial fit to the differences; Dashed curve: cubic fit.

CMDL measurements were all manometric. Figure 3 is one demonstration (out of many) that lower scatter or reproducibility by itself is clearly unrelated to accuracy. The scatter of the CMDL assignments of the Primaries around the WMO Scale of about 0.04 ppm is consistent with taking the average of five episodes in which the "noise" level is about 0.08 ppm (see Section 3 below). We believe that the inconsistency of successive Scripps determinations is caused by their technique of propagating the scale via NDIR measurements. All gases are measured against two references, called the "principal" and the "span", which are both in the ambient background range, typically 20 ppm apart. When gas mixtures are calibrated that are far outside of the range of the principal and span, a large extrapolation is necessary. The uncertainty of the measured difference between the principal and span gets multiplied several times over a large extrapolated range. In addition, the non-linear characteristics of the analyzer response are assumed to remain constant between major calibration episodes. These problems are especially evident in Figure 1 for cylinder numbers 110 (247 ppm), 107 (453 ppm), 132 (521 ppm).

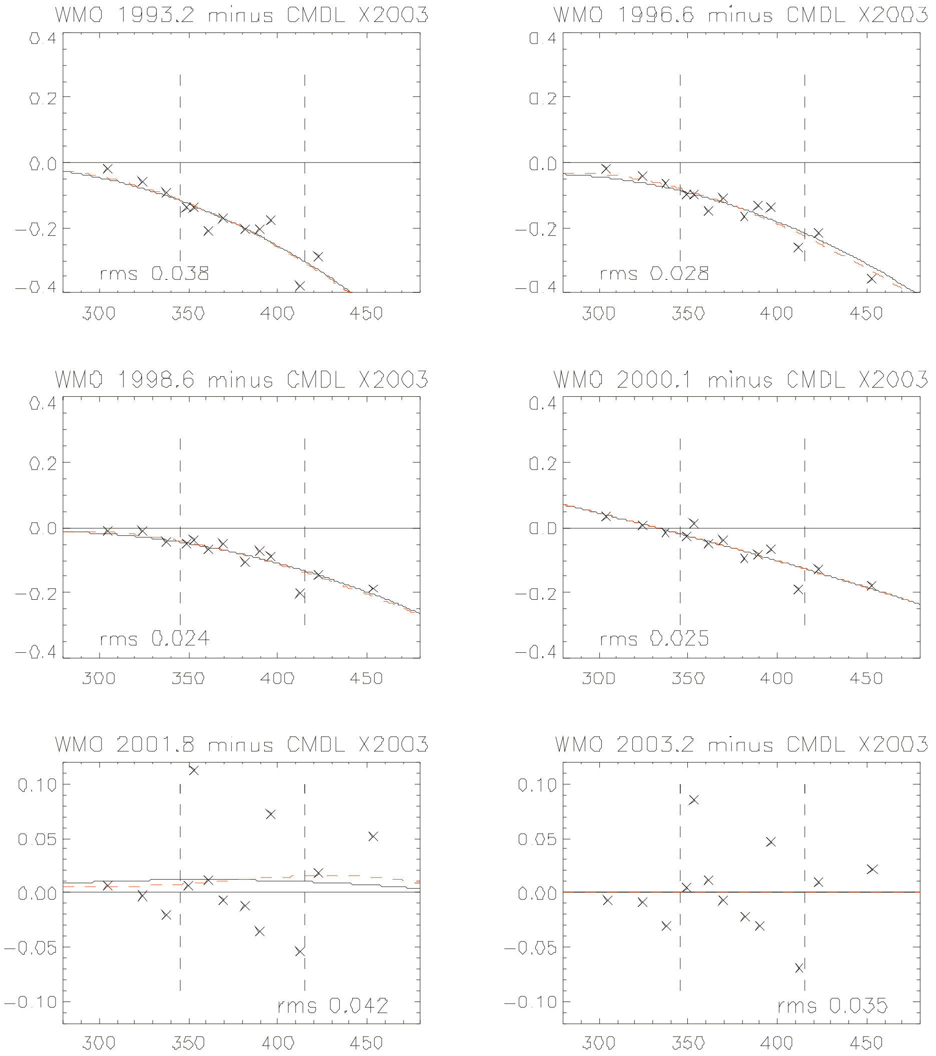


Figure 3: Differences of past assignments of the WMO Primaries compared to the current WMO Scale. The curves are fit as in Figure 2, dashed lines are often coincident with solid lines. Note the change in vertical scale for the lowest two panels.

3.2.3 Detection of drift of a primary standard

The standard deviation of differences between the means for each CMDL calibration episode is 0.08 ppm on average for all Primaries. With current procedures, any potential drift of a primary standard will have to be evaluated in light of a basic “noise” level of 0.08 ppm. We have carried out Monte Carlo simulations of drifting reference gas cylinders to get an idea of our current ability to detect drift of any of the Primaries. Figure 4 shows an example. In that case we simulated a cylinder with a real drift rate of 0.01 ppm/year, and a manometric calibration episode once every 1.5 years with randomly assigned noise of 0.08 ppm for every episode. The results of chi-square tests for goodness-of-fit are printed on the graphs for a 1-parameter fit (assuming a constant value, no drift), and a 2-parameter fit (assuming drift linear in time). For example, after 4 episodes the 1-parameter reduced chi-square equals 1.22, and a look-up table shows that there is a 30% chance to obtain such a value or higher in case there is no drift. Therefore, one cannot reject the hypothesis that this cylinder is stable. In our example even after 8 years the chances of obtaining a 1-parameter reduced chi-square value of 0.81 or higher are 55%, which implies that a constant value still provides a good fit to the data. In the lowest panel of Figure 4, after 15 calibrations and 21 years, one can be pretty sure that the cylinder is indeed drifting. There is only a 1% probability that a 1-parameter reduced chi-square value of 2.11 or larger will be found. Therefore, a constant value is not a good fit. In this case there is a 25% chance that a reduced chi-square of 1.24 or larger will be found for the 2-parameter fit. Therefore we accept the hypothesis that the cylinder is drifting linearly over time because it cannot be rejected.

Of course, a larger rate of drift will be detected sooner. If the linear rate of drift is as much as 0.025 ppm/year, the drift will in most cases have been detected with good confidence in 10 years. If the variance of successive calibration episodes can be decreased, we would be able to statistically detect cylinder drift sooner, but the reality of such detection would still be in doubt in case the standard deviation of successive calibrations would be substantially smaller than the estimated absolute accuracy of the measurements. In that case we would have no way to prove that our procedures have not undergone a gradual change that we are not aware of, or cannot quantify accurately. In Zhao et al. (1997) the one-sigma absolute accuracy of our method was estimated to be 0.07 ppm. This also illustrates that it is essential to have independent confirmation of the absolute accuracy of the WMO Scale, such as comparisons with gravimetric scales as well as with the manometric scale maintained at Scripps.

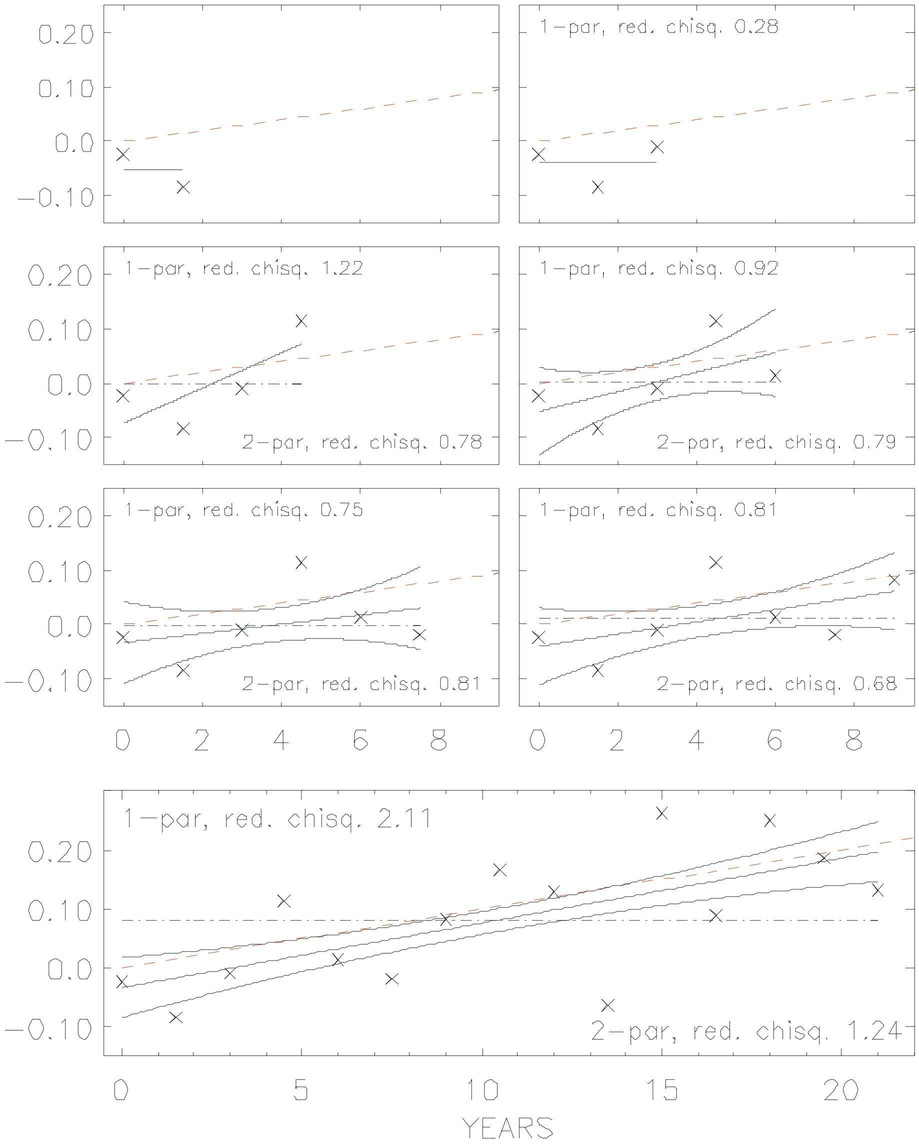


Figure 4: Simulated successive calibrations of a drifting Primary cylinder. The real drift is depicted as the dashed upward sloping line. Chi-square tests are used to detect the statistical significance of drift. A straight line (dash-dot) is fitted to successive calibrations (shown as crosses) on the assumption that there is no drift. A 2-parameter fit assuming linear drift and one-sigma confidence intervals about the mean and slope are drawn as well.

3.2.4 Can drift of reference gases be detected without using absolute measurements?

Since it is a common practice in many laboratories to perform consistency checks among cylinders in order to detect drift of one or more cylinders, we have done a second set of Monte Carlo simulations to clarify what can or cannot be concluded from such consistency checks. One of these simulations is shown in Figure 5. A hypothetical laboratory has six high level standards, two of which are close together. We have shown as crosses on the top panel the drift of individual cylinders that has occurred over a given amount of time relative to each of their initial values. The cylinders have experienced real, but unknown, drift. The scale, defined in this case between 335 and 380 ppm, is determined by a curve fit to the response of a NDIR or other analyzer to the set of cylinders. If this laboratory normally determines its scale by a quadratic fit to the highest level reference gases, the real drift of the scale in this case is determined by a quadratic fit to the deviations shown in the top panel. Therefore, a set of polynomial curves has been fitted to the individual deviations that define the actual drift of the scale. The lower panels show the residuals of the individual cylinders to each of the curve fits.

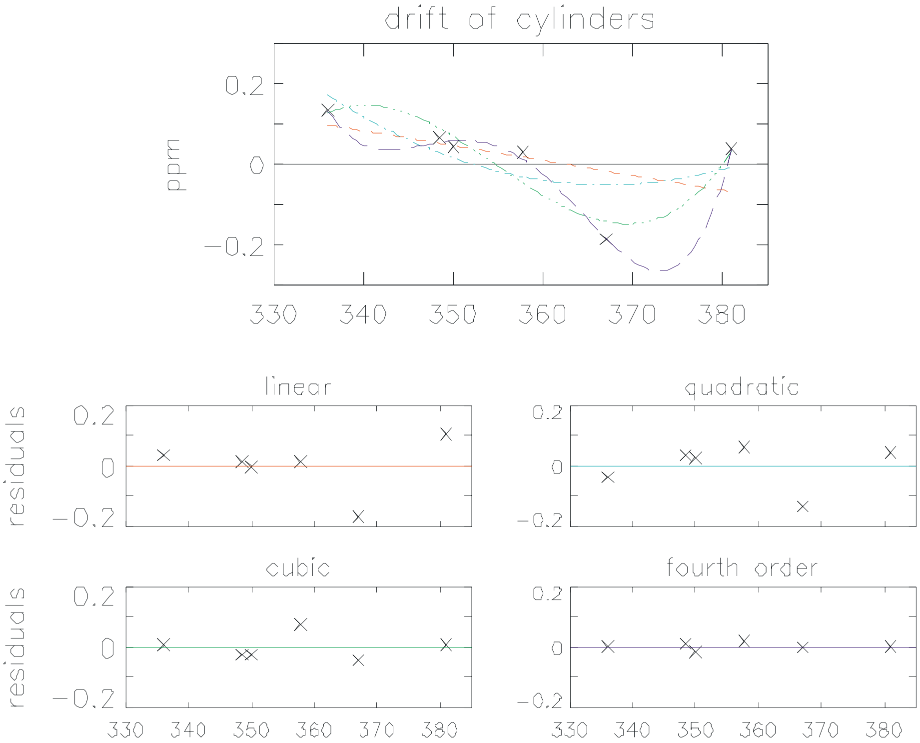


Figure 5: Simulation of consistency checks among cylinders to detect drift. Upper panel: Hypothetical drift of 6 standard reference cylinders over time, with their nominal concentrations plotted along the x-axis. A linear (short dashed line), quadratic (dot+dash), cubic (3 dots+dash), and fourth order polynomial (long dashes) are fit to the changes of the 6 standards. Next rows of plots: residuals of the 4 curve fits above.

What conclusions can we draw from this example? In reality the low end of the scale went up and the standard at 367 ppm went down. In case the scale is normally defined by fitting a linear function to the reference gases the tilting of the scale cannot be detected, nor can any overall average movement be detected by looking at the residuals. In case the scale is defined by a quadratic curve, any change in curvature between the ends and the middle is added to the information lost. What is left is that one may be able to detect in some cases whether a single gas is likely drifting relative to its close neighbours. Even that ability is lost in this example when a cubic or higher order fit is used. In the cubic case there is effectively only one degree of freedom left because two standards out of the six are very close together at 350 ppm. In many cases a much larger set of reference gases than six is needed just for detecting drift of an individual cylinder. Drift of the major features of the entire scale cannot be detected, even with a larger set of reference gases. All one has in that case is that the chance of major features drifting is perhaps lower.

3.2.5 Propagation of the scale

In order to lengthen the useful life of its highest level standards CMDL has always propagated the scale via a set of Secondary standards, which in turn are used to calibrate almost all other standards. The Secondaries are calibrated twice per year against the Primaries. The Secondaries last from 3-5 years. All calibration transfers from a higher level to a lower level are done with 4 higher level standards always bracketing the concentrations of the 2 or 4 lower level standards that are being calibrated. All of our transfer calibrations have been done with NDIR, but with a succession of different instruments.

There are several issues pertinent to the transfer calibrations that we would like to mention here:

a. A calibration scale, relating instrument response to mole fraction of the gas being measured, is defined by a curve fit to a set of well-defined reference gas mixtures. Ideally one would like the scale to be uniquely defined by the set of reference gases because that allows the scale to be transferred between laboratories. There is a limit to the accuracy with which this can be done. We have found that, when the same gases are run through three NDIR analyzers (Siemens Ultramat 3, Licor 6252, and Licor 7000) in direct sequence, the residuals of such a curve fit are different for each analyzer at the level of 0.01-0.03 ppm. The differences remain when the experiment is repeated at a later time. They are thus a property of the analyzer, and do not transfer when a set of reference gases is sent to another laboratory.

b. Especially at the low and the high end the definition of the scale is more sensitive to individual gas mixtures, namely the gas mixtures with the lowest and the highest mole fraction. Furthermore, while using the same set of reference gas mixtures the definition of scale also depends on the number of parameters used to define the instrument response curve, for example, a quadratic or a cubic polynomial.

c. The mole fraction assignments of the Primaries contain unavoidable errors and uncertainty (see Figure 2). If we substitute one of the Primary standards with a different one while calibrating the Secondaries, the calibration results are changed somewhat because of the errors in the Primaries. Such inconsistencies largely disappear if, for the purpose of transfer calibration only, we use not the actual assigned value of the Primaries but their value “corrected” to the overall curve fit to the entire Primary set. In other words, we subtract the residual of each Primary to the overall curve fit from its assigned value (last panel of Figure 3). In that way the Primaries represent the entire scale rather than only their own assigned value. We changed to this procedure in 2001.

d. Inconsistencies between successive Scripps calibrations and between Scripps and CMDL translated only gradually and partially into working level standards.

e. Based on the information presented above, a minor revision of the WMO CO_2 scale is due. All users of CO_2 reference gas mixtures calibrated by CMDL will be notified of changes to their calibrated values.

Reference

Zhao, C., P.P. Tans, and K.W. Thoning, A high precision manometric system for absolute calibrations of CO_2 in dry air, J. Geophys. Res. 102, 5885-5894, 1997.

3.3 Making Quality Measurements Without a Data Management Strategy

Ken Masarie

3.3.1 Introduction

The idea of a data management strategy is simple enough; organize and save atmospheric trace gas measurements made now so that we can later evaluate their quality and explore their meaning. Yet the carbon cycle measurement community has demonstrated the tendency to spend considerable effort developing the measurement technique while neglecting the development of a strategy for managing the observations that have been so carefully made. Data management is often an afterthought. In some instances the need for a data management strategy arises only after a data crisis occurs. Why do we tend to neglect data management when developing our measurement programmes?

The analytical method, calibration system, and data management strategy are all fundamental components of an ongoing measurement programme. If inadequate resources prevent us from establishing any one of these components, maintaining an ongoing programme becomes a tenuous proposition. Failing to develop an essential component is more likely related to the environment in which a programme is developed. Often we obtain a source of funding to develop a measurement technique (e.g., test the feasibility of making Ứ^{13}C (CH_4) measurements from the air remaining in a CMDL network flask after all other measurements have been made). Funding is typically for a fixed time period and supports temporary personnel. Periodic reports to the funding agency document progress. This process establishes an environment driven by short-term objectives: develop the technique, measure atmospheric samples, and interpret initial results. Managing the data is typically not one of the short term objectives. However, if the technique is feasible and can be adapted to making ongoing measurements, there is often some urgency to begin as soon as possible. It is during this transition when the short-term project is converted into a long-term programme where development of a data management strategy is often overlooked. All too often, the management tools (e.g., lab notebooks, text files, spreadsheets) used to meet the short-term objectives become by default the basis for the long-term strategy. In time, it becomes painfully clear that ***we cannot sustain a quality measurement programme without an equal commitment to a quality data management strategy***.

3.3.2 Flow of Data

Within an ongoing measurement programme, the natural flow of information is from data in its rawest form (e.g., detector response) to data in its most processed form (e.g., averaged mixing ratios). Intermediate steps establish a hierarchical data structure (Figure 1). This tiered data structure is critical to an atmospheric trace gas data management strategy because it enables us to retroactively revise numbers at any level in the hierarchy and automatically propagate the changes to affected data at lower levels. In practice, the flow of information is more complicated and includes information about the observations and details on how to treat data produced using different methods. Not only must we manage the measurement data, we must manage all supporting information (metadata). Our data management strategy must guarantee that we can, at any time in the future, unambiguously reprocess large amounts of raw data to exactly reproduce our current results.

3.3.3 Data Management

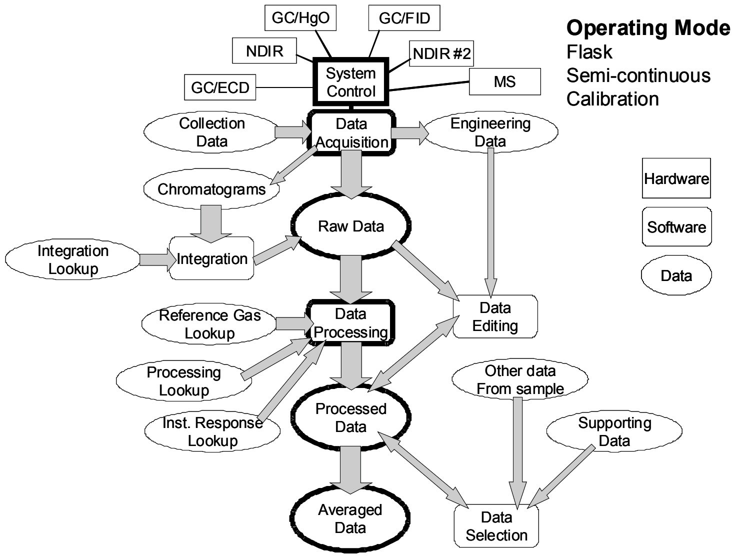


Figure 1: Data flow in an atmospheric trace gas measurement programme. An underlying hierarchical flow of data (shown in bold) simplifies automatic retroactive revisions due to changes in calibration or methodology.

Managing data requires a strategy that has at its core a database management system (DBMS). The DBMS has two primary components: a DB engine and a set of features that simplify access to the database. All DBMSs share basic features. A DBMS is a collection of tables related to the measurement process. Each table is a collection of data about a specific aspect of the measurement process. Tables are a matrix of columns and rows. Each column has a user-assigned attribute (e.g., site ID, collection date, sample ID). The intersection of a row and column is a field. Tables may be stored as text or binary files. If tables are related to each other, e.g., by sharing one or more attributes (keys), the DBMS is called a “relational” DBMS or RDBMS. Attributes whose fields never change once assigned make suitable keys. For example, a unique event number automatically assigned to the collection of a flask air sample is a good key because it has no meaning beyond linking collection details to related information residing in other tables. Non-key data stored in a RDBMS typically exist in a single location and are not repeated in other tables. A well-constructed RDBMS makes few assumptions about how data are related or how they will be extracted from the database. “Queries” are used to extract, append, remove, and alter data.

RDBMS manufacturers recommend using a RDBMS when 1) data are dynamic; 2) the volume of data is large and increasing; 3) routine and automatic data updates are required; 4) queries may be initiated from external applications (e.g., C, Perl, PHP, IDL); 5) external applications are required to derive, process, and analyze data; 6) tables must relate; 7) many users will be accessing the same data; and 8) strategies for data exploration are many and varied.

Several RDBMS products are commercially available including Paradox (Borland), Access (Microsoft), IQ (Sybase), Informix (IBM), and MySQL. In recent years, the cost of these products has fallen considerably making commercial packages a viable option for managing atmospheric trace gas data.

An ongoing atmospheric trace gas measurement programme, regardless of size, requires a data management strategy that includes some type of RDBMS. Working with a RDBMS does require an understanding of general data management concepts, the RDBMS architecture and a working knowledge of Standard Query Language (SQL), the language used by most RDBMSs. These prerequisites may present a barrier. Unfortunately, there are no acceptable alternatives.

A spreadsheet application is not a RDBMS. Spreadsheet manufacturers recommend using a spreadsheet when 1) data are static; 2) the volume of data is small and fixed; and 3) the spreadsheet owner is the primary user of the data. These criteria are not consistent with an ongoing atmospheric trace gas measurement programme. Nevertheless, many of us have, on occasion, opted to use a spreadsheet to “manage” observing data because it was readily available and easy to use. With little effort, we are able to quickly perform calculations and graph data. The spreadsheet works well for awhile but in time, fails as a data management strategy. The price to disentangle from the spreadsheet and migrate to a proper RDBMS can be painfully high.

3.3.4 Developing a Strategy

The first step in developing a data management system is to formulate a strategy. The WMO document No. 150 entitled "Updated Guidelines for Atmospheric Trace Gas Data Management" [*WMO*, 2003; *WMO*, 1998] is intended to serve as a starting point for new and existing laboratories ready to develop a data management strategy. The document includes an introduction to general data management terms and concepts, a recipe for developing a strategy, and a discussion on selecting the RDBMS. It describes the CMDL data management strategy (at the time of publication) and highlights its strength and weaknesses. The document is only an introduction; many references are readily available that provide a much more thorough investigation of this topic.

3.3.5 Evolution of the CMDL carbon cycle RDBMS

The CMDL CCGG data management strategy evolved somewhat haphazardly (see Figure 2). Flask air and in situ measurements of CO_2 began more than 25 years ago when computing technology was relatively new and expensive. As the CMDL observing programme slowly expanded, each new measurement project made use of the latest available technology which was more powerful and affordable. As a result, CMDL used several independent data management strategies simultaneously. Metadata that could have been shared between projects were instead being entered and managed independently. Prior to 1992, for example, sample collection details from the cooperative air sampling network were manually entered into four independent databases. Differences in interpreting collection details hand recorded by field operators led to discrepancies among the databases. This eventually led to serious problems as the network projects increasingly relied on comparisons among the trace gases and isotopes measured from the same air sample to assess the quality of samples and interpret the results.

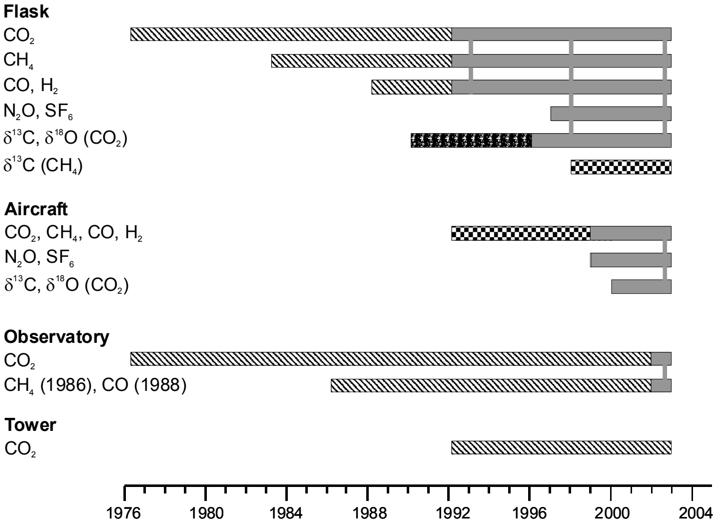


Figure 2:* *Evolution of the CMDL data management strategy. Bars with backward slashes represent independent RDBMS strategies. Bars with checkered hashes represent data stored, processed and manipulated in spreadsheets. Solid bars indicate an integrated RDBMS strategy. All isotope measurements are made by the Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado.

In 1991, CMDL formalized a strategy for managing data from the cooperative air sampling network. The strategy required standardizing data structures, sharing metadata, and adapting software for use with all measured trace gases. At the time, the cost of commercially available RDBMS applications was prohibitively expensive requiring CMDL to develop its own text-based RDBMS [*WMO*, 2003]. CMDL network data and analysis procedures were quickly adapted to the new RDBMS, however, ingesting isotope data from analyses made by INSTAAR was more difficult. At the time, CMDL was using an HP computer network running UNIX that allowed CMDL users and analytical systems central access to the data file server. INSTAAR, on the other hand, had limited network capabilities particularly with the computers and software used to control the mass spectrometers. As a result, INSTAAR relied on spreadsheets to "manage" the network isotope data. With time, access speed degraded, multiple versions of files led to confusion, and comparison of isotope data and CMDL whole air data became exceedingly difficult. By 1995, both labs were compelled to resolve this problem. It took one full year to reconcile INSTAAR data with CMDL data and to develop the necessary software and procedures to process and manage the INSTAAR data using the CMDL data structure and RDBMS. In 1998, computer and software constraints again created similar problems for the fledgling INSTAAR $\delta^{13}C$ in CH_4 measurement programme. With few options, INSTAAR again resorted to using a spreadsheet until a proper strategy could be developed. Aircraft data and in situ data from the CMDL baseline observatories are now being managed by the CMDL RDBMS. Work is currently underway to adapt in situ tower data and methane isotope data into the CMDL RDBMS.

CMDL is currently establishing additional tower and aircraft sampling sites in North America as part of the North American Carbon Programme (NACP) and expanding the global cooperative air sampling network [see map from Tom Conway's contribution]. By 2010, CMDL will likely increase by an order of magnitude the volume of data currently managed. This prospect requires ongoing development of the CMDL data management strategy to ensure that CMDL can continue to assess the quality of the data and interpret their meaning in a timely manner. Recent changes to the CMDL RDBMS are described elsewhere in this document [Masarie and Tans].

3.3.6 Summary

CMDL has learned, by trial-and-error, that an atmospheric trace gas measurement laboratory cannot sustain a quality measurement programme without an equal commitment to a quality data management strategy. While the lure of a spreadsheet is great, particularly when meeting short-term objectives, we must resist the temptation and instead focus on developing a long-term strategy. A data management strategy must ensure that we can routinely assess the quality of our growing volume of data, automatically revise data when required, and promote the exploration and interpretation of the observations. As the observing network evolves, so too must our data management strategy.

References

Masarie, K.A. and P.P. Tans, "Updated Guidelines for Atmospheric Trace Gas Data Management", Global Atmospheric Watch Report Series No. 150, World Meteorological Organization, TD No. 1149, Geneva, 2003.

Masarie, K.A. and P.P. Tans, "Guidelines for Atmospheric Trace Gas Data Management", Global Atmospheric Watch Report Series No. 129, World Meteorological Organization, TD No. 907, Geneva, 1998.

3.4 A Web-Based Interactive Atmospheric Data Visualization Tool: Near Real-Time Access to Data from the NOAA CMDL CCGG Observing Network

Ken Masarie and Pieter Tans

3.4.1 Introduction

Managing a growing volume of atmospheric data, providing tools to help detect problems quickly, and making data available in a timely manner is an ongoing challenge. In 2003, CCGG added several new projects including semi-continuous measurements of CO_2 at 2 levels on a tall tower in the north-eastern United States; and discrete measurements of CO_2, CH_4, CO, H_2, N_2O, SF_6, and the stable isotopes of CO_2 at 4 locations using aircraft and at 2 surface locations. Table 1 summarizes the current CCGG measurement programmes. Nearly 9000 discrete samples are collected annually, and 19 streams of continuous data are downloaded to Boulder daily. In the next several years, CCGG plans to greatly expand its observational network with intensive ongoing sampling from aircraft and tall towers in North America (our commitment to the North American Carbon Programme (NACP)) and continued expansion of the global cooperative air sampling network into under-sampled regions of the world. This planned expansion will increase, by an order of magnitude, the volume of data we manage.

3.4.2 Improvements to CCGG Data Management

A recent assessment of our current data management strategy and quality control procedures focused on our ability to maintain the level of standard we require for data produced by this laboratory under the expansion scenario. We identified several limitations of our current strategy and have improved our ability to manipulate and probe data between the flask, aircraft, tower, and observatory programmes. Figure 1 shows schematically the current data management strategy (see Masarie elsewhere in this document). Individual projects are required to adopt a standardized data structure but can remain somewhat independent from each other. Standardization is advantageous to individual projects because they can utilize shared metadata and make use of existing tools within CCGG to manipulate and view data. The structure is hierarchical to match the flow of information in the measurement laboratory. The tiered structure enables us to retroactively revise numbers at any level in the hierarchy and automatically propagate the changes to affected data at lower levels. The strategy uses text files and a commercial relational database management system (RDBMS). Measurement results are managed by MySQL which greatly improves our ability to quickly manipulate and compare data between the different measurement programmes (e.g., flask network, aircraft, tower, observatory). MySQL was selected because it is 1) freely available; 2) fast; 3) simple; 4) widely used; 5) well maintained and documented; 6) supported by several programming environments (e.g., C, Perl, PHP; and 7) accessible across distributed networks.

3.4.3 Interactive Web Site

Improvements to our data management strategy enabled us to introduce a Web-based interactive atmospheric data visualization (IADV) tool (Figure 2 and http://www.cmdl.noaa.gov/ccgg/iadv/). The IADV Web site is intended to improve our ability to assess the quality of a growing volume of data and is designed to better serve users outside CCGG including students, educators, the press, business, and policy makers as well as the scientific research community. To achieve these objectives the IADV tool 1) accesses our operational database in order to make all data available including our most up-to-date measurements; 2) centralizes access to a growing library of graphing tools developed within CCGG; 3) requires minimal maintenance; 4) ensures flexibility and adaptability; 5) provides an environment in which users can easily manipulate the data and prepare custom graphs that can be saved in a variety of formats; 6) uses simple development tools that do not require users to download plug-ins, add-ons, or updates; 7) performs consistently on a variety of computers and browsers; and 8) serves users with typical internet access speeds. Additionally, because users can view near real-time data that have not yet been screened for calibration or experimental problems, these “preliminary” data are clearly identified and their limitations explicitly stated.

The IADV Web site was launched in May 2003. Since May, the site has been visited more than 2250 times (~ 250 per month) from 49 countries. The site currently provides details on each sampling location; acknowledges our cooperating and sponsoring agencies; presents graphs depicting time series, average seasonal patterns, vertical profiles, south-to-north latitudinal distributions, global surfaces, and flask/in situ comparisons; and enables users to create custom graphs using data from multiple sites and multiple trace gases. To maximize the usefulness of the site, we routinely and automatically prepare thousands of the most frequently requested graphs (Figure 3). This ensures that the majority of requests can be displayed with no delay. Advanced graphing functions allow users to select any number of data sets and manipulate, compare, and plot data in whatever manner they choose. A custom request takes several seconds to process as data are extracted from the database and the graph prepared according to user-defined preferences.

3.4.5 Future Plans

The IADV Web site is not yet fully functional and will continue to evolve with time. Future plans include expanding the selection of prepared graphs and providing the ability to highlight a region on the global map and display all flask, aircraft, tower, and observatory data derived from within the region. Additional functionality will be added as users and project leaders discover new ways to explore and evaluate the CCGG observations.

Because the IADV tool is optimized for plotting near real-time atmospheric greenhouse gas observations, it may be of interest to other atmospheric carbon cycle measurement laboratories. Our design strategy lends itself to making this product easily available to interested laboratories. As other laboratories develop similar capabilities, we will encourage the community to standardize the look and feel of the sites so that together we can provide a powerful resource whereby visitors can easily move among a "network" of atmospheric data Web sites maintained by the various measurement laboratories.

Table 2: Current CCGG Measurement Programmes.

Discrete Sampling			
Global Cooperative Air Sampling Network ~6500 samples yr^{-1} (160,000 Total)		Aircraft Sampling Network ~2400 samples yr^{-1} (12,500 Total)	
	Year		Year
CO_2	1967	CO_2	1992
CH_4	1983	CH_4	1992
CO,H_2	1988	CO,H_2	1992
$\delta^{13}X$, $\delta^{18}O$ (CO_2)	1990	N_2O,SF_6	1997
N_2O,SF_6	1997	$\delta^{13}X$, $\delta^{18}O$ (CO_2)	2000
$\delta^{13}C$ (CH_4)	1998		
Semi-continuous Sampling			
CMDL Observatories (4 sites)		Tall Tower Network (3 sites)	
	Year		Year
CO_2 (BRW, MLO, SMO, SPO)	1974	CO_2	1992
CH_4 (BRW, MLO)	1986		
CO (BRW, MLO)	1988		

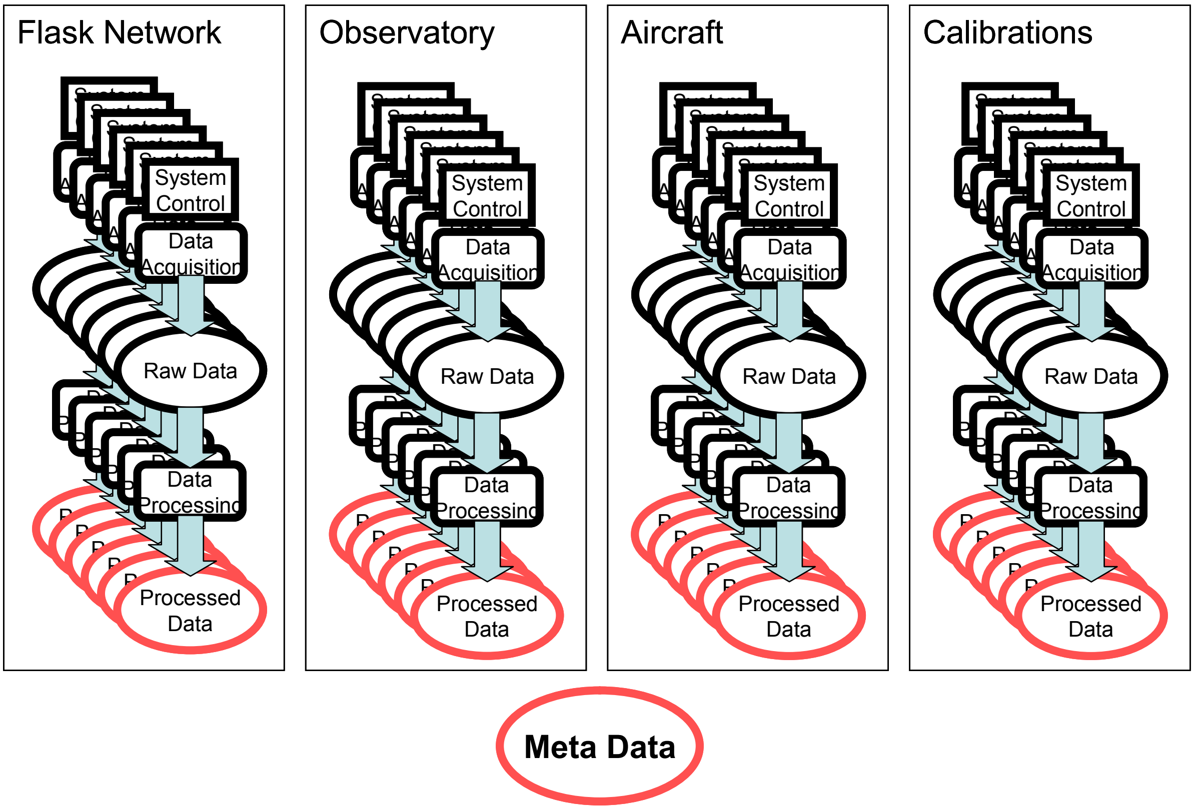
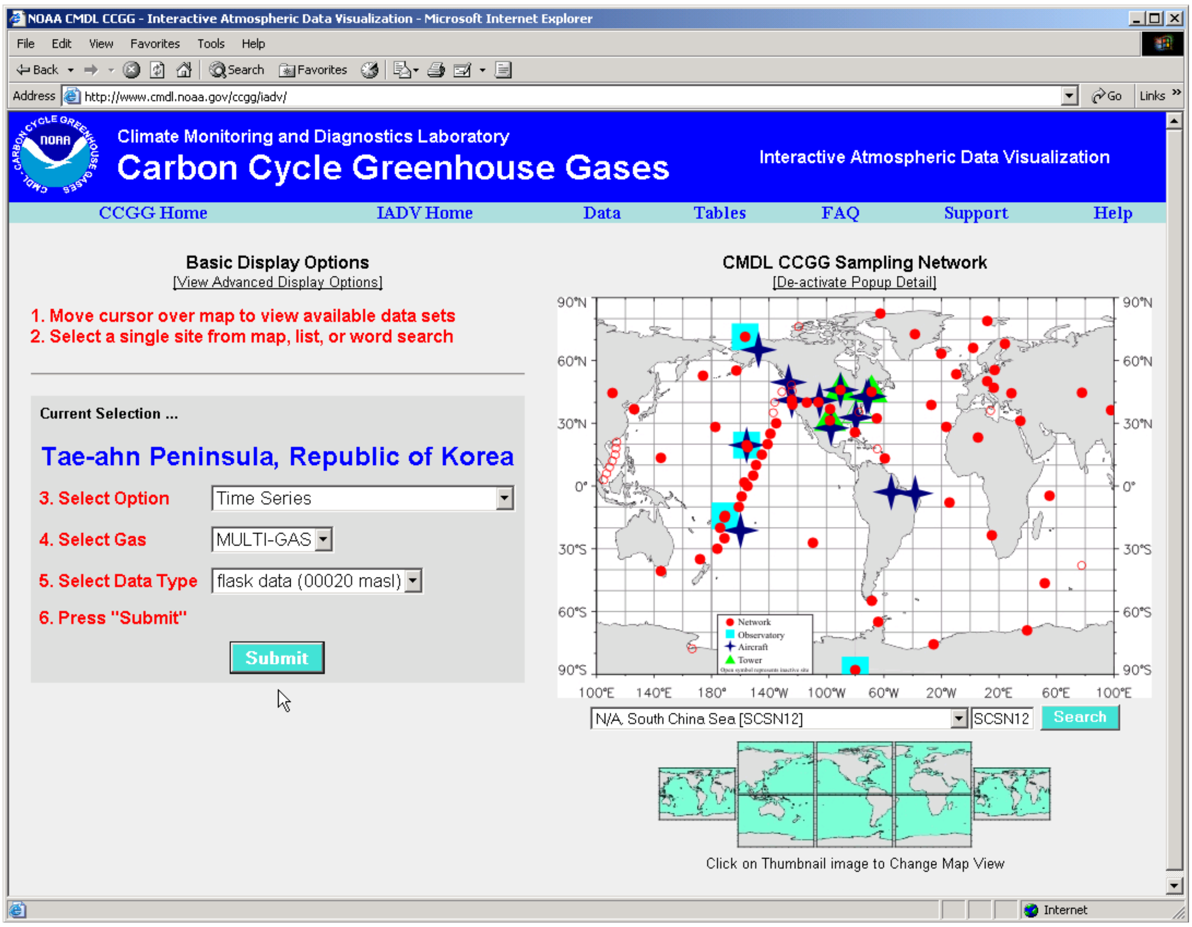


Figure 1: Schematic of CCGG Data Management System. Parallel structure within each programme represents data flow of each measured trace gas species.
The tall-tower programme is not represented.



NOAA CMDL CCGG - Interactive Atmospheric Data Visualization - Microsoft Internet Explorer

Address http://www.cmdl.noaa.gov/ccgg/iadv/

Climate Monitoring and Diagnostics Laboratory

Carbon Cycle Greenhouse Gases

Interactive Atmospheric Data Visualization

Basic Display Options

[View Advanced Display Options]

1. Move cursor over map to view available data sets
2. Select a single site from map, list, or word search

Current Selection ...

Tae-ahn Peninsula, Republic of Korea

3. Select Option: Time Series

4. Select Gas: MULTI-GAS

5. Select Data Type: flask data (00020 masl)

6. Press "Submit"

CMDL CCGG Sampling Network

[De-activate Popup Detail]

N/A, South China Sea [SCSN12]

SCSN12

Click on Thumbnail image to Change Map View

Figure 2: Interactive Atmospheric Data Visualization (IADV) home page.

Web address: http://www.cmdl.noaa.gov/ccgg/iadv/.

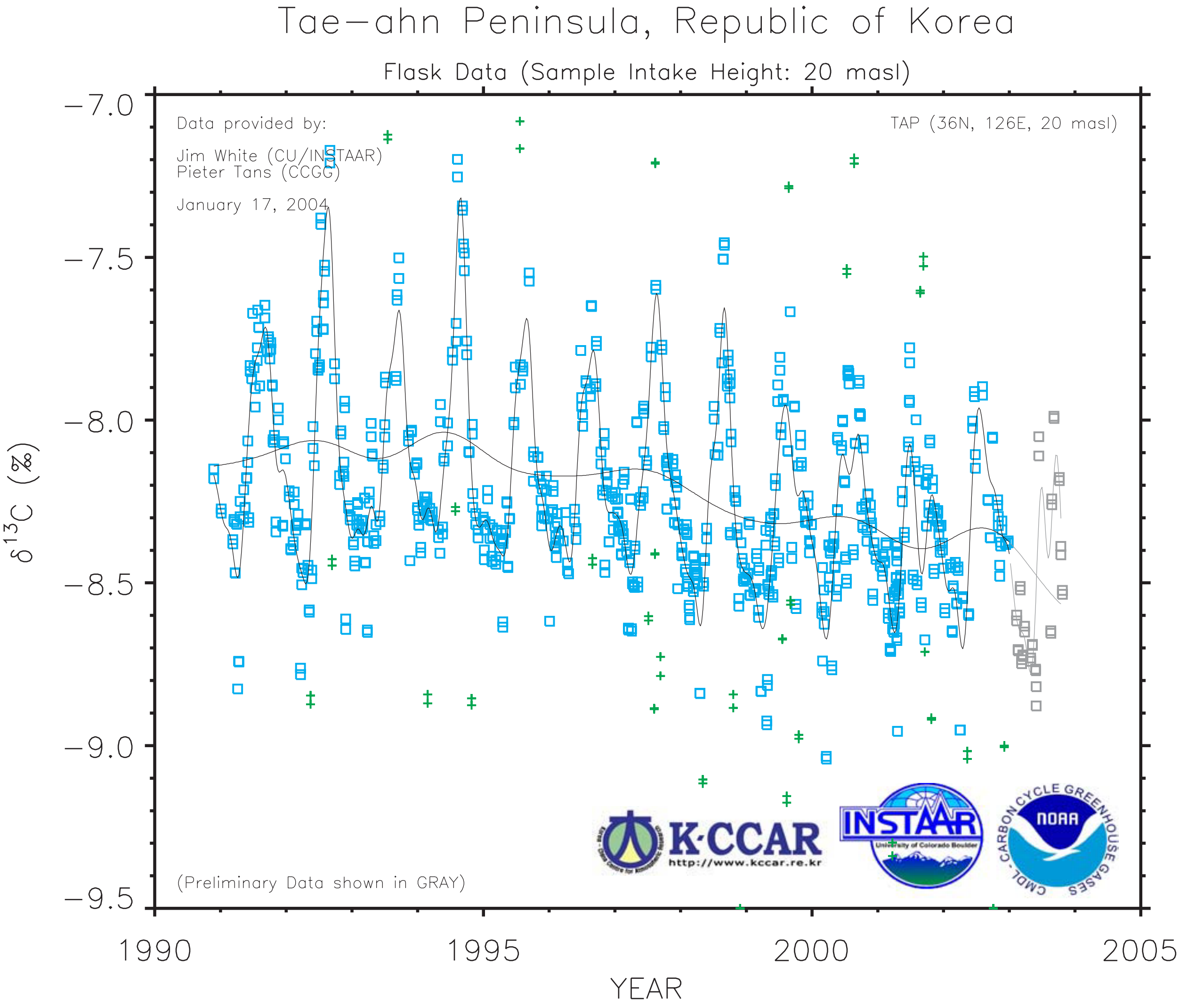


Figure 3: Graph produced from IADV Web site. The principal investigators and cooperating agencies are identified in the upper left and lower right portions of the graph. Preliminary data and curves derived from preliminary data are clearly identified in grey.

4. ISOTOPES IN CARBON DIOXIDE

4.1 Isotopic Analysis of CO_2 in Air Samples: Requirements for a New CO_2-In-Air Standard and Preparation of an Air-CO_2 Reference Mixture from Calcite Material

Prosenjit Ghosh and Willi A. Brand[‡]

Abstract

An *a*cid *r*eaction and *a*ir *mi*xing *s*tation (*ARAMIS*) is described which is capable to introduce COỨ at ambient levels into an air mixture (without CO_2) at the precision level required for air monitoring of the CO_2 isotopes. The mixing station is used for generating CO_2 by a conventional acid reaction (at 47°C carbonate powder is reacted with pure ortho-phosphoric acid) and mixing the reaction gas with synthetic air. The mixture is distributed into a number of glass flasks (5l volume, 1.6 bar) attached to the system. The isotopic composition was recovered by measurement of the flask air samples using the two automated cryogenic extraction line / mass spectrometer systems in the Jena isotope facility.

Using the same protocol we have generated CO_2-in-air mixtures from NBS-19 and other internationally available carbonate standards for assigning isotopic values to our new carbonate reference material (MAR-J1). The isotopic record in a number of batches prepared over the course of several months is presented. In addition, the relationship with existing CO_2-in-air scales (e.g. CG-99, based on calibration of pure CO_2 gas) has been evaluated by direct CO_2 admixture to synthetic air using the same setup.

4.1.1 Introduction

The isotopic composition and concentration of atmospheric air samples are useful parameters required for deriving the flux information of atmospheric CO_2 into terrestrial and marine compartments. In the terrestrial regime plant photosynthesis strongly discriminates against ^{13}C, while oceanic uptake and release of CO_2 do not significantly fractionate these isotopes relative to atmospheric values. As a consequence, the isotopic signal in atmospheric CO_2 is rather small and approaches the detection limit of modern analytical techniques[1]. Calculating fluxes with a small uncertainty requires a comparable precision in the analysis of $\delta^{13}C$ values as well as in the determination of CO_2 mole fractions. Current fossil fuel emissions of ~6 Gt C yr^{-1} result in a long term change of the CO_2 mixing ratio of 1.6 ppm yr^{-1} and a $\delta^{13}C$ change of about -0.025 ‰ yr^{-1}. While CO_2 analyses typically can be made with a precision of 0.1 ppm or better, $\delta^{13}C$ precision is near 0.01 ‰ at best[2].

In recent years there is a growing concern about climate change and consequent proposed actions to limit atmospheric levels of green house gases, in particular CO_2. An obvious requirement is much improved inter-laboratory calibration, with new laboratories participating in routine measurements, thus permitting high precision merging of data from a variety of sources. Wider comparison of CO_2 stable isotopic composition data between laboratories is possible provided an air-CO_2 reference material (reflecting the composition of air) is made available with a short, direct

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[1] *P. Ghosh and W.A. Brand, Stable isotope ratio mass spectrometry in global climate change research, Int. J. Mass Spectrom. 228 (2003) 1-33*

[2] *Masarie, K.A., R.L. Langenfelds, C.E. Allison, T.J. Conway, E.J. Dlugokencky, R.J. Francey, P.C. Novelli, L.P. Steele, P.P. Tans, B. Vaughn, and J.W.C. White, NOAA/ CSIRO Flask Air Intercomparison Experiment: A strategy for directly assessing consistency among atmospheric measurements made by independent laboratories, J. Geophys. Res. 106, (2001) 20445-20464*

link to V-PDB. This link also requires a high precision of about 0.015 ‰ in the case of carbon and 0.03 ‰ in the case of oxygen isotopes[3].

4.1.2 Background Information

There were several attempts in the past to tightly link the air-CO_2 isotopic measurement scale to V-PDB. The V-PDB scale for carbon and oxygen stable isotopes replaced the PDB scale in 1987[4]. V-PDB was defined by assigning $\delta^{13}C_{VPDB} = +1.95$ ‰ and $\delta^{18}O_{VPDB} = 2.2$ ‰ (exact) to the international reference material NBS-19. In order to report to this scale, isotope laboratories generate carbon dioxide by reacting NBS-19 carbonate with 100 % phosphoric acid as well as extract CO_2 from air cryogenically. By measuring the resulting CO_2 gases against each other stable isotope values are assigned to the respective laboratory air standard (in a high pressure tank) used for routine measurement.

The stable isotope laboratory at CSIRO (Atmospheric Research, AR) in Aspendale, Australia, which has been involved in air-CO_2 isotopic measurement since 1982 started with the calibration of a laboratory reference CO_2 gas (HC 453) using NBS-19. The original values were -6.396 ± 0.029 ‰ and -13.176 ± 0.083 ‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively[5]. These values were used subsequently for assigning δ-values to standard air in high pressure tanks which led to the now more widely recognized CG-99 scale[6].

More recently, in order to reduce the uncertainty associated with CO_2 isotopic measurements in different laboratories, CSIRO (AR) prepared 10 high pressure cylinders of air for the IAEA/WMO CLASSICS project (Circulation of Laboratory Air Standards for Stable Isotope inter-Comparisons) with the CO_2 concentration and stable isotope composition spanning the present background atmosphere values. In addition, two containers of high-purity CO_2 were included in the circulation. All gases were circulated twice and measured independently by four laboratories using their individual analysis systems and protocols for routine isotopic determinations.

The results of this inter-comparison exercise were presented at the 11th IAEA/WMO CO_2 experts meeting in Tokyo[3]. Significant differences in the mean isotopic values reported by the different laboratories were found. Moreover, the data for determinations made two years apart from each other often exceeded the target precision for merging data considerably (0.015 ‰)[2,3]. A number of possible causes for the observed discrepancies were discussed: (1) errors in the preparation of CO_2 gas from NBS-19 carbonate standard and initial assignment on the (V-)PDB-CO_2 scale, (2) propagation of initial assignment errors to subsequent working standards and hence to the sample and (3) systematic effects like ^{17}O correction, drift correction and cross contamination during gas switching in the ion source of the mass spectrometer (‘eta-effect’).

In order to improve the link to primary reference material (NBS-19, but also NBS-18, IAEA-CO-1 and others) we have devised an experiment where we tried to strictly follow the rule of identical treatment. In this approach, CO_2 was extracted from NBS-19 carbonate following a standard procedure. Instead of using the CO_2 gas directly for comparative isotopic measurement we mixed it with CO_2-free synthetic air. The resultant mixture of air containing CO_2 was transferred into three 5 litre flasks at 1.6 bar pressure for routine mass spectrometric measurement. In this

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[3] *Allison, C.E., R.J. Francey, J.W.C. White, B. Vaughn, M. Wahlen and A. Bollenbacher and T. Nakazawa, What have we learnt about Stable Isotope Measurement from the IAEA CLASSIC? WMO Report 148 (2003), 17-30*

[4] *see for instance: IAEA-TECDOC-825, available from the IAEA in Vienna: (http://www.iaea.org/worldatom/publications/catalogue.html)*

[5] *R.F. Francey, and H.S. Goodman in: Baseline Atmospheric Programme 1983-1984, ed. R.J. Francey and B.W. Forgan, CSIRO Australia, Division of Atmospheric Research, (1985)*

[6] *C.E. Allison and R. J. Francey, 'δ-^{13}C of atmospheric CO_2 at Cape Grim: The in situ record, the flask record, air standards and the CG92 calibration scale'. In: J.L. Gras, N. Derek, N.W. Tindale and A.L.Dick (eds.), Baseline Atmospheric Programme Australia 1996, Bureau of Meteorology and CSIRO Atmospheric Research, Melbourne, 1999; pp. 45-56*

preparation we obtained a reproducibility of 0.019 ‰ in case of carbon and 0.034 ‰ in case of oxygen as a longer term reproducibility for different batches of CO_2 in air.

4.1.3 Jena 'CG99' isotope scale

In Jena we implemented a local CG-99 scale on the basis of 6 high pressure reference air cylinders filled and supplied by CSIRO (AR), Melbourne, Australia. These cylinders have assigned δ values based on the CG99 scale at CSIRO. The corresponding measurements were made at the end of 1999. The cylinder with identification number CA01656 was chosen for positioning our measurements on the international scale. It's assigned CO_2 isotopic composition was $\delta^{13}C = -8.078 \pm 0.017$ ‰ and $\delta^{18}O = -0.847 \pm 0.033$ ‰. From the six cylinders, these values together with the mixing ratios of the trace gases were the closest to current atmospheric values. The other tanks of the suite serve as quality and drift control standards.

4.1.4 Experimental set up and flask preparation

The air preparation system ('ARAMIS', Acid Reaction and Air Mixing Station) in Figure 1, mounted on a mobile platform, is constructed mainly using ¼" stainless steel internally electropolished tubing (ULTRON, Dockweiler, Neustadt-Glewe, www.dockweiler.com).

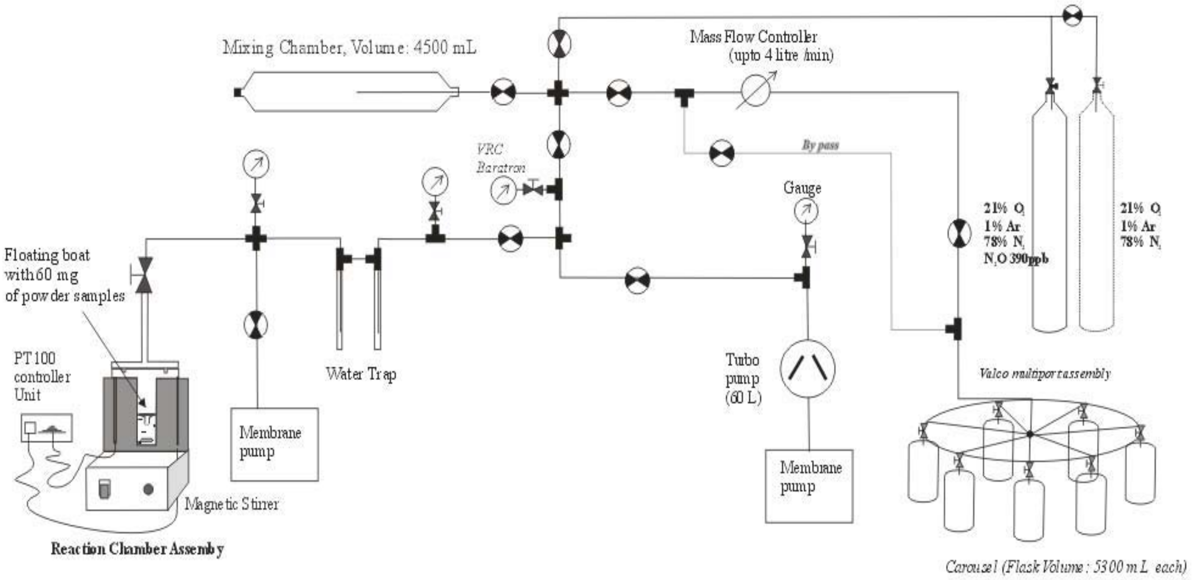

Figure 1: Layout of the Acid Reaction and Air Mixing System (ARAMIS).

The twin water trap comprises two ½" ULTRON tubes (30 cm in length) also internally electropolished. A set of three gauges were installed for pressure reading at three locations in the extraction line and close to the mixing chamber. Gauges 1 and 2 have coarse vacuum readouts whereas gauge 3 (Baratron, MKS, Andover, USA, www.mksinst.com) is designed for pressures up to 2100 ± 2mb. Prior to starting a new batch the whole setup is evacuated using a Pfeiffer membrane pump (model MVP 015-4; 1.5 m^3/min, located close to the reaction chamber) and subsequently by a 60 l/s hybrid-turbo pump (Pfeiffer model TMH071 with MVP 015-04 backup pump).

The sequence of events in preparing a set of reference air samples is as follows:

- Carbon dioxide is produced using the classical calcite reaction with H_3PO_4 at constant temperature. The resulting CO_2 is allowed to equilibrate with the Mixing Chamber (MC) for 20 minutes keeping the water trap at -77°C (dry ice / ethanol mixture). Here, expansion of CO_2 from the reaction chamber to the MC is done in a stepwise fashion (within 5 minutes following completion of reaction).
- An inlet close to the mixing chamber is included for introducing CO_2-free air from a high pressure tank. Following equilibration of CO_2 throughout the system (20mins) the CO_2 in the mixing chamber is isolated from the rest of the preparation system, sacrificing about 1/10th of the gas.
- Synthetic air is then added to the CO_2 in the MC up to pressure of ~1450mb. The mixture of CO_2 and synthetic air inside the MC is allowed to equilibrate for another 20 minutes.
- The mixture is then expanded from the MC through a mass flow controller (MKS model 1179AX53CS18V) into 3 evacuated 5 litre flasks attached to 3 ports of a multi-port (8 port) Valco valve using an initial flow rate of 3 l/min. The final pressure of the initial expansion is about 200mb.
- Final addition of synthetic air into the three flasks is made at 3 l/min until a pressure of 1.6 bar in the flasks is observed.
- The last step is two hours equilibration with the MC and the 3 flasks communicating before closing the individual flasks.

The resulting air-CO_2 mixtures in the 3 separate 5 l flasks are measured together with ordinary air samples within a single sequence on one of our BGC-Airtrap/ IRMS systems[7]. δ–values are reported on the Jena-implementation of the CG99 scale.

4.1.5 Preparation of CO_2 from carbonate reference material

Carbonate powder

Laboratory carbonate reference powder was prepared from a (TS limestone) marble slab purchased from a local vendor (about A3 size). The slab was broken into chips, crushed into fine grains, and sieved. The <250 µ size fraction weighing about 0.9 kg was labelled 'MAR-J1' ('Marble-Jena1'). Texture and appearance of the powder is similar to the NBS19 carbonate material. Other fractions 250-315 µ (~0.5 kg) and 315-400 µ (~300 g), were designated as 'Mar-J2' and 'Mar-J3' and stored for future preparation. Other carbonate reference materials (NBS-19, NBS-18, Cal1, Cal2) were used in an identical fashion during our experiments.

Phosphoric acid

Preparation of the phosphoric acid involves 500 ml of ortho-phosphoric acid (99 %, MERCK, Darmstadt) and 25 g of phosphorus pentoxide, heated to 150°C for 2 hours. Final specific gravity at room temperature was 1.92 and 1.94. The acid is kept in a sealed container prior to use.

Reaction chamber

The reaction chamber was custom made from a block of copper in the workshop of the MPI-BGC. The volume of the reaction chamber is about 35 ml. The reaction chamber is connected to the vacuum line using a flat base glass lid and a Viton O-ring clamp. The reaction chamber is housed in a tight fit brass housing regulated to provide a constant temperature (± 0.1°C) using a Pt-100 resistor. About 10 ml of acid is filled into the reaction chamber and stirred. The whole assembly of reaction chamber and acid fitted with glass joint is kept under vacuum for more than one hour. After this time the stirrer is switched off shortly, the reaction chamber is opened and a quartz boat with 60 mg of MAR-J1 powder is added. The quartz boat is designed to allow free floating on the acid. The glass joint is fitted back to the reaction chamber and same sequence of evacuation is applied. The carbonate reaction is started manually by tilting the quartz boat using a permanent magnet applied from outside.

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[7] *R.A. Werner, M. Rothe and W.A. Brand, Extraction of CO2 from air samples for isotopic analysis and limits to ultra high precision d18O determination in CO2 gas. Rapid Comm. Mass Spectrom. 15 (2001) 2152-2167*

A similar set of experiments was performed with a glass reaction chamber. Compared to glass we noticed improved temperature stability during the reaction using copper.

Temperature of reaction

The role of temperature on the oxygen isotopic composition of CO_2 produced during reaction has been recognized long ago[8]. Based on a number of experiments it was concluded that isotopic fidelity maybe obtained by using a procedure in which carbonate samples are reacted with 100 % H_3PO_4 at 25°C, with the product CO_2 being retained in the reaction vessel until dissolution is complete. In order to decrease the reaction time and help degassing of the acid higher temperatures up to 90°C have been employed later (for a review see reference 1). However, the temperature dependence of the reaction is not known with sufficient accuracy[9,10]. In order to evaluate the temperature dependence of the $^{18}O/^{16}O$ ratio with higher resolution and precision we conducted measurements at a number of temperatures between 25°C and 47°C using the ARAMIS line. The results indicated a strictly linear relationship with a slope of the observed $\delta^{18}O$ of -0.03576 ‰/°C. There was no detectable dependence of the $\delta^{13}C$ values within the studied temperature range and precision (0.019 ‰). Further details of these experiments will be presented elsewhere[11]. Based on this experience we decided to set the default reaction temperature to 47°C.

Timing of the reaction

60 mg of MAR-J1 powder were weighed in for reaction with phosphoric acid. The reaction was allowed to proceed for time periods between 40 and 90 minutes. In this set of experiments we observed an initial change in the oxygen isotopic composition of the CO_2 produced. The carbon isotopic composition remained constant within the measurement uncertainty. Based on this set of experiment we established 60 minutes as the default duration time for our reaction. With this timing the isotopic results were both, consistent and reproducible. Further details about the experiment and the conclusions will be presented elsewhere[11].

4.1.6 Results

Mass spectrometric analysis involves extraction of CO_2 + N_2O. We made two sets of experiments adding two different types of synthetic air to CO_2 evolved from reaction of carbonate samples: air (1) had 390 ppb of N_2O and air (2) was without any N_2O. The online extraction system coupled with the mass spectrometer and the measurement protocol are described in detail elsewhere[7,12]. Our laboratory uses air as working as well as quality control standards. These air standards in high pressure cylinders are processed together with regular air samples in our daily routine operation using the same experimental protocols.

Results from these air standards are used to monitor and correct systematic influences on all aspects of CO_2 extraction, sample handling, analysis, and ion correction.

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[8] *McCrea, J.M., On the isotopic chemistry of carbonates and a paleotemperature scale. J. Chem. Phys., 18 (1950) 849-857*

[9] *Kim ST, O'Neil JR, Geochim. et Cosmochim. Acta 61(1997) 3461-3475*

[10] *Swart PK, Burns SJ, Leder JJ, Chem. Geol. 86 (1991) 89-96*

[11] *Ghosh et al. 2004, in preparation*

[12] *P. Ghosh and W.A. Brand, The effect of N_2O on the isotopic composition of air-CO_2 samples, submitted to Rapid Comm. Mass Spectrom. 2003*

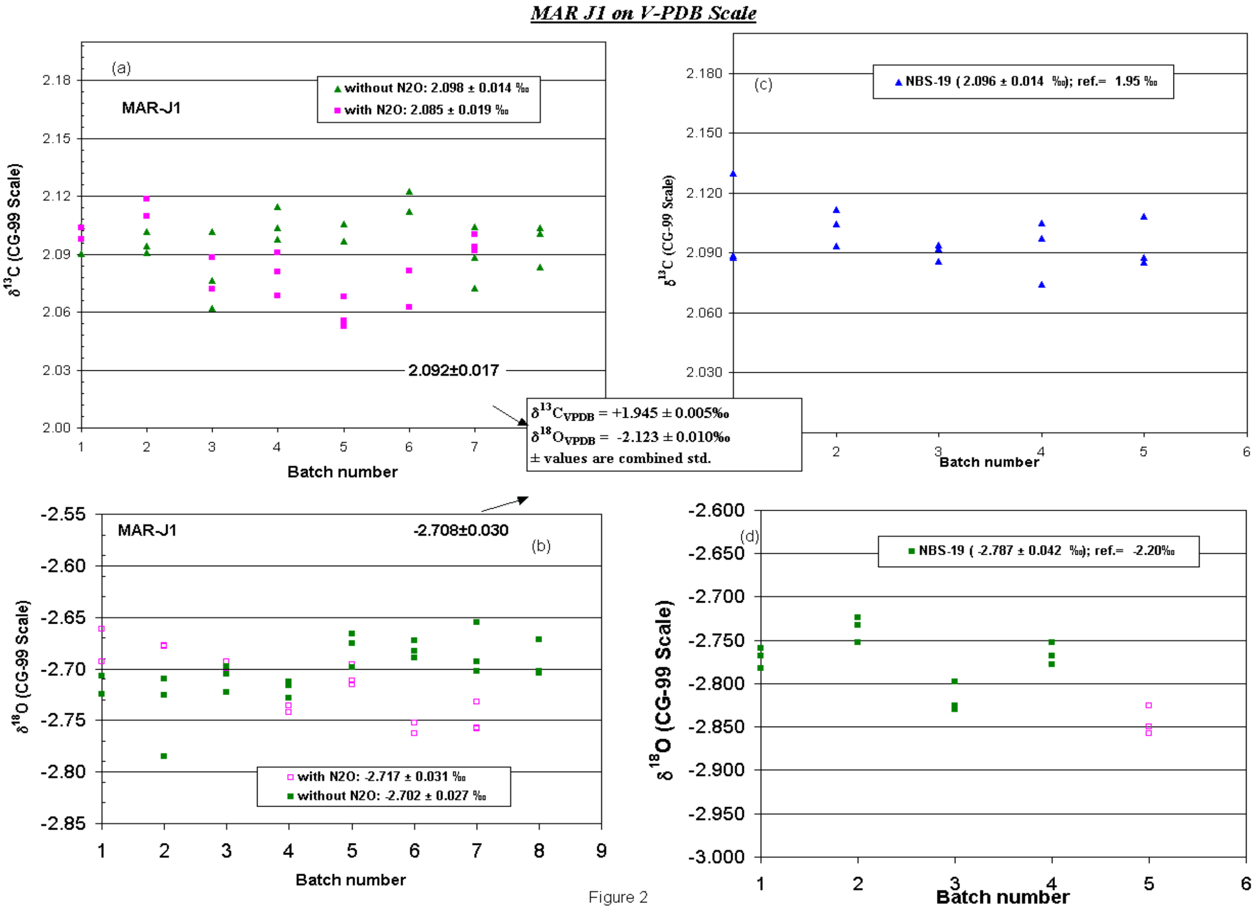

Figure 2: Determination of the isotopic composition of MAR-J1 using NBS19.

4.1.7 δ^{13}C of MAR-J1 analyses

Results from 15 batches of MAR-J1 flasks are shown in Figure 2a. Each batch comprises three samples. The set contains seven preparations made with synthetic air containing N_2O. Eight preparations were made without N_2O. Correction of the N_2O contribution was made using measured concentrations and a modified mass balance correction (for details see reference 12). There is no significant difference in the mean values of δ^{13}C obtained from the analyses and the results are close to the target precision of 0.01 ‰ for air sample analyses. The means and standard deviations for MAR-J1 CO_2 with and without N_2O admixture were 2.085 ± 0.019 ‰ and 2.098 ± .014 ‰ respectively. We obtained an average value of 2.092 ± 0.019 ‰ from all analyses. The observed mean was consistent with the uncertainty arising from sample preparation.

4.1.8 δ^{13}C of NBS-19 analyses

In a second series of experiments we prepared artificial mixtures of air with CO_2 from NBS-19. As already mentioned, the NBS-19 δ^{13}C and δ^{18}O values have been set to +1.95 ‰ and -2.2 ‰ respectively[13]. The isotopic composition of the CO_2 added in the mixture was established

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[13] *T.B. Coplen, New Guidelines for reporting stable hydrogen, carbon, and oxygen isotope ratio data, Geochim. Cosmochim. Acta 60(17) (1996) 3359-3360*

independently with repeated measurements giving a consistent precision of 0.02 ‰ for $\delta^{13}C$. The results plotted in Figure 2b show the intra-batch variability and heterogeneity in preparation. We obtained an average value of 2.096 ± 0.014 ‰ based on 5 batches of NBS-19 preparations. Comparison of MAR-J1 and NBS-19 preparation based on these analyses indicate indistinguishable $\delta^{13}C$ values within analytical uncertainty for both materials. This implies that MAR-J1 is very close to NBS-19 in $\delta^{13}C$ and that it can be used reliably as working carbonate reference material because of its isotopic homogeneity.

4.1.9 *$\delta^{18}O$ of MAR-J1 analyses*

The $\delta^{18}O$ results of batches of MAR-J1 are plotted in Figure 2c. The results obtained from individual sample are displayed in a similar way as in the case of carbon. The mean and standard deviation of MAR-J1 CO_2 were 2.717 ± 0.031 ‰ and 2.702 ± 0.027 ‰ respectively with and without N_2O added to the mixture. We obtained an overall average value of 2.708 ± 0.03 ‰ from all analyses. The average is consistent with the uncertainty arising from sample preparation with and without N_2O.

4.1.10 *$\delta^{18}O$ of NBS-19 analyses*

The $\delta^{18}O$ of batches of NBS-19 are plotted in Figure 2d. The results obtained from individual samples denote a higher degree of heterogeneity between preparations in comparison to MAR-J1. However, the number of preparations is too small for judging the statistical significance of the observation. The mean for NBS-19 CO_2 without N_2O admixture was 2.787 ± 0.042 ‰.

4.1.11 *The CG99 scale and other reference material measurements using the ARAMIS preparation line*

In addition to NBS-19 we have analyzed a set of common carbonate standard reference materials (NBS-18, IAEA-CO-1, IAEA-CO-8) for further evaluating the scale offset seen in our measurements of NBS-19. Table 1 is a summary of all analyses made so far.

The CG99 scale offset we observed was 0.146 ‰ for carbon and 0.188 ‰ for oxygen respectively. In order to check for a possible scale contraction we have analysed NBS-18 carbonatite and obtained values consistent with the NBS-19 data when correcting the scale for the observed offset. The other carbonate standards provide a slightly less consistent picture when comparing accepted and obtained results.

The results for MAR-J1 are listed separately in order to show the different $\delta^{18}O$ values present in the mineral and in the respective gas at 25°C and 47°C. The synthetic air mixture intended for use as CO_2-in-air SRM obviously is made by releasing CO_2 from MAR-J1 at 47°C.

In order to separate effects in the carbonate reaction from pure gas mixing effects we also mixed and analysed two batches of HC-453 CO_2. The results were internally consistent but the resulting offsets after scale adjustment were considerably different from zero (-0.059 ‰ and -0.266 ‰). We conclude from this finding that the original preparation[5] combined with the transfer to the CG99 scale and cryogenic extraction of CO_2 from the reference air[6] differs from our carbonate preparation / gas mixing in terms of consistency. With the latter offsets closer to zero, a conclusion would have been possible that the observed CG99 scale offset might arise from the extraction process exclusively, not from the carbonate reaction. This is obviously not the case. However, all data presented in Table 1 are preliminary. We do not feel confident, yet, to draw farther reaching conclusions and we will continue to examine our system and our procedures for possible sources of fractionation at the precision level presented. Revised data and conclusions will be published separately.[11]

Table 1: Summary table.

Standards (# of analyses)	Jena' CG-99 scale (measured)				corrected to VPDB (this work)				accepted or in use (VPDB)			
	$\delta^{13}C$		$\delta^{18}O$		$\delta^{13}C$		$\delta^{18}O$		$\delta^{13}C$		$\delta^{18}O$	
	Mean	StdDev	Mean	StdDev	Mean	StdDev	Mean	StdDev	Mean	StdErr	Mean	StdErr
NBS-19 (15)	2.096	0.013	-2.012	0.041	1.95		-2.2		1.95		-2.2	
CG99 scale offset	0.146	0.013	0.188	0.041								
other carbonate standards												
NBS-18 (5)	-4.857	0.011	-22.929	0.021	-5.002	0.011	-23.113	0.021	-5.01	0.05	-23.035	0.172
IAEA-CO-1 (6)	2.581	0.012	-2.332	0.027	2.434	0.012	-2.520	*0.027*	2.480	0.025	-2.437	0.073
IAEA-CO-8 (3)	-5.651	0.010	-23.458	0.022	-5.796	0.010	-23.642	0.022	-5.749	0.063	-22.667	0.187
CAL-1 (2)	-45.963	0.019	-22.272	0.012	-46.10969	0.019	-22.462	0.012	-45.764	0.018	-22.036	0.033
CAL-2 (2)	-2.383	0.000	-12.58	0.009	-2.529	0.000	-12.770	0.009	-2.558	0.009	-12.549	0.028
NBS-19 (CO2-gas)					1.950		-2.20 + (10.25)					
MAR-J1 (mineral)					1.945	0.017	-2.122	0.030	1.945	0.005	2.123	0.010
MAR-J1 (gas, 25°C))					1.945		-2.123 + (10.25)					
MAR-J1 (gas, 47°C))					1.945		-2.123 + (9.475)					
Air standard (MARJ1 (47°) vs. VPDB-gas)					1.945		-2.897		1.945	?	-2.897	?
HC-453 (6)	-6.324	0.023	-13.280	0.015	-6.469	0.023	-13.466	0.015	-6.410	0.020	-13.200	0.030
Offset vs assigned					-0.059		-0.266					

4.1.12 Conclusions and outlook: open issues and plans for the future

Before a new CO_2-in-air standard reference material can be established we must arrive at a conclusive picture regarding the offset discussed above. Once this point is reached, we will be able to produce the SRM in the form of 5l glass containers at a pressure up to 2 bar. This amount of air is sufficient for a larger number of isotopic determinations even when about 500 ml (STP) of air are consumed in a single preparation. We plan to always ship two such flasks in order to provide a consistency check. When extracting CO_2 from these air-SRM containers on one of the sample ports, isotopic determination of a local working standard that is being used as the major referencing material in daily routine analysis can be made with a high level of precision. If systematic fractionation occurs in this procedure, or if other systematic errors are present in the data evaluation and corrections applied, the errors will tend to cancel for other air samples provided these are close to ambient concentrations and isotopic compositions with the exception that the air-SRM has an offset of about +10 ‰ for $\delta^{13}C$. It would be advantageous to also have a sibling air-SRM with $\delta^{13}C$ close to air-CO_2. This would, however, require a calcite with the texture and homogeneity of NBS19 that has a $\delta^{13}C$ value close to -8 ‰.

4.1.13 Acknowledgements

We gratefully acknowledge the cooperation of the Gaslab people at CSIRO, in particular Colin Allison, who kindly sent us two freshly filled glass ampoules of HC453 CO_2. We are also grateful to Lin Huang for sharing her acid recipe with us and for sending us aliquots of Cal1 and Cal2 carbonate material. Michael Rothe (MPI-BGC) made all isotopic determinations referred to in this contribution. He also assisted in the preparation of the flasks.

Our appreciation goes to Manfred Groening of the IAEA in Vienna for supporting our project with an extra set of NBS19 reference material. The IAEA also supported the presentation of the data at the Toronto meeting.

Setting up of the ARAMIS system as well as a post-doctoral fellowship for PG were made possible by the TACOS project (EU, EVR1-CT-2001-40015). The financial support is greatly appreciated.

4.2 Inter-Comparison Of Isotope Ratios For CO_2 Using Several Reference Materials

Hitoshi Mukai

4.2.1 Introduction

Isotope analysis of CO_2 is useful to estimate CO_2 budget in the atmosphere. International analytical primary standard for carbon isotope ratio is NBS19 carbonate. In general, it is not easy to get high precision (e.g. 0.01 per mil level) in isotope analysis for atmospheric CO_2 because of many reasons. One difficulty of the analysis comes from standard. NBS19 is carbonate and has different isotope value from CO_2 in the atmosphere. Chemical treatments needed for carbonate and analysis by mass spectrometry for CO_2, which has different isotope ratios from standard, may cause some deviation of measured value from true value.

Therefore, international gas standard (CO_2) is helpful to calibrate mass spectrometry. In last WMO/IAEA meeting in 2001 in Tokyo, one CO_2 reference material (NIES Atmospheric Reference CO_2 for Isotopic Study (NARCIS)) was prepared by NIES (Mukai, 2003). It was prepared as 1500 glass tubes, which was distributed to over 40 labs for inter-comparison. Isotope value is close to CO_2 from the air. (like GS-19 and 20). Another reference material was prepared this time, which is NARCIS-II having different isotope value from the first NARCIS (-I). To check produced homemade NBS19-CO_2 by each laboratory the isotope ratios of NARCIS-II were adjusted to the values close to CO_2 produced from NBS19 carbonate. Because NBS19-CO_2 is prepared in each laboratory, the isotope value may be affected by the method of acid treatment in each laboratory. If sample CO_2 has similar isotope value to NBS19-CO_2, analytical error by MASS must be negligibly small. Therefore, by the comparison of NARCIS-II, difference of produced CO_2 from NBS19 between laboratories will be checked.

On the other hand, measurements of pure CO_2 and air sample may be different, because air sample will be affected by CO_2 extraction method and N_2O influence at the MASS analysis. Some laboratories use CO_2 in natural air, compressed in a cylinder as standard. Air standard can cancel out such effects by treating it as a working standard. Therefore, if air standard was well calibrated against NBS-19, it is very good tracer for calculating air sample.

Thus, as each laboratory has own sample extraction method, standard system and analytical instrument, it is not easy to compare our data directly to each other. We need careful studies from calibration scale to sample treatment procedure. By using NARCIS CO_2 samples, basic calibration scale used in each laboratory can be compared. Such pure CO_2 scale should be compared to air standard scale.

4.2.2 Preparing NARCIS I and II

Several regent carbonates were analyzed. They showed a large range from -40 to 2 per mil in $\delta^{13}C$. Two kinds of carbonate were mixed and adjusted $\delta^{13}C$ value to the target value, which were -8.5 and 1.95 for I and II respectively. About 12g of mixed carbonate was placed in a glass flask (2L) and the flask was evacuated. Phosphoric acid was added slowly and produced CO_2 was trapped in a glass trap by liquid nitrogen. Water was also trapped in another –50 °C trap before the CO_2 trap. Trapped CO_2 was introduced to another 2L-flask, where seawater (150 ml) was cooled to -100 degree C and air was evaluated. Delta ^{18}O was adjusted to about zero per mil by one-day equilibration with seawater. Again, CO_2 was trapped in the glass trap dipped in liquid nitrogen after water was removed. At the last stage, about 2.5-3 litre of CO_2 was collected in a 2 litre-glass bottle. The pressure in the glass bottle was about 1.5 atmosphere. We waited for over 5 days to mix CO_2 fully in the bottle.

About 2ml of CO_2 was collected in a 6 mm glass tube by using a special manifold (Figure 1) from the bottle. To avoid isotopic fractionation, each sample was very carefully trapped and sealed. Five samples were produced at the same time. Over 1500 samples were prepared after all.

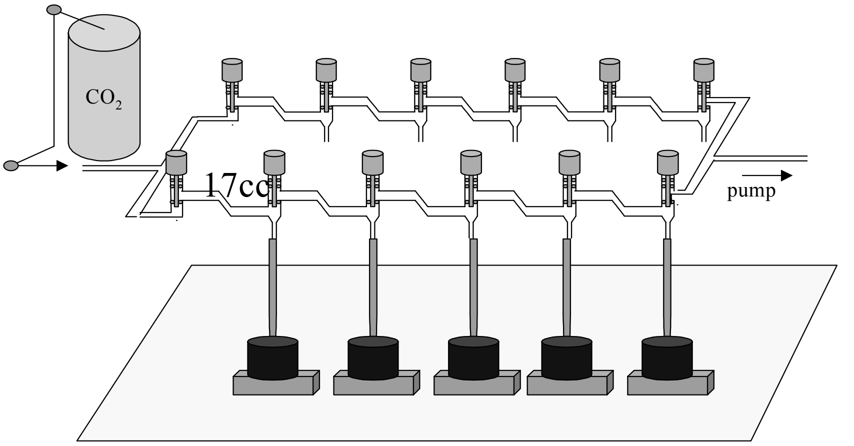

Figure 1: Special manifold for collecting constant volume of CO_2.

Inter-comparison using NARCIS-I

NARCIS-I (five samples set) was distributed to over 40 labs, and about 20 labs reported the values, which were indicated in Table 1. NARCIS-I is pure CO_2 having similar isotope ratio to air CO_2. Preliminary results were plotted in Figure 2.

Average value was -8.548 per mil with 0.014 per mil (95% confidence limit) in δ^{13}C (n=19) and -0.690 per mil with 0.028 per mil (95% confidence limit) in δ^{18}O (n=17) respectively. Median value was -8.550 per mil and -0.701 per mil respectively. If these averages are compared to the values reported by NIST, these average values were a little heavier than the values (-8.580 and -0.750) from NIST.

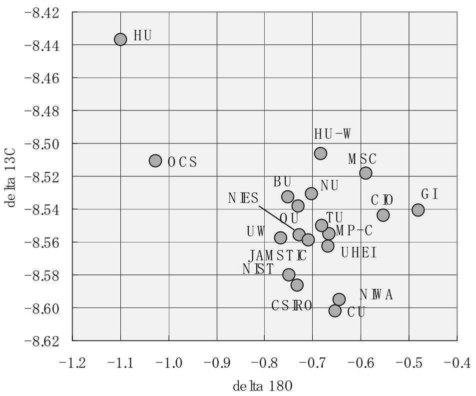

Figure 2: Scatter plot of reported isotope value for NARCIS-I.

Histogram of reported isotope values were shown in Figure 3 (a) and (b). It was found that our analytical accuracy for pure CO_2 (NARCIS-I) was about 0.08 per mil in δ^{13}C (-8.60 to -8.52) and 0.16 per mil in δ^{18}O (-0.76 to -0.6).

In general, main two causes of deviation from real value are possible. One is from phosphoric acid treatment for NBS-19 carbonate (especially for ^{18}O). Another came from cross contamination effect on mass spectrometric analysis.

In the case of carbon isotope ratio, phosphoric acid treatment may not affect so much, if 100% of carbonate reacted with acid. Therefore, cross contamination effect at mass analysis could largely affect the deviation of measured value. Delta ^{13}C of NBS19 is 1.95 per mil, which is about 10 per mil different from that of air CO_2 (e.g.-8 per mil). On the other hand, cross contamination effect for δ^{18}O may be relatively small, because δ^{18}O of NBS19 is -2.2, which is only about 2 per mil different from air CO_2. Supposed cross contamination effect for δ^{13}C was about

0.016 per mil for the MAT252 (VISC open case) installed in my institute, while about 0.004 per mil in $\delta^{18}O$.

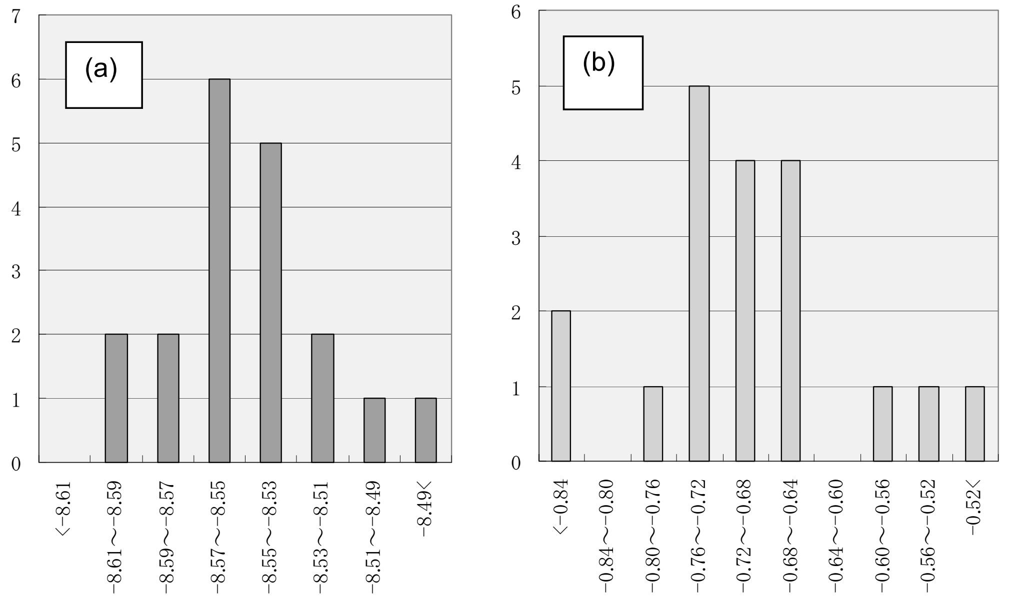

Figure 3: Histogram of reported isotopic value (per mil) (a) delta ^{13}C and (b) delta ^{18}O for NARCIS-I

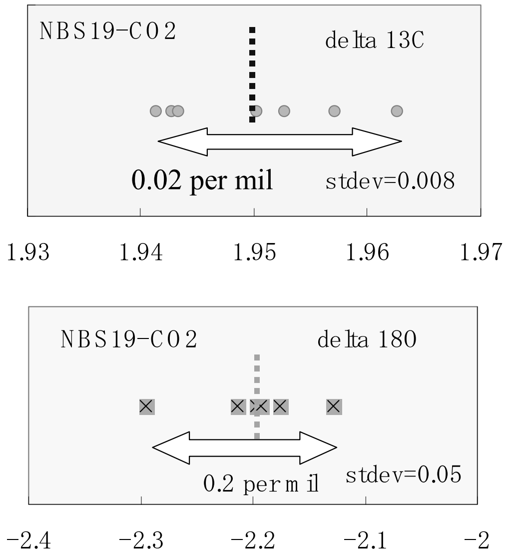

Figure 4: NBS19-CO_2 reproducibility. Seven samples were produced at the same time. Sample size was over 20mg.

However, $\delta^{18}O$ of CO_2 can be altered by fractionation at phosphoric acid treatment, because supposed fractionation at that time is 10.25 per mil at 25 degree C. If we look at the variation of $\delta^{18}O$ of CO_2 produced by NBS19 acid treatment, reproducibility of NBS19-CO_2 was about 0.008 per mil (range 0.02 per mil) in $\delta^{13}C$ but 0.05 per mil (range was 0.2 per mil) in $\delta^{18}O$. Therefore, $\delta^{18}O$ was surely affected more than $\delta^{13}C$ by such chemical treatment (Verkouteren, 2003).

Another cause of deviation is how to calculate the delta values from delta 45 and delta 46, which are observed by mass spectrometer. In most cases, Craig correction is used basically in this inter-comparison. If IAEA recommended method (Allison et al., 1995) was used, 0.01 per mil difference was estimated at most. However, observed difference was much larger than that.

Production of NARCIS-II

Isotopic values for NARCIS-II were adjusted to the values of NBS19-CO_2. Tentative values are 1.927 ±0.005 per mil in $\delta^{13}C$ and -2.589 ±0.013 in $\delta^{18}O$. These values are very close to NBS19-CO_2 (1.95 and -2.20). As mentioned before, NBS19-CO_2 reproducibility is not good enough to determine working standard gas precisely. Therefore, a gas standard is more convenient to be used for primary standard in general. NARCIS-II may provide the hint of reason why NARCIS-I has such scatter in the reported values.

Because in most cases working standard gases are first determined by NBS19-CO_2, if NBS19-CO_2 was not prepared properly, the isotopic values of working standard gas may be incorrect. To compare homemade NBS19-CO_2 without mass cross contamination effect, NARCIS-II is useful, because we don't have a large volume batch of NBS19-CO_2. Now NARCIS-II is being distributed to the related labs.

4.2.3 Inter-comparison of pure CO_2 and air sample

CO_2 must be extracted from the air sample for measuring isotope values. Some labs used air standard for isotope analysis to compensate the extraction effect on the isotope analysis. In this case, however, air standard must be precisely determined by pure CO_2 standard. Therefore, in either case, extraction process must be checked.

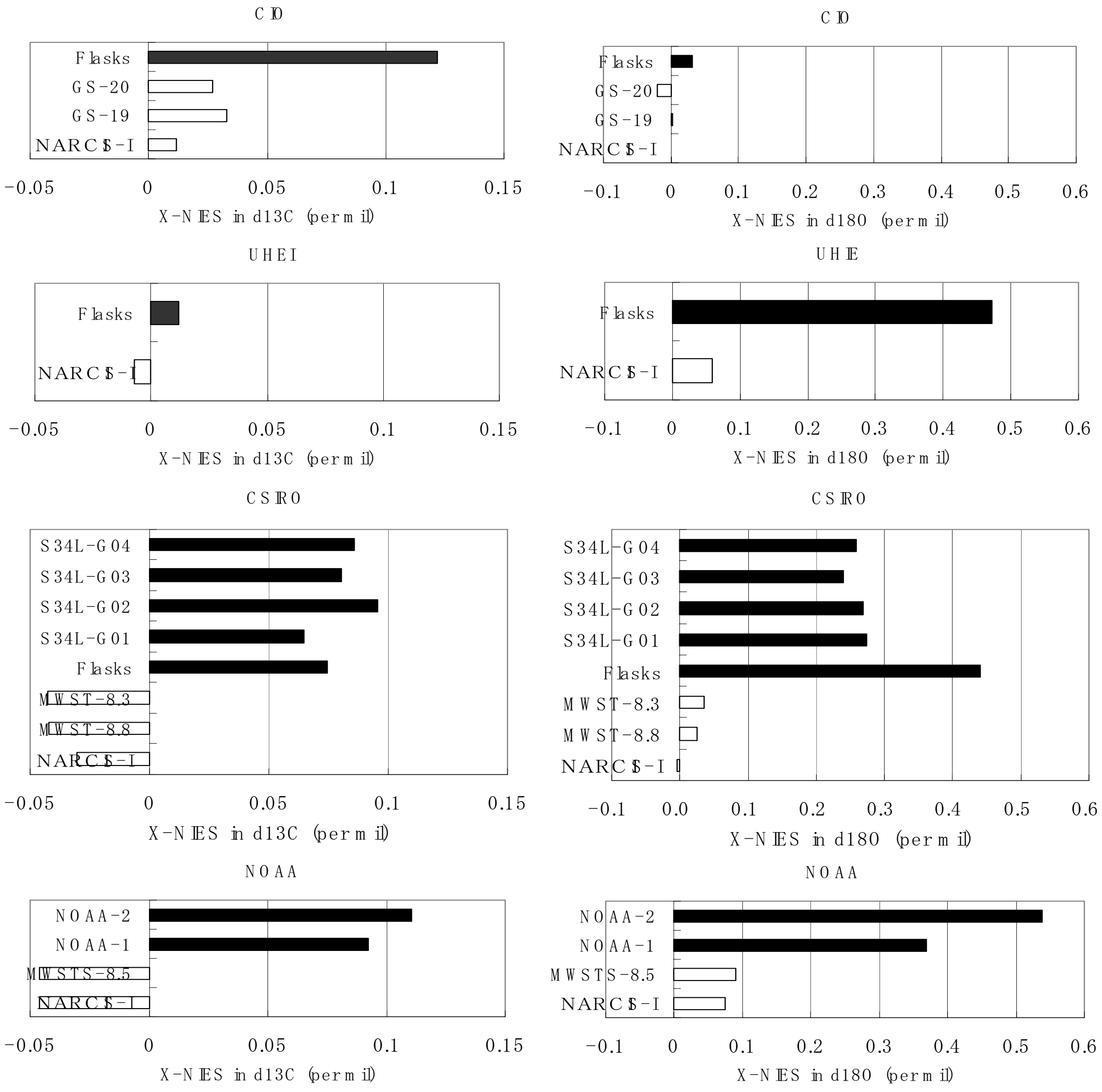

Figure 5: Differences of measured values between NIES and other institutes (X) on several air samples (black rectangle) and pure CO_2 references (white rectangle).

In order to compare pure CO_2 scale in isotope ratios to the scale for air sample including N_2O correction, several comparisons were performed by using the air in NOAA high-pressure cylinder and in stainless steel containers (so called "melon") provided from CSIRO. In addition, we attended periodical inter-comparison activity in Europe conducted by UHEI-UP (Schmidt et al. 2003). Tentative results were summarized in Figure 5.

Several reference materials including GS-19, GS-20 (Meijer, 1995) and NIES workings were used to compare CO_2 scale. During pure CO_2 references, the differences between them were small and consistent with each other. However, the differences in air samples were quite different from those from pure CO_2. Up to 0.15 per mil difference compared from CO_2 standards was observed in $\delta^{13}C$ for air samples. In the case of $\delta^{18}O$, up to 0.3 per mil difference was observed. Such differences may include effects on CO_2 extraction and N_2O correction. However, the effect related N_2O correction must be under 0.1 per mil for both $\delta^{13}C$ and $\delta^{18}O$. Therefore, CO_2 extraction effect must be checked as a source of difference between air CO_2 and pure CO_2 measurement.

Three extraction lines in NIES were tested on their extraction performances. NARCIS-I was diluted by zero air and made artificial air CO_2 sample (about 350 ppm). This sample was extracted by three extraction lines and their isotope values were measured and compared to original NARCIS-I values. The results showed that the deviation in $\delta^{13}C$ from original NARCIS-I value was 0.01 per mil at most. On the other hand, 0.1 per mil deviation was sometimes observed in the case of $\delta^{18}O$ for one extraction line. In either case, these differences were much smaller than the case observed in inter-comparison for air sample.

Another possibility of the causes of discrepancy of the differences between pure CO_2 and air sample should be studied. For instance, if air standard is used for the measurement of real air sample, the scales for pure CO_2 may not match with that of working air CO_2 standard.

Thus, each step for measurement such as pure CO_2 scale, air standard scale, CO_2 extraction, N_2O effect and calculation method should be checked in the future.

4.2.4 Conclusion

NIES reference CO_2 (NARCIS-I) inter-comparison showed good example of accuracy of isotope analysis. The data scattered with the range of 0.08 per mil in $\delta^{13}C$ and 0.22 per mil in $\delta^{18}O$. Such ranges may be caused by both cross contamination effect at the mass spectrometry analysis and NBS19-CO_2 reproducibility.

NARCIS-II, which had fairly close isotope values to NBS19-CO_2, was produced to check homemade NBS19-CO_2 in each laboratory, which is used as primary standard.

Pure CO_2 and air sample inter-comparison showed large discrepancy in their data, suggesting that scales for pure CO_2 and air standard seemed to be different, if extraction process did not affect so much to the isotope analysis.

Acknowledgement

Author would like to thank people who took part in this inter-comparison activity.

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Meijer, H., The isotopic composition of the Groningen GS-19 and GS-20pure CO_2 standards, Reference and intercomparison materials for stable isotopes of light elements, IAEA-TECDC-825, pp.81-84, 1995.

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Schmidt, M., Ciais, P., Levin, I., Meijer, H., Neubert, R., Ramonet, M., Brand, W. A. and Francey, R., The European intercomparison project for greenhouse gas monitoring (TACOS-Infrastructure), Report of the eleventh WMO/IAEA meeting of experts on carbon dioxide concentration and related tracer measurement techniques, WMO-GAW No.148, 32-54, 2003.

Verkouteren, M., The NIST-IAEA measurement intercomparison of carbon and oxygen stable isotope reference materials, Report of Investigation 837-02-03, pp 1-56, 2003.

Table 1: Tentative reported values for NARCIS-I December 2003).

Table 1. Tentative reported values for NARCIS-I (2003. Dec)

Institute or University	delta 13C - VPDB-CO2							delta 18O - VPDB-CO2						
	Sample							Sample						
	1	2	3	4	5	AVG	SD	1	2	3	4	5	AVG	SD
UO(J)	-8.543	-8.517	-8.545	-8.551	-8.535	-8.538	0.013	-0.726	-0.724	-0.738	-0.735	-0.733	-0.731	0.006
GCI	-8.546	-8.558	-8.526	-8.536	-8.537	-8.541	0.012	-0.474	-0.496	-0.480	-0.468	-0.483	-0.480	0.011
COS	-8.514	-8.526	-8.485	-8.524	-8.504	-8.511	0.017	-1.049	-1.020	-0.961	-1.069	-1.040	-1.028	0.041
NU(J)	-8.513	-8.509	-8.523	-8.572	-8.536	-8.531	0.025	-0.660	-0.683	-0.709	-0.763	-0.705	-0.704	0.038
CSIRO	-8.582	-8.583	-8.584	-8.591	-8.590	-8.586	0.004	-0.708	-0.718	-0.747	-0.757	-0.738	-0.734	0.020
TU(J)	-8.596	-8.538	-8.557	-8.531	-8.528	-8.550	0.028	-0.784	-0.687	-0.668	-0.631	-0.637	-0.681	0.062
NIES(J)	-8.566	-8.571	-8.569	-8.571	-8.571	-8.556	0.002	-0.699	-0.702	-0.688	-0.697	-0.697	-0.729	0.005
NIST	-8.595	-8.572	-8.571	-8.581		-8.580	0.011	-0.788	-0.741	-0.742	-0.728		-0.750	0.026
MSC	-8.508	-8.514	-8.512	-8.520	-8.536	-8.518	0.011	-0.578	-0.592	-0.592	-0.595	-0.596	-0.591	0.007
CIO	-8.545	-8.557	-8.608	-8.556	-8.516	-8.544	0.019	-0.571	-0.561	-0.681	-0.596	-0.488	-0.554	0.046
MPI-C	-8.542	-8.542	-8.578	-8.560	-8.554	-8.555	0.015	-0.666	-0.664	-0.671	-0.637	-0.691	-0.666	0.019
WU	-8.559	-8.559	-8.557	-8.554	-8.560	-8.558	0.002	-0.806	-0.748	-0.771	-0.769	-0.745	-0.768	0.024
HU(J)	-8.452	-8.449	-8.421	-8.426		-8.437	0.016	-1.111	-1.193	-1.027	-1.071		-1.101	0.071
CU	-8.602	-8.606	-8.598	-8.607	-8.595	-8.602	0.005	-0.658	-0.661	-0.646	-0.659	-0.646	-0.654	0.007
BU	-8.538	-8.519	-8.528	-8.541	-8.536	-8.532	0.009	-0.749	-0.735	-0.743	-0.747	-0.791	-0.753	0.022
HU2(J)	-8.520	-8.501	-8.500	-8.503	-8.508	-8.506	0.008	-0.694	-0.679	-0.674	-0.691	-0.679	-0.683	0.009
JAMSTIC(J)	-8.554	-8.553	-8.557	-8.565	-8.564	-8.559	0.006	-0.694	-0.689	-0.724	-0.718	-0.718	-0.709	0.016
UHEI	-8.569	-8.546	-8.563	-8.563	-8.571	-8.562	0.010	-0.640	-0.676	-0.655	-0.686	-0.689	-0.669	0.021
NIWA	-8.595					-8.595	0.001	-0.646					-0.646	0.002
SIO	-8.494	-8.493	-8.496	-8.496	-8.499	-8.495	0.001	-0.692	-0.695	-0.705	-0.719	-0.693	-0.701	0.002

4.3 Trace gases, $\delta^{13}C$ and $\delta^{18}O$ of CO_2-in-air samples: Storage in glass flasks using PCTFE seals and other effects

Michael Rothe, Armin Jordan and Willi A. Brand[‡]

Abstract

The storage properties of air in borosilicate glass flasks have been studied over extended periods of time. Changes of the trace gas composition as well as the stable isotope ratios of CO_2 have been observed and quantified. Different types of sealing materials are discussed and the role of permeation is reiterated. The effects of two types of sealing materials (PFA and PCTFE) have been investigated more closely. Except for a small increase in the CO concentration over time, PCTFE in general seems much better suited than PFA owing to the much lower permeation rates for most gases. In particular, no change could be detected for the CO_2 mixing ratio over a time period of 250 days.

The isotopic composition of CO_2 remains constant for $\delta^{13}C$ in both materials. $\delta^{18}O$, on the other hand, exhibits a pronounced change over time with a trend close to -0.2 ‰ in 100 days. Possible causes are discussed including traces of H_2O or exchange with OH bonds inside the borosilicate glass.

4.3.1 Introduction

Owing to the small size of seasonal and longer term alterations trace gas measurements as well as CO_2 carbon and oxygen isotope ratios in air samples collected in glass flasks require the highest attainable precision.[1] Among the limitations to improve such measurements is the integrity of the samples during storage. The option to measure samples within a short time period following collection is not always given. Logistical problems in sample transport from the often remote sampling stations (e.g. Siberia, Antarctica) require that samples remain unaltered over months before analysis can be made. On top of the time aspect, temperatures during storage as well as outside pressures may vary considerably.

Samples are usually collected in duplicate in order to exclude results from flask pairs that differ by more than a certain margin. Systematic errors, however, that arise during storage and alter the respective sample air in a similar fashion in both flasks, are not detectable using such a strategy. Loss of air through the O-ring seals via diffusion is such a case.

4.3.2 Diffusion through O-rings

Permeation is a function of the sealing material, the geometry of the seal, the temperature, partial pressure difference and, most importantly, of the molecular species diffusing through the seal[2]. Diffusion through a single O-ring can be described by

$$(1) \qquad d(pV)/dt = D_g(T) \bullet A/d_y \bullet (p_i-p_A)$$

with A= exhibited O-ring area, d_y = O-ring diffusion length, $D_g(T)$ = Gas diffusion constant, T = Temperature and (p_i-p_A) denoting the pressure difference between the inside and outside of the flask. The gas diffusion constant or permeation coefficient $D_g(T)$ differs widely for the diffusing gas and for the O-ring material. Some literature constants have been compiled in reference 2. For CO_2 the permeation coefficient for instance varies between $4 \bullet 10^{-17}$ $m^2/s\ mb^{-1}$ (PCTFE) and 2.3

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[1] *R.J Francey, C.E. Allison, D.M. Etheridge, I.G. Trudinger, M. Enting, M. Leuenberger, R.L. Langenfelds, E. Michel, L.P. Steele, Tellus B 51 (1999) 170*

[2] *P. Sturm, M. Leuenberger, C. Sirignano, R. Neubert, H.A.J. Meijer, R. Langenfelds, W.A. Brand and Y. Tohjiama, Permeation of atmospheric gases through polymer O-rings used in flasks for air sampling, J. Geophys. Res. (2004) accepted for publication*

•10^{-12} m^2/s mb^{-1} (Silicone), i.e. 5 orders of magnitude. For other gases the situation is similar and the relevance of the effect for flask sampling of air has been recognized[2].

4.3.3 Flask conditioning

Measurements of trace gases in atmospheric air as well as determination of isotopic composition of CO_2 in air samples must be made with a high focus on precision and accuracy. In order to avoid a spill over of 'bad' air into the next sample (we have seen samples with organic material from a spill over of kerosene in air campaigns, we occasionally have samples with a considerable water background and we often have flasks filled with soil or close-to-ground air) or other forms of memory we have installed a routine flask conditioning unit where all flasks have to pass through in between sampling. Figure 1 depicts the major components of the unit. Dry conditioning air (clean air, originally manufactured for scuba diving) is dried further with $Mg(ClO_4)_2$. A backpressure regulator and mass flow controller bracket the flask 'sausages' (series of flasks connected with Cajon Ultratorr adapters) attached to a wide-bore Valco 6-port valve.

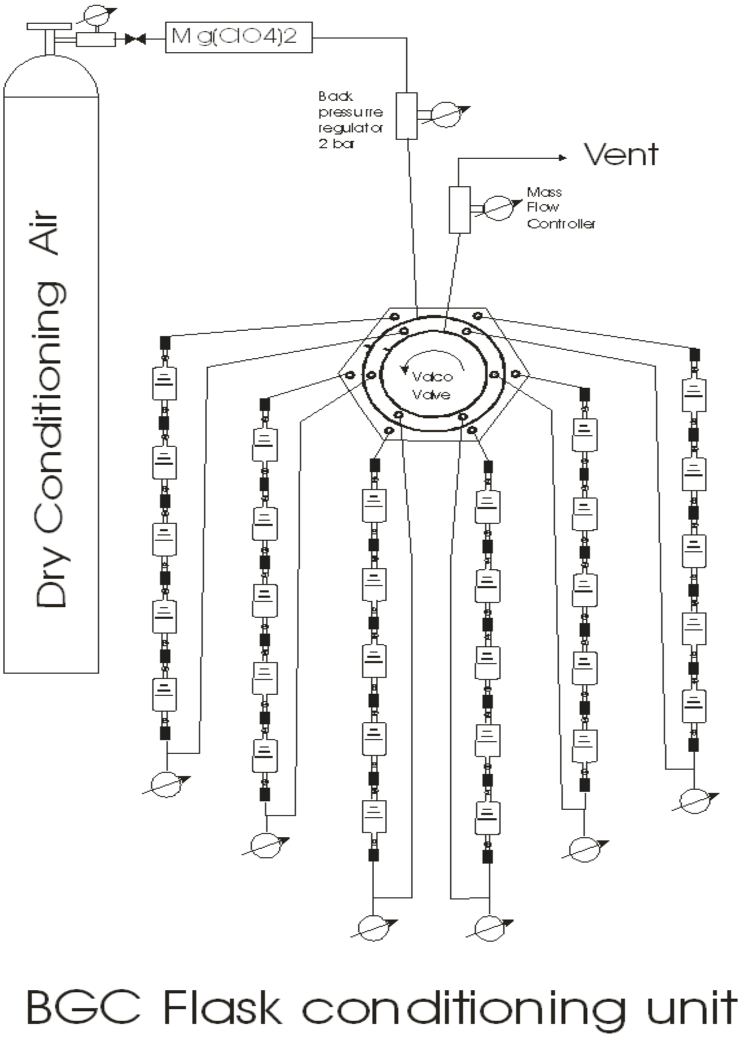

Figure 1: Layout of the flask conditioning station at MPI-BGC Jena. Five flasks in a row are flushed with dry air at the final pressure of 2 bar (3 l/min, ½ h).

Conditioning is made at the final pressure of 2 bar using a flow of 3 l/min for 1/2 h for every 5-flask sausage. Hence, a total amount of 90 l of conditioning air passes the 1-liter flasks, thereby exchanging the total volume 9 times. We have carefully checked whether the flasks within a sausage differ for instance from the first to the last, but we have never found any significant difference for any of the measurements we routinely perform, including O_2/N_2 ratios (see reference [3] in this volume). We also have occasionally checked for deviations from one sausage to the next for adjacent fillings. Also here, we were unable to find differences so far.

4.3.4 Trace gas stability

A number of our standard flasks have been filled with dry air using the procedure described above in order to study the stability of trace gas mixing ratios over elongated periods of time.

Some of the flasks were equipped with PFA O-rings, another set of flasks had a PCTFE seal as shown in Figure 2. The storage tests were made by analysing flasks from a common sausage at different times. The data are shown in Figure 3 for CO_2, CH_4 and N_2O and in Figure 4 for CO.

Figure 2: Glass flask with PCTFE-on-glass seat[4]. The shaft seal is made using two Viton O-rings. The flasks are protected against ex- or implosion hazards by a heat shrink hose (black).

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[3] *Willi A. Brand, O_2/N_2 Storage Aspects and Open Split Mass Spectrometric Determination, Proceedings of the 12th IAEA/WMO meeting of CO2 experts, Toronto, Sept. 2003, WMO-GAW Report, ed. D. Worthy (2004, this volume)*

[4] *The flasks and seal have been developed with QVF AG in Ilmenau (www.glasapparate.de) The flasks are available commercially from this source. The PCTFE seals also fit valves from GE, Australia.*

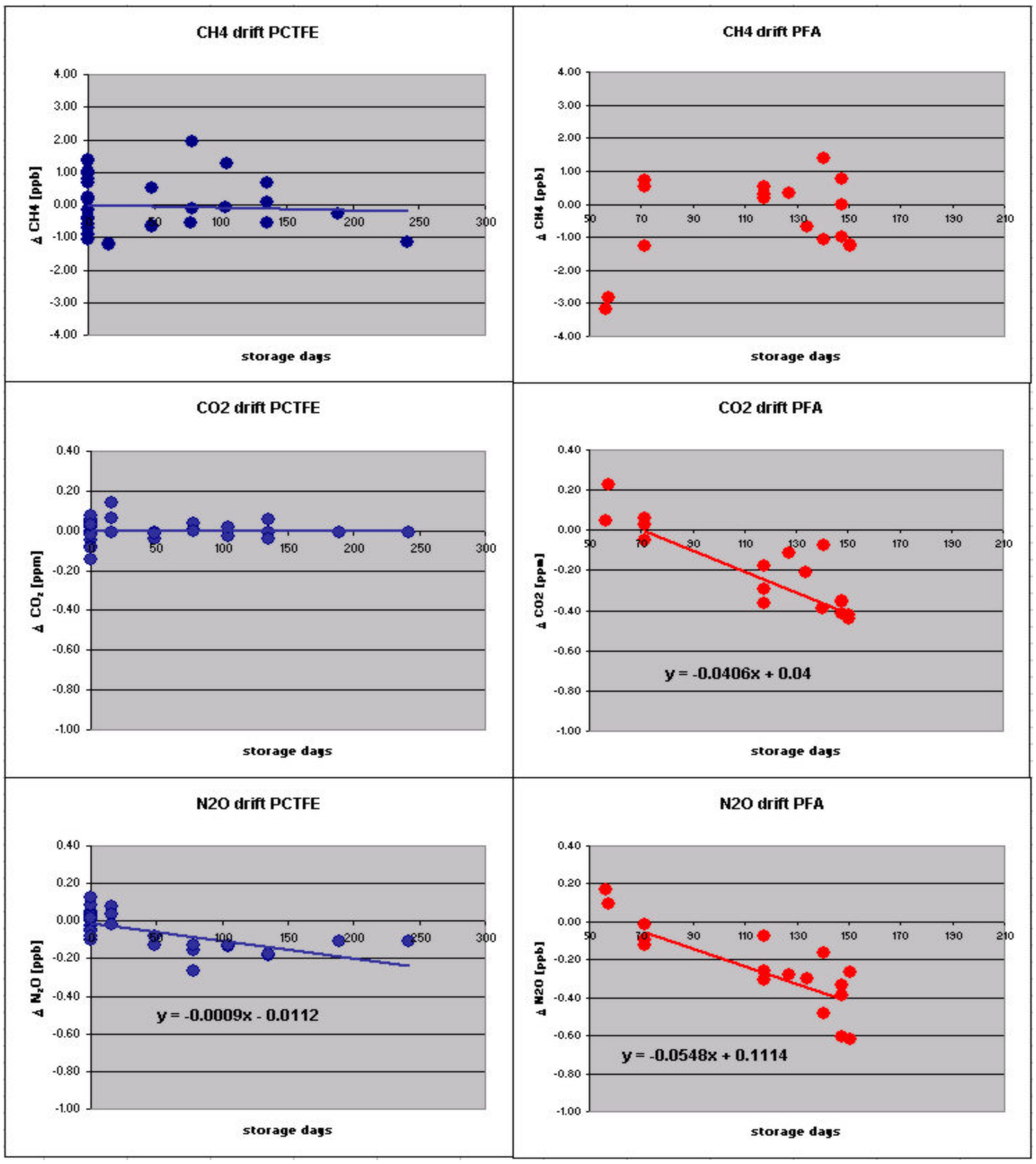

Figure 3: Storage data for the mixing ratios of CO_2, CH_4, and N_2O. The right hand panels are for PFA O-rings, results for the new PCTFE flasks are on the left.

Each data point in these figures represents the mean of triplicate analysis of a single flask, i.e. all flasks were stored under the pressure of 2 bar until measurement. The PFA flasks were part of an ongoing bilateral intercomparison programme filled in Heidelberg by I. Levin using a procedure close to the one described above. The PFA flasks exhibit a clear preferential loss of CO_2 (about -0.4 ppm in 100 days) and of N_2O (about 0.5 ppb in 100 days) over time. The mixing ratio of CH_4 seems to be stable. For the flasks equipped with PCTFE the trend in CO_2 is completely eliminated, CH_4 is again stable over time and the drift in the N_2O mixing ratio has declined to less than 1/5th (if any) of the PFA value. The stability of CO, however, seems to deteriorate slightly when replacing PFA O-rings with PCTFE (Figure 4). An increase of CO of almost 6 ppb in 100 days is observed. The phenomenon has first been noticed by Ray Langenfelds of the CSIRO Atmospheric Research division in Aspendale, Australia. He observed a growth of about 7 ppb in 100 days in flasks equipped with a different geometry of the PCTFE seal[5]. The origin of the finding is not clear and warrants further observation. We speculate that it may be an outgassing effect that should decline over time.

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[5] *Ray Langenfelds, personal communication*

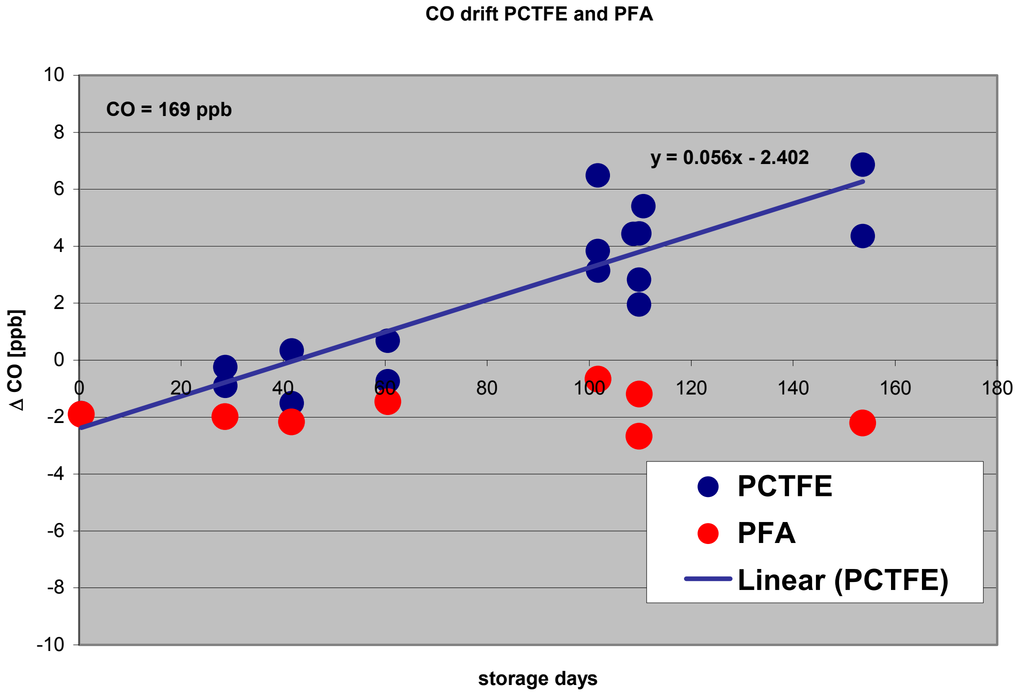

Figure 4: Storage data for the CO mixing ratio in air samples. PCTFE sealed flasks seem to develop CO over time. An outgassing effect of the polymer is suspected to be the cause.

In any case: The effect is small in comparison to the observed variability of CO in atmospheric samples. The data for H_2 and for SF_6 are not shown in the figures. Within measurement precision these data were essentially flat with time for both types of sealing materials.

Storage effects for the stable isotope ratios of CO_2 in air

Measurements of $^{13}C/^{12}C$ ratios from air-CO_2 stored in glass flasks have mostly been reliable in the past. Extensive intercomparison programmes have revealed a high level of comparability of such data and exchange of air in glass flasks is used to monitor and diagnose mutual drifts caused by either the measurement equipment or by the standardization procedures in the participating laboratories[6].

It is therefore not surprising that our findings confirm that there is no change of the measured $\delta^{13}C$ values over longer periods of time (Figure 5). Each sample was measured twice with the corresponding storage time in between the two determinations. The error bars represent the average long term single measurement precision of our isotopic measurements. $\Delta\delta^{13}C$ denotes again the difference between the first and the second determination of the isotopic composition. The trend lines are not significant. Although there seems to be an increase in the scatter of the data points as a function of time, we believe that this is not significant. The overall precision of about 0.02 ‰ for both types of flasks is in line with our normal flask pair deviation. Figure 6 shows the corresponding situation for $\Delta\delta^{18}O$ of CO_2 in the same samples.

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[6] *Masarie, K.A., R.L. Langenfelds, C.E. Allison, T.J. Conway, E.J. Dlugokencky, R.J. Francey, P.C. Novelli, L.P. Steele, P.P. Tans, B. Vaughn, and J.W.C. White, NOAA/ CSIRO Flask Air Intercomparison Experiment: .A strategy for directly assessing consistency among atmospheric measurements made by independent laboratories, J. Geophys. Res. 106, (2001) 20445-20464.*

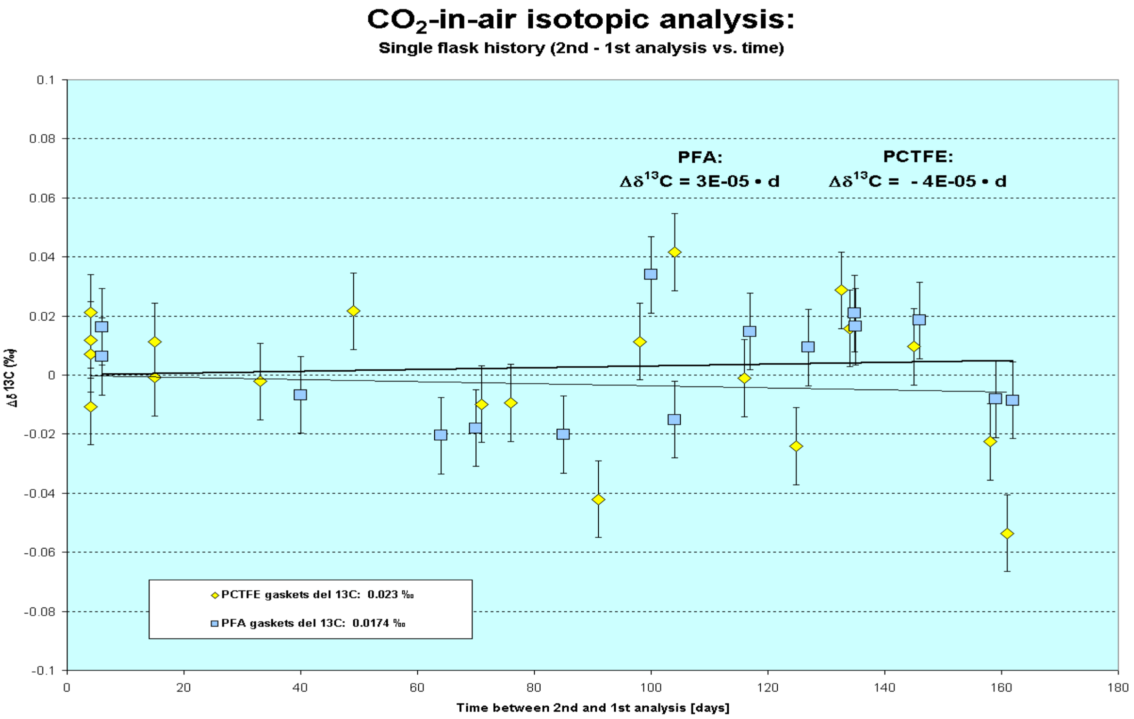

Figure 5: ^{13}C/^{12}C isotope ratio results for CO$_2$ in air samples. Two measurements per sample with the difference between the second and the first determination plotted as a function of time.

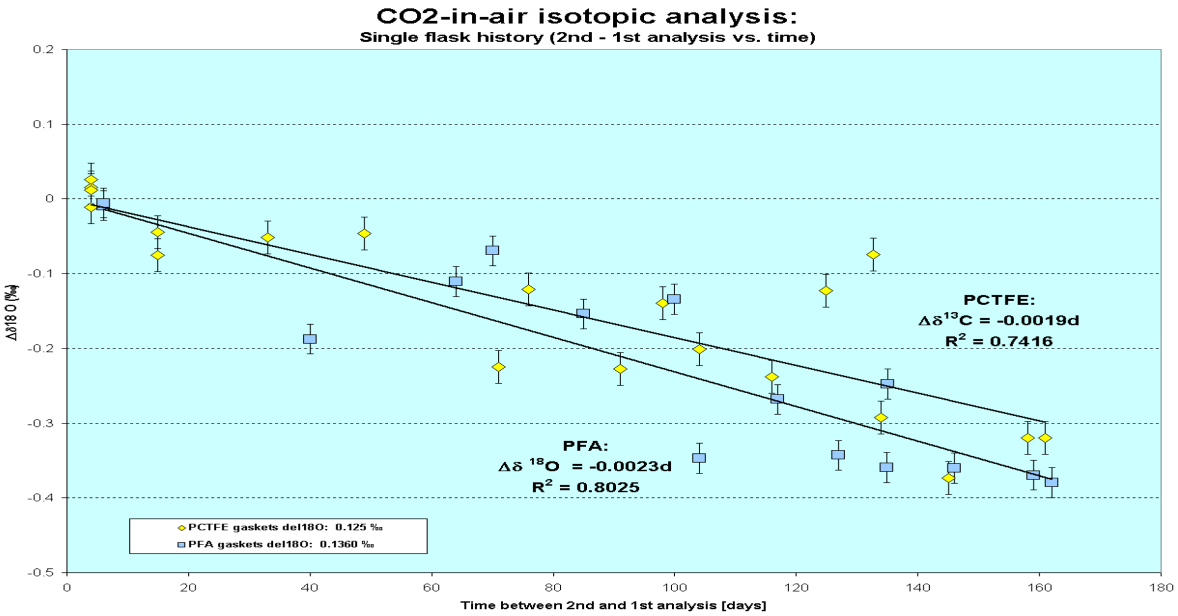

Figure 6: ^{18}O/^{16}O isotope ratio results for CO$_2$ in air samples. Data are from the same measurements as those in Figure 5.

Contrary to ^{13}C there is a clear negative trend with a slope of about -0.2 ‰ in 100 days. In light of the single determination measurement precision indicated by the error bars, the trend is statistically significant with $R^2>0.7$ for both types of flasks. The trend is also large in comparison to the measurement precision that is necessary for explaining the fate of CO_2 regarding the cycling through different compartments of the environment. Moreover, there is an increase in the scatter of the data over time, rendering a possible drift correction almost impossible. We believe that the observed trend is in line with the inconsistencies observed in ^{18}O records and in intercomparisons between laboratories. If we find a cure for this behaviour we will certainly improve on these issues and make better use of ^{18}O data in the future.

One of the prime candidates for causing ^{18}O drifts is water in the flasks, present either from the start or added over time through permeation. The latter should show up in the data as a pronounced difference in the ^{18}O behaviour between the PFA and the PCTFE flasks owing to the differences in permeation rates. Such differences are not seen (yet) in the data set. Water on the glass walls, on the other hand, should come to an equilibrium with the CO_2 in the flasks within a rather short period of time. Complete exchange of large amounts of CO_2 with liquid water is achieved within less than a single day. Hence, if water is responsible for the observed change of δ^{18}O over time, it must reside inside the glass, not on the surface and diffuse slowly from there. Alternatively, the rate limiting step can also be a diffusion of CO_2 in and back out of the glass. Exchange then must take place inside the glass. Borosilicate glass (Pyrex®, Duran®, our flasks are made from the latter) is carrying a large number of OH groups which are part of the glass structure and not mobile. We suspect that this structure itself, not water trapped inside, is able to slowly exchange oxygen isotopes with CO_2. Whether other types of glass are better suited or whether a coating of the surface with another type of glass would be a solution remains to be seen in the future.

5.3.5 Acknowledgments

We are indebted to Ray Langenfelds of CSIRO-AR for communicating his PCTFE storage tests to us. Ingeborg Levin has filled the PFA flasks which we have used for the mixing ratio measurements in this study. Financial support from the EU-TACOS project (contract No. is EVR1-CT-2001-40015) is gratefully acknowledged.

We also would like to thank QVF AG, Ilmenau (www.glasapparate.de), the manufacturers of our flasks for developing the PCTFE valve with us and make it available commercially.

5. SAMPLING STRATEGIES

5.1 Determination of CO_2 Sources and Sinks on the Continental and Regional Scales

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Abstract

We examine how to us observations of atmospheric and ecological quantities over continental land areas to determine regional and continental scale CO_2 fluxes, in particular by using integrated land surface-atmospheric models. Observations over continental areas necessarily reflect both near-field and far-field influences, and the observations and the model constructs used to analyze them must both be capable of distinguishing and quantitatively resolving these influences.

The net exchange of CO_2 between the surface and the atmosphere is a key parameter of the global carbon cycle. Particular interest attaches to regional and continental scales, where the specifics of human intervention and impacts of climate variations can be examined and understood. Two basic approaches have been taken to study large-scale carbon budgets:

1. *Classic inverse modelling* of CO_2 fluxes ["Top-down"] solves an optimization problem in which gridded fluxes are introduced into a model of atmospheric transport, and the resulting patterns of concentrations are matched against atmospheric data. The atmosphere integrates over large areas, and observations are limited in time and space, thus inverse models generally work best at very large scales with fluxes aggregated into only a few domains [e.g., *Fan et al.*, 1998; *Rayner et al.*, 1999]. *Down-scaling* to regional fluxes is under-constrained.

2. *Ecosystem modelling* of CO_2 flux ["Bottom-up"] uses detailed information on spatially distributed vegetation, from vegetation inventories, remote sensing, and soil surveys, and simulate ecosystem carbon fluxes using models with varying degrees of mechanistic realism [e.g. *Hurtt et al.*, 1998]. Model parameters are adopted from ecological and tower flux studies, and thus large-scale constraints from the atmosphere are not incorporated. *Up-scaling* to landscape, regional and continental scales is under-constrained, like down-scaling.

Recent studies have started the process of bringing together top-down and bottom-up approaches. Land-surface models of increasing sophistication have been incorporated into "inverse models", and "ecosystem models" are being coupled interactively with atmospheric models to assess the atmospheric concentration gradients [e.g. *Denning et al., 2003*]. The resulting models begin to approximate model-data assimilation systems, allowing in principle the incorporation into the optimization process of ecological and atmospheric data with very different spatial and temporal scales.

Ultimately models must accurately simulate multi-scale data, since land-atmosphere exchanges measurably influence atmospheric CO_2 on all spatial and temporal scales: near-field influences are inevitably mixed with larger scale effects, thus representation errors may be large, and biases may result from the inability to mechanistically represent key processes at intermediate scales, e.g. transport in and out of the Planetary Boundary Layer (PBL). If these processes are not properly represented the variability present in atmospheric CO_2 -which contains signals of underlying fluxes and such important vegetation parameters as type, biomass, and phenology— ends up as noise. To merge top-down and bottom-up approaches, we must make land-surface and atmospheric observations on all spatial and temporal scales, and develop modelling and synthesis capabilities that can use these data to constrain land-atmospheric exchanges on all scales.

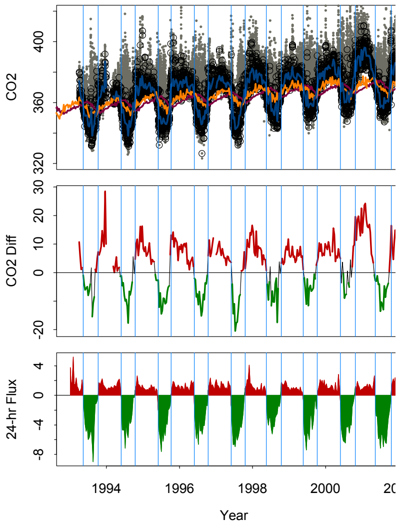

Figure 1a: CO$_2$ land vs sea. (upper) Hourly data (ppm) from Harvard Forest (grey), midday data (black), and 10-day means of midday data (blue); data from Bermuda (orange) and Mauna Loa (red) for comparison. (centre) Difference between Harvard Forest midday and Bermuda. (lower) 24-hr tower fluxes (● emission; ● uptake; μmole m^{-2}s^{-1}).

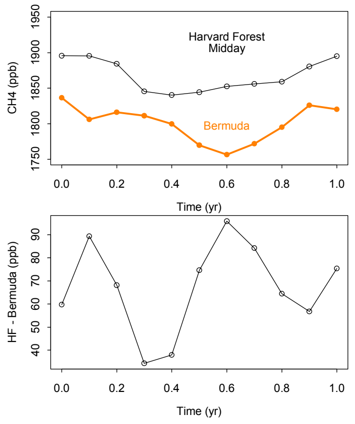

Figure 1b: CH$_4$ land vs sea. (upper) Midday data (black) from Harvaqrd Forest and data from Bermuda (orange) for comparison. (lower) Difference between Harvard Forest midday and Bermuda. (lower).

Figure 1*a* illustrates the multi-scale properties of data from continental sites. Hourly CO$_2$ at 30 m in Central Massachusetts, are influenced by local, regional and large-scale processes (*upper*). Midday data accurately reflect global trends. But regional effects are evidenced by differences with the closest marine site (Bermuda, in the Atlantic 700 km to the south; *centre*). The Harvard Forest data respond directly to regional uptake and release by New England's forests (*cf. eddy correlation fluxes, lower*). Figure 1*b* shows an analogous land-sea difference for CH$_4$ data. In this case there is no seasonal reversal of the flux, and likewise no reversal of the concentration differences.

Figure. 2 shows the large variations of CO$_2$ and H$_2$O in the PBL due to eddy-scale turbulence, one of several processes giving rise to *representation error* [*Gerbig et al.*, 2003; *Lin et al.*, 2004], associated with difference between a point measurement and the mean concentration in the grid square of a model.

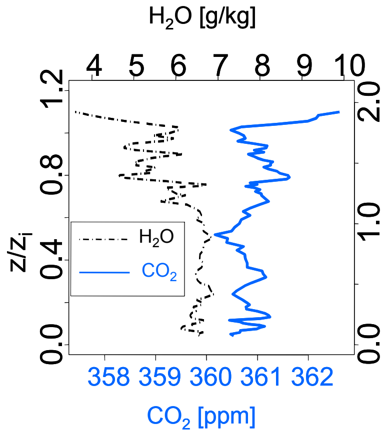

Figure 2: CO$_2$ and H$_2$O in the PBL ($Z_i \equiv$ PBL top). Large, inversely-correlated variations reflect the inhomogeneous daytime mixing of overlying air with moist, CO$_2$-depleted air affected by a vigorous forest canopy [from Gerbig et al., 2003a].

Figure 3 shows the large-scale concentration gradients observed over North America in the CO$_2$ Budget and Regional Airborne (COBRA) experiment carried out in the summer of 2000. The PBL was strongly depleted in CO$_2$ when the aircraft sampled air passing over forests supplied with ample sunshine and moisture, but there was excess CO$_2$ over drought-stressed vegetation under cloudy conditions.

The temporal and spatial variations in Figures 1-3 quantitatively reflect atmosphere-biosphere fluxes at large scales over land. If we develop a conceptual framework to use this information we will be able to quantitatively measure land-atmosphere fluxes of greenhouse gases for climate-relevant time scales (months, years, decades and spatial domains (10^2 – 10^3 or 10^4 km). We must develop models that accurately simulate the joint effects on CO_2 of near-field, regional, and global processes, and design measurements to reduce the impact of non-representative data and similar sources of error. In effect we will convert variance usually treated as unresolved variance ("nose") into signal providing us with information about terrestrial fluxes of CO_2.

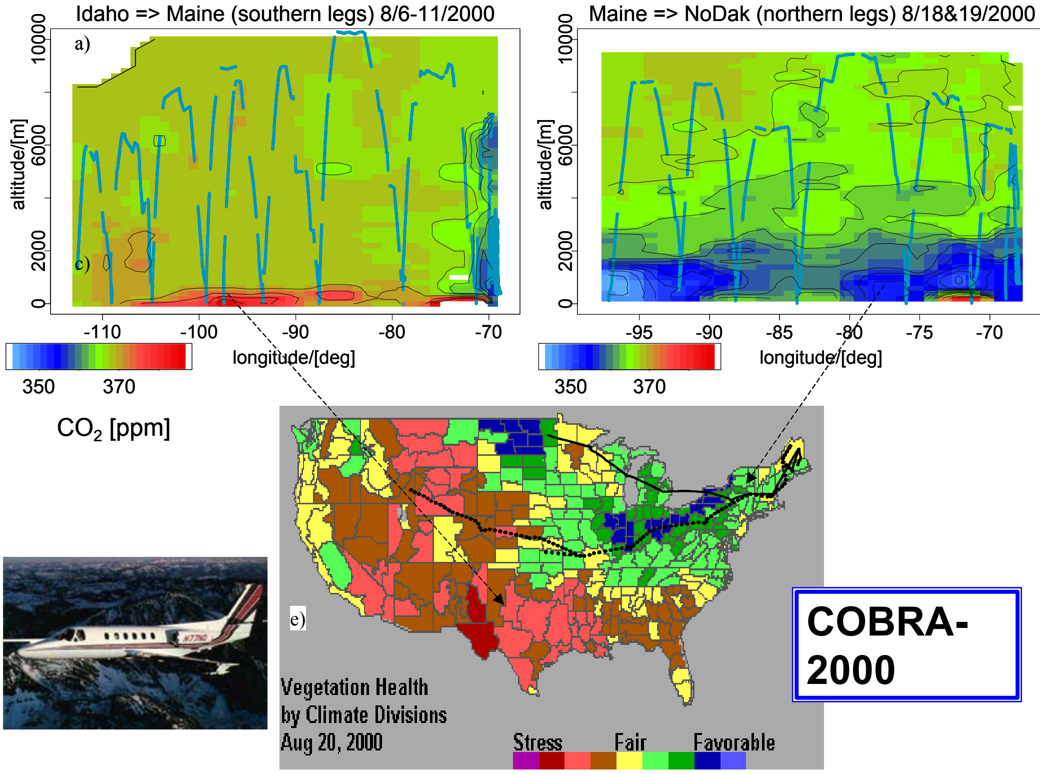

Figure 3: Cross sections of atmospheric CO_2 concentrations over North America in August, 2000 (upper left, southern transect; upper right, northern transect), for flight tracks with numerous vertical soundings (blue lines on the cross sections), obtained using the U. of North Dakota Citation II aircraft (inset, lower left). (Lower, centre) Soil moisture was ample across the northern transect, and it was also sunnier, whereas clouds and drought-stressed vegetation dominated along the southern transect. [COBRA-2000 data from Gerbig et al., 2003a. b and Lin et al., 2003].

Gerbig et al. [*2003a, b*] and Lin et al. [*2003*] introduced the Stochastic Time-Inverted Lagrangian Transport (**STILT**) model, combined with a simple mechanistic picture of the functional behaviour of the biosphere (**GSB**, the Greatly'Simplified Biosphere) to create the prototype of a conceptual framework for assimilating information from diverse sources, including atmospheric concentrations from aircraft, towers, and remote stations, as well as data for CO_2 sources and sinks from eddy flux sites and remote sensing data on vegetation type, soil moisture, solar inputs, etc.

STILT is a receptor-oriented modelling framework that quantitatively relates local measurements to the upwind flux distribution at high spatial and temporal resolution. Given a tracer concentration $C(\mathbf{x}_r, t_r)$ at location $\mathbf{x}_r$ measured at time t_r, the influence function $I(\mathbf{x}_r, t_r \mid \mathbf{x}, t)$ quantitatively links surface sources or sinks $S(\mathbf{x}, t)$, for a conserved tracer emitted at location $\mathbf{x}$ and at time t, to the tracer concentration $C(\mathbf{x}, t)$at a receptor [*Holzer and Hall*, 2000; *Lin et al.*, 2003]:

$$C(\mathbf{x}_r, t_r) = \int_{t_0}^{t_r} dt \int_V d^3\mathrm{x}\ I(\mathbf{x}_r, t_r \mid \mathbf{x}, t) S(\mathbf{x}, t)$$

$$+ \int_V d^3\mathrm{x}\ I(\mathbf{x}_r, t_r \mid \mathbf{x}, t_0) C(\mathbf{x}, t_0) \quad (1)$$

The first term on the RHS represents changes in the concentration at the receptor due to surface fluxes in the domain V between initialization time t_0 and t_r. Influence I has units of inverse volume (a density) and, since we use mixing ratios for C (ppm), S has units of ppm/s. The second term is the advected contribution from the initial tracer field $C(\mathbf{x}, t_0)$. Since surface fluxes in equation 1 can be represented as interior (volume) sources or sinks [Holzer, 2000 #30], the first term in equation 1 can be rewritten to:

$$\Delta C(\mathbf{x}_r, t_r) = \int_{t_0}^{t_r} dt \int_A d^2\mathrm{x} f(\mathbf{x}_r, t_r \mid \mathbf{x}, t) F(\mathbf{x}, t) \quad (2)$$

Here F is the surface flux in μmol/m^2/s, and the function f is the footprint of the receptor observations derived from $I(\boldsymbol{x}, \boldsymbol{t})$ and the factor $m_{air}/(h\,\rho)$.

STILT extracts footprint information from assimilated meteorological data by computing transport *backward* in time for an ensemble of representative particles released at a receptor (the measurement location), using winds and turbulence statistics from a high-resolution meteorological assimilation (presently capabilities include RAMS, EDAS, MM5, etc). The particles represent air parcels of equal mass, transported by mean winds and sub-grid turbulent winds calculated from surface sensible heat and momentum fluxes, extracted from the assimilated meteorological fields. The local density of these particles is directly related to the influence density (details see [*Lin et al.*, 2003]). The time-reversed computation obtains the influence functions *I* for the surface domain from high-resolution meteorological assimilated products (from RAMS, MM5, or EDAS), including the effects of PBL turbulence represented as a stochastic Markov chain, simply by counting particles in the surface-influenced box. Considerable care must be taken to insure conservation of mass in the calculations. Recent versions of STILT incorporate transport in deep convection using the Grell scheme [*Grell and Devenyi*, 2002]. We obtain the footprint function from $\Delta t_{p,i,k,j}$, the time which each individual trajectory *p* spends in the near-surface volume above cell *j*,*k*, during the time interval Δt,

This approach has major advantages for many problems, as discussed in detail by Gerbig et al. [*2003b*] and Lin et al. [*2003*]. The footprint is similar to the "adjoint" of a Eulerian transport model [*Errico*, 1997]: each footprint element is equivalent to the sensitivity of the mixing ratio at a given receptor location with respect to a change in boundary (surface) flux. Interpolation of winds down to the exact location of a measurement enables footprints to be derived at a higher spatial resolution than the driving meteorological data, a requirement to represent influences from sources in the near field, close to the receptor. This is a capability needed to interpret the signals observed over land, as illustrated by Figures. 1-3. Also, modelling turbulent transport as the ensemble of stochastically transported particles more closely approximates the stochastic nature of air parcels transported by turbulence than typical parameterizations (e.g., diffusion coefficients). The fact that the model runs backward in time makes it very efficient, such that only a single reversed-time model run is required to extract the spatially and temporally resolved footprint for emissions at all previous times.

Gerbig et al. [*2003b*] computed the advected background from CMDL data at remote marine sites, and computed the influence of combustion-derived CO_2 using observations of CO from the aircraft. They were thus able to obtain “observed” values for ỨC due to vegetation for the transects in COBRA-2000 (Figure 3). They then computed the footprints shown in Figure 4 using EDAS analyzed wind fields. In order to determine the surface fluxes that best reproduced the observed ΔCO_2, they adopted a simple equation (the GSB) describing the dependence of assimilation (*GEE*) and respiration (*R*) on sunlight and temperature (using shortwave radiation (*SWRF*) and temperature (*T*) from EDAS fields). Terrestrial fluxes of CO_2 were modelled by linearly scaling eddy covariance observations of net ecosystem exchange (*NEE*) from the AmeriFlux network [*Baldocchi et al.*, 2001] for different vegetation types (denoted by *i*), projected regionally using land-cover data:

$$NEE_i = \lambda_{i,R} \cdot R_i + \lambda_{i,GEE} \cdot GEE_i \tag{3a}$$

$$R_i = \beta_i T \ ; \qquad GEE_i = \frac{a_i \cdot SWRF}{b_i + SWRF} \tag{3b}$$

Here $\lambda_{i,R}$ and $\lambda_{i,GEE}$ are parameters for up-scaling (see below). The parameters β_i (temperature coefficient for respiration flux, autotrophic + heterotrophic), a_i (maximum GEE), and b_i (with a_i/b_i as the quantum efficiency) were obtained from least-square fits to the hourly AmeriFlux data (available under http://public.ornl.gov/ameriflux) for each vegetation class over the months July and August in 2000. This model (GSB) explained most of the hourly variance for the crop site (r^2=0.79) and for forests (r^2=0.56).

The International Geosphere Biosphere Programme 1-km resolution vegetation data [*Belward et al., 1999*] were regridded to the relevant domain at the different horizontal resolutions starting at 1/6°Lat.×1/4°Lon., to give relative coverage for each vegetation type. Since tower flux data are not available for each of the 17 different vegetation classes, the vegetation classification was simplified into 5 classes: forests, shrublands (open and closed shrublands, savannas, grassland, and barren or sparsely vegetated), croplands (croplands and cropland/natural vegetation mosaic), wetlands, and water bodies. The scaling factors $\lambda_{i,R}$ and $\lambda_{i,GEE}$ account for the up-scaling from flux-sites to the larger regions and represent the adjustable parameters for the biospheric CO_2 flux. They were estimated using a Bayesian optimization with the AmeriFlux values (all λ=1) as priors.

Figure 5 summarizes the complete framework for assimilating the following datastreams: atmospheric data from COBRA, AmeriFlux tower data for functional dependence of CO_2 flux on environmental parameters, IGBP land cover data, CMDL remote measurements of CO_2 and CO, inventories of fossil fuel emissions and observed CO/CO_2 ratios from forest fires, and meteorological fields (including winds and drivers for the vegetation, e.g. sunlight) from EDAS. Most of the GSB model parameters were strongly constrained by the atmospheric data, as indicated by the small magnitude of the conservative error bars in the figure. Some parameters appear to have been close to the prior values (λ=1) but others were significantly changed.

The parameterized GSB provides large-scale flux estimates for a time interval before or after the COBRA flights, for which parameters remain significantly unchanged—an interval of 1-2 weeks as indicated by AmeriFlux data. We need only input the relevant driver fields (sunlight and T for this version of the GSB; later versions will use also soil moisture information derived from remote sensing). In this manner we can make estimates of the carbon budget for much of the northeastern and central US that are constrained by diverse data sets characterizing the key components system.

COBRA-2000 was a pilot study of data assimilation approaches to constraining CO_2 net fluxes at continental scale. It showed that it is feasible to obtain accurate constraints on continental carbon budgets, with a temporal resolution of days, weeks, or months and spatial resolution of ~1000 km, using the data sets listed in Figure 5. The time and space scales are set by properties of the atmosphere and by the response of ecosystems to environmental forcing.

The work has also shown us where efforts should be concentrated to develop an accurate and reliable framework. Current meteorological products do not contain important information needed to carry out assessment of CO_2 budgets (e.g. turbulent and convective mass fluxes, height of the PBL; see *Gerbig et al., 2003b*; Lin et al., *2004*) and in many cases do not conserve mass with sufficient accuracy and do not verify well in comparison with the aircraft data for winds, cloudiness, and related driver variables. A quantitative description of modelling uncertainties such as in transport (advection error due to imperfect winds) [*Lin and Gerbig 2004*], as well as in the biosphere representation, is essential for unbiased estimates of fluxes. Improvements in other data products are also needed, especially increases in the number of continuous measurements of CO_2 and related trace gases at tower sites, traceable to CMDL standards. Currently this type of measurement is available at just a few sites. The model-data fusion approach summarized here can potentially resolve a number of critical issues in understanding the key factors in the carbon cycle, and thus development of coordinated programmes to obtain improved meteorological fields and atmospheric data sets merit a high priority.

5.1.1 Acknowledgements

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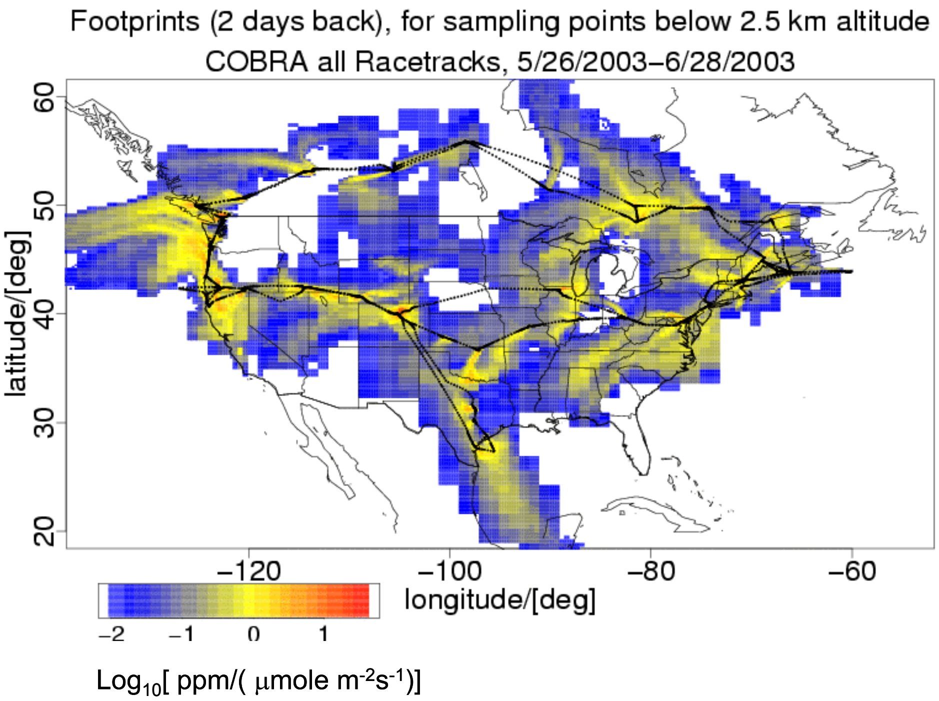

Figure 4: Footprints calculated for 2 days travel back in time, from receptors located along the cross sections of CO_2 concentrations shown in Figure 3. The Southern transect sampled mostly drought-stressed vegetation south and west of the ground track, while the Northern transect sampled north and along its ground track in well-watered vegetation.

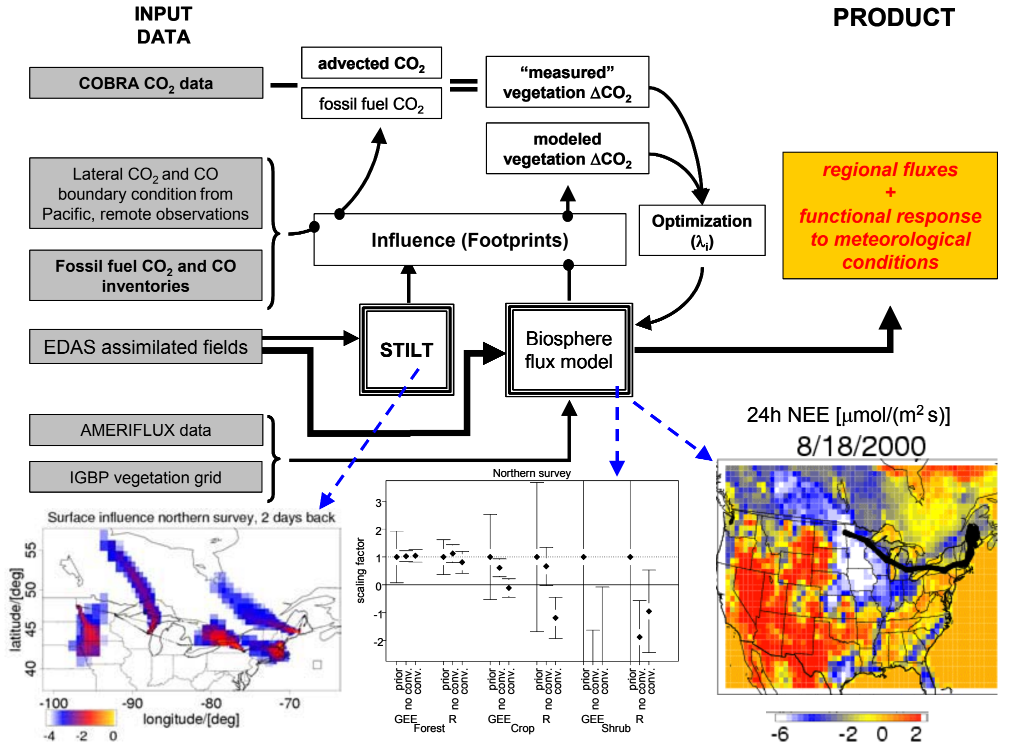

Figure 5: Schematic summarizing model-data assimilation. Starting with COBRA-2000 data and the other data sets on the left, the STILT model computes the atmospheric signals (example shown in the lower left panel) and the GSB computes the atmosphere-biosphere fluxes. The parameters of the GSB are optimized using a Baysian with priors from the IGBP vegetation grid and associated AmeriFlux data fields to give well-constrained values, some being close to the priors but several of which are notably different. The GSB can then provide 24-hour mean fluxes (i.e. daily carbon budgets) for the eastern US when driven with assimilated meteorological products, for a time period where parameters of the GSB have not changed significantly (a few weeks, as indicated by AmeriFlux data).

5.2 The NOAA/CMDL Carbon Cycle Greenhouse Gases Group Observation Programme: Expansion and Technology

T. Conway

The NOAA/CMDL Carbon Cycle Greenhouse Gases observational programme currently (March 2004) consists of 4 baseline observatories; a global network of 55 surface air sampling sites, plus sampling aboard two containerships in the Pacific Ocean; aircraft vertical profiles at 12 sites, using Programmable Flask Sampling Packages (PFPs); and 3 instrumented very tall towers (Figure 1). The in situ and flask CO_2 measurements are made using LICOR non dispersive infrared analyzers and reference gases traceable to the CCL primary standards. The flask samples from both the surface sites and aircraft are measured for several other gases and isotopic ratios as shown in Table 1.

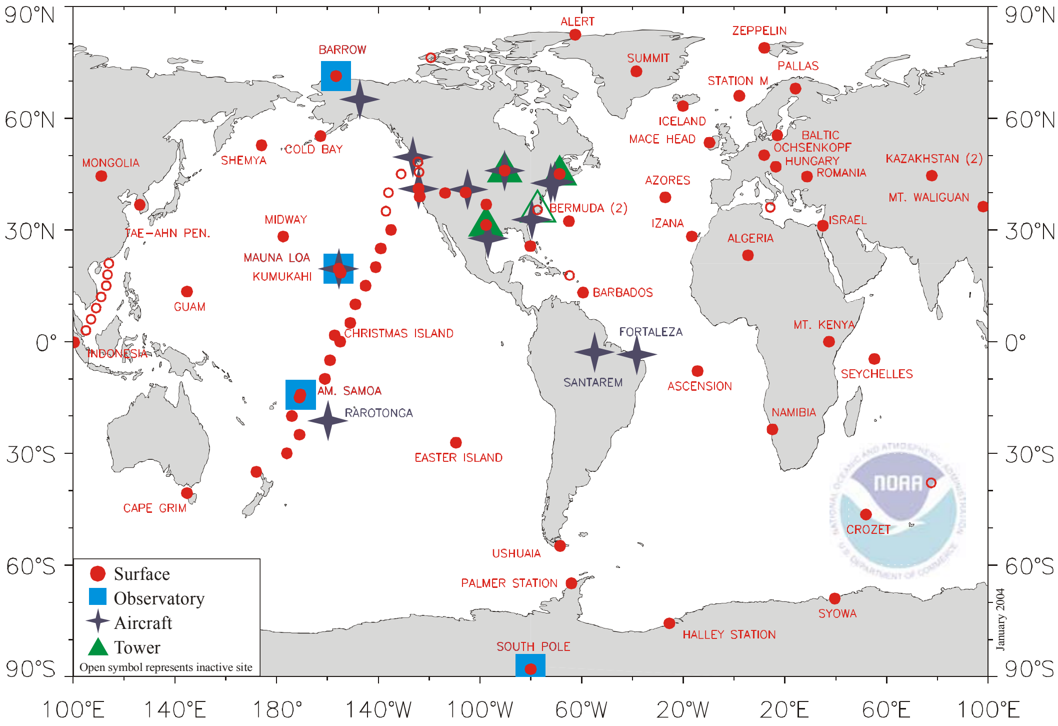

Figure 1: Map showing the locations and types of measurements of the NOAA/CMDL observation programme.

At the Cooperative Global Air Sampling Network sites samples are collected in 2.5 L glass flasks equipped with Teflon O-ring stopcocks. These samples are collected using portable battery-powered pumping units. At most sites in the tropics and on the ships, the sampler includes a thermoelectric condenser, cooled to ~5° C, to remove some of the water vapour from the sample air.

Table 1: Trace gases and isotopic species measured in the flask samples from the Cooperative Global Air Sampling Network and the aircraft vertical profile PFPs.

Species	Start Date	Method	Precision	Collaborators
CO_2	1967	NDIR	0.07 ppm	
CH_4	1983	GC/FID	1 ppb	
CO	1988	GC/RGD	0.5 ppb	
H_2	1988	GC/RGD	2 ppb	
^{13}C, CO_2	1990	IRMS	0.01 ‰	CU/INSTAAR
^{18}O, CO_2	1990	IRMS	0.03 ‰	CU/INSTAAR
N_2O	1996	GC/ECD	0.2 ppb	
SF_6	1996	CG/ECD	0.03 ppt	
^{13}C, CH_4	1998	GC/IRMS	0.06 ‰	CU/INSTAAR

A major expansion of the CMDL observation programme is currently underway. The main thrust of this expansion is the implementation of the North American Carbon Programme (NACP). The purpose of the NACP is to reduce the uncertainty on estimates of carbon sources and sinks in North America, and to understand the underlying processes. The CMDL contribution to the NACP will include an extensive network of measurements of CO_2 and other tracers (CH_4, CO SF_6, $^{13}CO_2$, etc.) from small private aircraft (18 by 2005; 25-30 by 2007) and on very tall towers (6 by 2005; 12 by 2007). The vertical profiles from aircraft will be measured up to twice per week at each site. This increased collection of samples will require a corresponding increase in the analytical capability at the CMDL laboratory in Boulder. Figure 2 shows a rough idea of what the CMDL NACP network might look like in 2007.

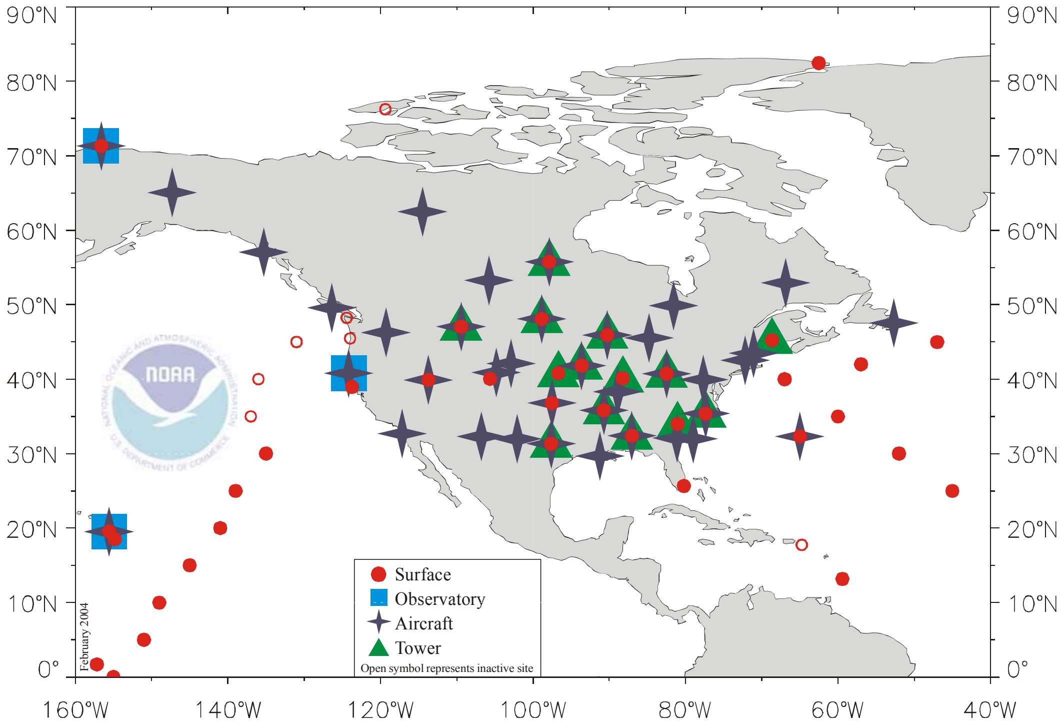

Figure 2: Map showing what the NOAA/CMDL measurement network for the North American Carbon Programme might look like in 2007.

In addition to the expanded measurement programme in North America, CMDL is undertaking a more modest expansion of the Cooperative Global Air Sampling Network. The purpose of this expansion is to increase the measurement density in undersampled regions, especially the Atlantic, Pacific, and Southern Oceans, as well as Africa, South America, and Asia. To this end, sampling began in 2002 on two ships in the Pacific Ocean - a resumption of the long-running shipboard sampling programme that ended in 2000. The shipboard sampling is now being done in coordination with the NOAA Voluntary Observing Ship programme which is affiliated with the Global Ocean Observing System (GOOS) and the Global Climate Observing System (GCOS). In spring of 2004 CMDL is planning to initiate sampling on board a containership making regular voyages across the Atlantic Ocean between New York City and Cape Town, South Africa.

In 2003 air sampling began at the GAW stations at Bukit Kototabang, Indonesia and Mt. Kenya, Kenya. In 2004 measurements should begin at the GAW station at Arembepe, Brazil; Obninsk, Russia; Huancayo, Peru; and a site in Bolivia. The search continues for suitable ships in the Southern and Pacific Oceans, as well as suitable locations on land.

CMDL currently participates in four Intercomparison Programmes (ICPs) with CSIRO, MSC, NIWA, and MPI-BGC. The Global Network expansion plan calls for additional ICPs.

The planned increase in the number of aircraft vertical profile sites will require deployment of a large number of automated Programmable Flask Sampling Packages. The design of the PFP has evolved within the existing CMDL aircraft vertical profile programme. A private company in Boulder (Atmospheric Observing Systems) is now manufacturing the PFPs. The current design contains 12 one litre flasks which can be filled automatically according to time, location, altitude, etc. In addition to obtaining vertical profiles, it is anticipated that the PFPs will be used in various applications including on ships, offshore platforms, or land-based sites that cannot be visited frequently by a sample collector.

The obvious advantages of collecting air samples in flasks are 1) measurements can be made at many locations with less expense than deploying instruments to every site, 2) the measurements are made in a laboratory where the environmental conditions are more easily controlled and the instrument performance is more easily monitored, and 3) the samples can be analyzed for many different gases, including isotopic ratios, which would be difficult, if not impossible, to measure in the field. The major disadvantage to flask sampling is the severe limitation on sampling frequency. Sample density is very limited and high frequency signals cannot be captured.

These limitations to flask sampling have motivated an effort to develop a fast response CO_2 sensor that could be used in a variety of field applications. To be useful, the instrument will need to be very robust, light weight, automated, low cost and need only small amounts of calibration gases. Such an instrument is currently being developed by AOS, Inc. with funding from the NOAA Small Business Innovation and Research (SBIR) programme. A prototype is currently being tested at the CMDL observatory at Trinidad Head, California. The instrument is being designed so that it could be deployed at remote, unattended sampling sites, as well as on ships, buoys, and aircraft.

5.3 The Carbo-Europe Atmospheric CO_2 Sampling Strategy

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5.3.1 The CARBOEUROPE programme

The CARBOEUROPE research programme has been developed with the overarching aim to "understand, quantify and predict the terrestrial carbon balance of Europe and associated uncertainties at local, regional and continental scale." Meeting that ambitious goal requires an integrated approach to be built, where regionally denser atmospheric concentration measurements, surface based ecological measurements of carbon fluxes and pools are collected, and interpreted using numerical models of land-atmosphere exchange and of atmospheric transport. CARBOEUROPE echoes similar initiatives to determine the carbon balance of North America (web site), and it is funded both by the EU and through national programmes. Currently CARBOEUROPE helps integrates and expands the research efforts of 65 European institutions. The programme has federated independent projects from 2000 to 2004, and will form a single integrated entity for the period 2004-2008

The key innovation of the CARBOEUROPE research programme is in the increase in spatial and temporal resolution of the observational and modelling programme allowing consistent application of the multiple constraint approach to determine the terrestrial carbon balance of Europe with its geographical patterns and variability. CARBOEUROPE aims to provide a system for full carbon accounting for the European continent. By increasing the resolution at which fluxes can be inferred, we expect to further investigate the main controlling mechanisms of carbon cycling in European ecosystems, such as climate (change) and variability, changing land management, and nitrogen deposition and provide future projections of the carbon cycle.

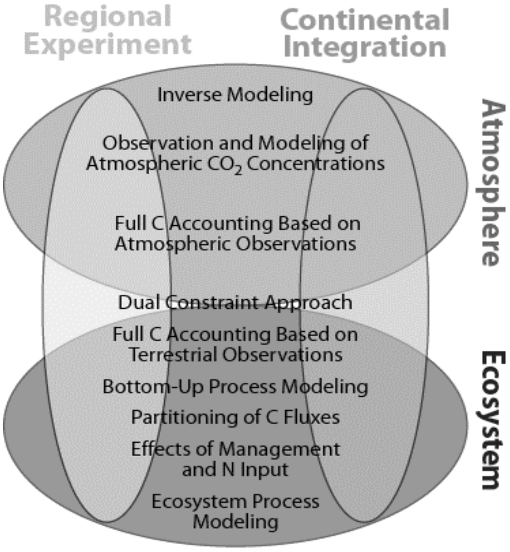

Figure 1: Graphical representation of the main objectives and their implementation in the Components of CARBOEUROPE.

The programme is structured into 4 complementary components, 3 dealing with the implementation of observations and one with the overall integration and modelling activities. The Ecosystem Component will expand the measurements of fluxes by eddy-covariance technique (90 towers scheduled), supplemented by biometric measurements and soil carbon inventories. There will be an intensive observation period, also called Regional Component, in the summer of 2005, over the *Les Landes* region in the South West of France, a rather flat area with contrasted forest and cropland cover, and relatively simple atmospheric boundary conditions for air masses coming from the Atlantic ocean. The Atmospheric Component is the main focus of this report and deal with regional measurements of CO_2 and related tracer used in high-resolution inverse models (in linkage with the Integration Component of the programme) to infer regional carbon fluxes and their variability.

5.3.2 Rationale and objectives of CARBOEUROPE atmospheric component

The atmosphere is a fast but incomplete mixer and integrator of spatially and temporally varying surface fluxes, and so the distribution and temporal evolution of CO_2 in the atmosphere can be used to quantify surface fluxes, using numerical models of atmospheric transport. This approach is known as inverse modelling. However, the atmospheric approach to derive fluxes from observations of concentration on a regional scale needs sites better adapted to the specific circumstances at the regional level, where the precision and representativity of the measurements should match that of the involved major source and sink processes. Because of their long atmospheric life times, the horizontal gradients of greenhouse gas concentrations, which carry the information on the magnitude and spatial distribution of sources and sinks, are quite small, and difficult to detect with a network of stations typically spaced at 2000 km.

Consider uptake by European forests as reported by forest biomass inventories as an illustration. Naaburs et al. recently estimated a sink of 0.3 PgC y-1, located in central European and Nordic forested areas. The induced annual mean horizontal CO_2 gradient induced by this forest uptake would be 0.1 ppm/day in the entire air column over this forested region or 0.3 ppm/day if confined to the boundary layer. This gradient can be captured with the current network of high precision atmospheric stations within Europe. Consider now the release of fossil fuel CO_2 from the Paris urban area, that is 7 million people over 2500 km^2 with a per-capita emission of 712 gC per day. Locally, the emissions from Paris would add 4.6 ppm/day to the boundary layer. This is a higher signal than the one from European forest uptake shown above, but the individual flux from Paris will be more difficult to infer from stations that are presently located at best 1000 km away from the source.

If we are to infer CO_2 fluxes at the regional level from atmospheric concentration gradients, it is thus necessary to sample close to the Earth's surface, on a continuous basis, and from a higher network density of stations to best capture the signal of surface fluxes. As the variance of the measured concentrations is the most relevant quantity for the precision achievable with inverse calculations, the number of measurements should be as high as possible. In addition, because of the interannual variability in ecosystem carbon exchange, largely driven by changing climate patterns that is superimposed on the mean carbon balance of Europe, we need long time series in the atmosphere. The challenge is to operate atmospheric measurements for several years at very high precision, with a stringent quality assurance procedure to check on possible drifts in calibration scales or inter-laboratory differences.

The overarching goal of the Atmospheric Component of CARBOEUROPE is to build the Atmospheric Observing System needed to quantify the European carbon balance and its regional distribution. The road towards that goal is paved with the following sub-objectives:

- Provide the high precision atmospheric concentration measurements needed to document the contribution of Europe to the Northern Hemisphere carbon budget, placed in the global context,
- Provide the atmospheric concentration time series needed to quantify the inter-annual variability in the European carbon balance, in relation to the controlling mechanisms,
- Provide the high-frequency atmospheric concentration measurements needed to invert sources and sinks at the sub-continental level within Europe, with typical resolution of sources and sink of at least 500 km,
- Develop innovative methodologies using carbon related tracers and isotopes to attribute the CO_2 concentration in the European air shed to each of the components of the fluxes: fossil, oceanic, and terrestrial,

In addition to CO_2, CH_4, N_2O, and SF_6 will also be analysed on a large number of samples, which will provide better understanding of the European sources of these species.

5.3.3 Existing Atmospheric Observing System (2000-2004)

The European existing atmospheric observing network builds upon the scientific heritage of the former EU and National supported efforts over at least the last decade. More recently, as part of FP5, within projects AEROCARB, CHIOTTO and TACOS, a coordinated pilot European Atmospheric Observing System has been set up to demonstrate the feasibility to infer the European carbon balance by means of inverse modelling. Four laboratories CIO-Groningen, MPI-Jena, UHEI-Heidelberg and LSCE-Gif sur Yvette developed the capacity to measure a suite of carbon cycle related tracers for attributing variability and trends in concentrations to the underlying processes : fossil fuel emissions, air-sea exchange and ecosystem sequestration. The pilot Atmospheric Observing System is composed of four complementary parts:

- A network of 8 ground level CO_2 and Rn-222 stations with continuous *in situ* measurements, at a “ring“ of background sites along the boundaries of Europe and stations in the interior of the continent at about 2000 km spacing,
- A network of 8 tall towers with continuous in-situ CO_2, CH_4, N_2O, SF6, CO, O_2/N2 and Rn-222 measurements,
- A network of 6 aircraft vertical profiles at bi-weekly frequency, including both flasks and at some sites continuous CO_2 and CO soundings, and
- Flask sampling of tracers at 21 air sampling sites within Europe and over the adjacent oceans, with high-precision analysis of CO_2, CH_4, N_2O, SF6, CO, O_2/N2, and δ13C, and δ18O in CO_2 in air samples to attribute carbon fluxes to processes

These data are delivered to atmospheric mesoscale and global tracer transport models run in an inverse mode. They have also been analysed with forward simulations of 5 mesoscale and global transport models based on different flux scenarios and using a cascade of spatial resolutions of transport and process models.

Evaluation of atmospheric transport models on synoptic time scales is a prerequisite to perform defensible regional inversions that make use of the high frequency variability in the atmospheric signal. Forward simulations using five different models and a same protocol were used to analyze the spread in their results, evaluating them against data and thus quantifying the main uncertainties related to modelled atmospheric mixing.

Radon (^{222}Rn) and CO_2 simulations showed that most of the models could capture the synoptic variability of ^{222}Rn and CO_2 concentrations in the atmosphere but that there were significant differences in their mixing rates, in particular in the vertical. For CO_2 those differences were mapped for each component of CO_2. The biospheric component was the most different between models, since there is a diurnal cycle for the fluxes, which covaries with boundary layer atmospheric transport and yields strong spatial and temporal gradients in the atmospheric signals. Daily variations in most cases are followed rather well in models, although the absolute amplitude of the variations usually is too low. From vertical profiles and comparison to the measurements it is clear that a more detailed and accurate treatment of the vertical structure of the lower atmosphere is most important for correctly describing the concentration at or near the surface, probably even more important than enhancing the horizontal or vertical resolution of the models. Overall, night-time CO_2 values are underestimated by all models. Daytime selected values are in better agreement with observations and deviates less among the models. At high altitude locations the smooth topography in models leads to a delay in the diurnal cycle compared to the observed one. The issue of selecting model results at model levels corresponding to the altitude of monitoring sites is therefore important when hourly observations from the many high altitude locations are used in the inversions.

The continuous data monthly averaged from 10 sites was used in an inverse procedure to deduce carbon fluxes over Europe at sub continental scale using different models with the same inversion protocol. These inversions involved using high resolution meso-scale (limited domain models), and global models (needed among others to prescribe the boundary conditions used by the meso-scale models). A number of 20 regions was used over Europe. Such refinement was mainly possible given the addition of new observation sites within the AEROCARB project that allow to distinguish the fluxes between the different sub-continental regions.

Results in Figure 2 show an example of the West to East sub-continental (broken down into 4 regions) European carbon budget and the geographic Europe total (on the right) for five models in different colours. On average, this result suggests that Western Europe as being a sink and Eastern Europe a source of carbon. However this result is sensitive to the network of stations used. For example, the same inversion without the Black Sea coast (BSC) station reduces considerably this west to east dipole in the fluxes. Also, this dipole is bound to the quality of the regional fossil fuel estimates that we have for these Eastern European regions since this component is subtracted (after transport) to execute the inversion. Figure 2 also show that correctly accounting for the boundary conditions of the limited domain models is fundamental to produce robust results using limited-domain models. In the figure, the models in light and dark blue have different (simpler but less realistic) boundary conditions than the other models.

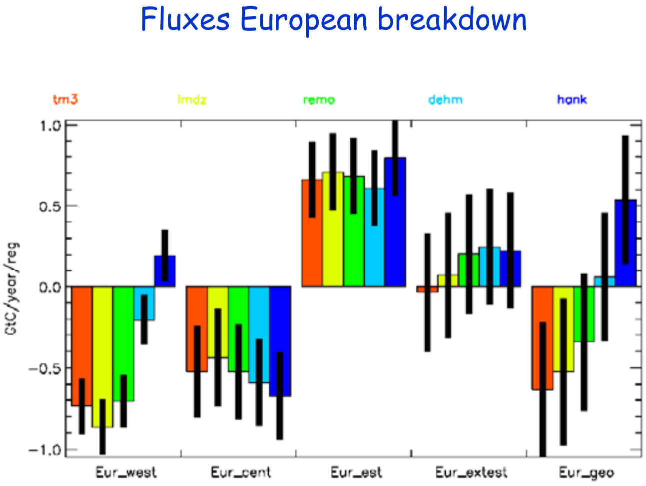
Fluxes European breakdown

Figure 2 : West to East sub-continental European breakdown of CO_2 annual fluxes and the geographical Europe total (on the right). The five models corresponding to the different colours are shown with the a posteriori error associated to the flux. This error is a result of the inversion formalism. Units are in GtC/year. The models are from left to right TM3 and LMDZ (global) and REMO, DEHM, MM5-HANK (limited area mesoscale models).

5.3.4 The future Atmospheric Observing System (funded 2004-2008)

Although some achievements have taken place to establish a pilot atmospheric network in Europe, enhancing, extending and optimizing atmospheric observations is needed.

First, the current observing atmospheric network has still insufficient horizontal spatial coverage, and must be expanded over Eastern and Southern Europe. In addition, we have learned that the current sampling frequency of the atmosphere in the vertical domain using aircraft must be increased to constrain regional fluxes, and that the aircraft measurement strategy is likely to be biased towards fair weather conditions. We must increase the aircraft sampling frequency because the „noise“ on concentrations induced by surface-atmosphere fluxes and atmospheric transport variance is high in the interior of Europe. Third, the current sampling strategy near the ground must be improved to minimize the influence of local sources and small scale transport, and eventually deliver selected atmospheric records that are fully representative of current models resolution, typically 50 km. To cope with these current limitations we propose to build a denser, and well intercalibrated Atmospheric Observing System suitable to determine regional fluxes of CO_2 and other greenhouse gases at a typical scale of 100-500km over the whole of Europe. This will be achieved by meeting the following specific objectives:

- Extending the atmospheric network spatial coverage over Southern and Eastern Europe, by adding new continuous monitoring stations,
- Increasing the frequency of vertical profile sampling through the Planetary Boundary Layer and aloft using aircraft from bi-weekly flights to sub-weekly flights, and if possible covering a wider range of synoptic weather conditions,
- Improving the atmospheric data selection, using *in situ* meteorological data and other tracer data such as Rn-222, to extract from continuous CO_2 time series representative measurements of regional sources and sinks activity

The guiding principles for reinforcing the existing Atmospheric Observing System and installing new stations, or new species measurements, does not only rely on atmospheric inverse models predictions, but also on geography, and on our present knowledge of regional fluxes across the various European ecosystems and industrial regions. The reason for this is that we already have some “a-priori“ knowledge of ecosystem source/sink distribution in Europe, as delivered from former projects results; and this information must be used in the atmospheric approach. Further, we expect the other components of CARBOEUROPE to deliver improved bottom-up estimates of ecosystem fluxes and fossil fuel emissions. These new assets will be used synergetically with the enhancement of the top-down atmospheric observations within a dual constraint, because results from one approach often place valuable constraints on the workings of the other two.

5.3.5 Methodology

The atmospheric CO_2 and auxiliary tracers measurements delivered by the Atmospheric Observing System of CARBOEUROPE will serve to quantify the European carbon fluxes quantified using different atmospheric transport models in an inverse mode. Integration of a continental atmospheric network of CO_2, CH_4 and carbon cycle related tracers in Europe is under achievement within FP5, and the approach has demonstrated its potential to downscale carbon fluxes from the hemispheric scale down to the European continent (>1000 km). Obtaining sub-continental flux estimates, with a spatial resolution of at least 1000 km, that are required to verify bottom up model estimates and eddy covariance towers up-scaling results is the next step. This will require a denser atmospheric network than what is already in place. The deployment of such a network has to account for the high diversity of landscapes and the ubiquitous presence of sources releasing fossil fuel CO_2 in Europe.

Ideally, to achieve the goals of the proposal, a measurement network would provide us with continuous high accuracy recording of the complete fields of CO_2, CO and CH_4 and their isotopes as well as a suite of transport tracers like SF6 and 222Rn in the lowermost 3 to 4 km of the troposphere. While the CO, CH_4 and $14CO_2$ fields would give information on fossil fuel and fossil fuel gas contributions to the observed CO_2 field, 13C in CO_2 would give information on land-biosphere atmosphere CO_2 exchange and transport tracers would help to test the realism of the simulation of air exchange between the planetary boundary layer and the free troposphere in models. The spatial structure of the data - horizontal concentration differences as well as differences between the planetary boundary layer and the free troposphere - and their interpretation with modelling of atmospheric transport would then permit to estimate carbon sources and sinks with high accuracy and high spatio-temporal density. This would build a base for further comparison with process studies carried out in the Ecosystem Component, to gain insight on the underlying mechanisms which control the European carbon balance.

The current technical possibilities do not permit such high-density and accurate sampling with affordable effort. Measurement methods probe currently small air volumes either continuously (CO_2, SF_6, CH_4, CO, N_2O, ^{222}Rn, O_2/N_2) or on discrete basis (e.g. weekly) with the help of flask sampling and subsequent analysis in the laboratory ($13CO_2$, $14CO_2$,). Continuous analyzers can in principle be used in aircraft to obtain vertical profile information, however the running and personal costs for this approach limit the density in time and space of this approach. The proposed Atmospheric Observing System thus consists of eight complementary activities that use a balanced choice of sampling and measurement strategies to obtain as complete a representation of the CO_2 field across Europe in the planetary boundary layer, and as far as possible, also of the concentration differences between the planetary boundary layer and the free troposphere. One important consideration underlying the sampling design is to try to take advantage of the mixing processes in the planetary boundary layer which smooth the high variability of land-biosphere atmosphere exchange CO2 signals close to the ground. Thus, the seven complementary activities which will form the core of the European Atmospheric Observing System are :

- A network of **ground based stations** measuring CO2 and Rn-222 located at „background“ locations, both around the coasts of Europe, and inside the continent on top of mountains. Sampling at these ground based stations is continuous (Figure 3). This network provides the „backbone“ data to estimate continental fluxes.

- A network of **tall tower stations** that are located roughly on a grid with horizontal distance on the order of 2000 km (Figure 3). Sampling at the tall towers is continuous and a suite of gases is measured (CO_2, CH_4, N2O, SF_6 and CO). In the afternoon, the measurements at the top of the towers sample the well mixed portion of the planetary boundary layer.

- A ring of **weekly flask sampling** stations along the coastline of Europe, including CMDL and European flask sampling programmes, completed by high altitude sites in the interior (Figure 3). Flask samples characterize boundary values of oceanic and free tropospheric reference CO_2. In addition, air in flasks gives access to isotopic signatures and carbon cycle tracers to apportion the fluxes into fossil, oceanic and biospheric components.

- A transect of **vertical aircraft profiles** of *in situ* CO_2 and flask sampling at locations where there is also a tall tower station. Airplane profiles will give guidance under which synoptic conditions the tall tower afternoon measurements are representative for PBL values. Airplanes will probe frequently (expected once a week after 2006) enough across the entire lower troposphere to deliver high-resolution snapshots of concentration fields that will place a constraint on vertical mixing in transport models, one of the largest sources of uncertainties in current inversions.

- A **quality control system** for atmospheric measurements, based on frequent exchange of intercomparison material for flask analysis and *in situ* stations. Rigorous inter-comparison procedures will detect differences between the European laboratories contributing to the Atmospheric Observing System. Use of this information will greatly improve calibration and measurement protocols, enabling us to reduce over time inter-laboratory differences in measurement scales, and *in fine* to safely merge European data with those of other international networks.

- A network of stations to quantify the fossil fuel component of atmospheric CO_2 over Europe using radiocarbon ($14CO_2$) and Carbon Monoxide (CO) measurements.

- A pilot network of **CO_2 concentration records on top of selected eddy covariance towers**. Establishing this pilot network will require a feasibility study to obtain calibrated CO_2 concentration records of moderate accuracy (± 0.5 ppm) at eddy-covariance towers and to test using transport models models constrained with the meteorological and heat flux information from the towers, how such an extension of the Atmospheric Observing System constrain regional fluxes.

Those seven complementary activities will map the CO_2 distribution over Europe with a spatial density of stations and a sampling frequency that is three to four times higher than currently operating over any other region in the world. Based upon these systematic observations, a detailed quantitative “top-down“ estimate of the European carbon balance will be obtained by using

multitracers measurements on air samples, and by applying **mesoscale transport models** run in an inverse mode, as described in the Integration Component. In return, we will perform model simulations of the atmospheric „network design“ to refine our sampling strategy for adding key stations and optimally sampling vertical profiles.

5.3.6 Ground level station measurements of CO_2 and Rn-222
(Contact M. Schmidt)

Europe has a long tradition in monitoring continental CO_2 concentration in the atmosphere. A number of 13 continuous stations are already in place (Table 1; Figure 3), with some records covering more than two decades. They comprise:

- High altitude stations such as Plateau Rosa (I), measuring the baseline free-troposphere reference,
- Coastal stations such as Mace-Head (Ir), acting as fenceposts to measure the boundary conditions of air coming into or going out of Europe,
- Mountain stations of moderate elevation such as Schauinsland (G) measuring the variability and the mean concentration signal related to regional and continental sources inside the continent.

These observations are often funded by national programmes, and are supported in CARBOEUROPE for ensuring that the records are available to a wider community and in the longer term for standardising the measurement and calibration protocols used. We expect to support the development of better data selection procedures at each site. The main issue to interpret ground level records is indeed representivity, i.e. how to compare point-wise station records[1] with transport model results of typical 50 km resolution. With that respect, Rn-222, a radioactive noble gas with half life of 3.8 days can serve as a tracer of PBL and synoptic transport processes and proves to be very valuable for selecting CO_2 data and evaluating when and where transport models can best represent observations.

5.3.7 Tall towers continuous measurements of CO_2, CH_4, SF_6, N_2O, CO, ^{222}Rn
(Contact A. Vermeulen)

Deriving fluxes from concentrations on a regional scale needs sites adapted to the specific circumstances at the regional level, where the precision and resolution in time and space of the measurements should match that of the major processes involved, and deliver as high as possible „signal to noise“ ratios to infer the mean fluxes out of transport and fluxes induced variability. This calls for measurements in the boundary layer. Tall towers are most promising platforms, where the cost of operations can be maintained relatively modest with the opportunity of using existing infrastructure such as TV transmission towers of heights up to 400m above ground in Europe. If the gases are measured at sufficient height above ground, then a fairly homogeneous signal that integrates fluxes over a footprint on the order of a range of 500 to 1000 km is obtained. Furthermore, continuous observations will enable us to optimise the data selection.

The CHIOTTO project led by A. Vermeulen started in 2002 to establish a new network of 8 tall towers in Europe (Figure 3) that complement the existing ground based stations. Here continuous measurements of CO_2 and other greenhouse gases like CH_4, CO, N_2O and transport tracers like SF_6 and ^{222}Rn will be sampled. At 5 tall towers, eddy-covariance fluxes are also measured, which will provide clues to connect the variability of tall towers vertical concentration profiles to local NEE patterns. We will to add one tall tower in the Northern Iberian This network will be completed by one tall tower for CO_2 only in Southern France for one year (2006-2007) as part of the Regional Experiment Component of the IP.

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[1] *For instance, mountain stations may probe alternatively the free troposphere and the boundary layer and prove difficult to represent in models lacking local circulation effects and local sources ; coastal stations can be affected by see-breeze effects and nearby land sources.*

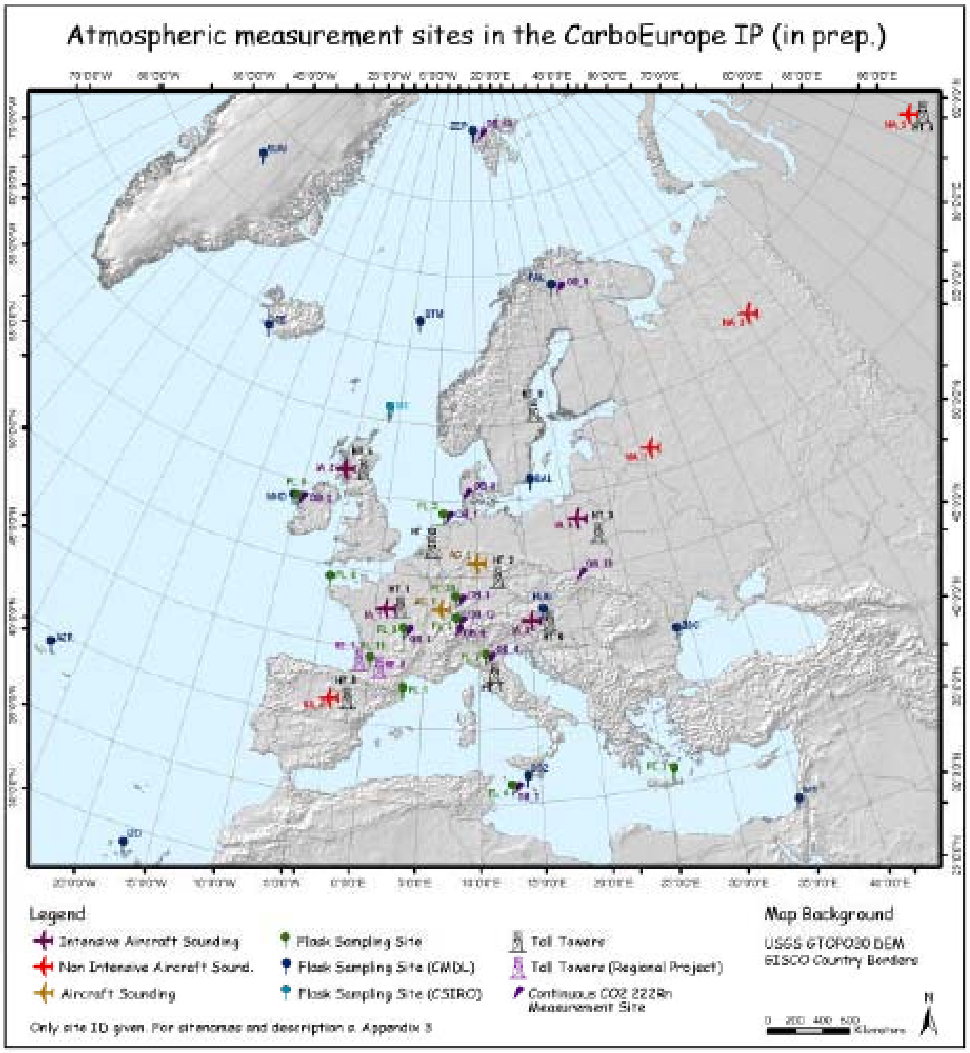

Figure 3: Atmospheric measurement site locations.

5.3.8 Flask air sampling for multiple species analysis (Contact M. Leuensberger)

Flask sampling sites, 21 in total in Europe for 115 around the Globe (Figure 3), collect discrete samples with weekly sampling frequency. Out of 21 flask sites, 12 are co-located with ground stations or tall towers in situ observatories and the remaining 9 sites are „flask sampling only“ stations which complete the Atmospheric Observing System[2]. In a 2L flask air sample, a wealth of information can be obtained via multiple species analysis of CH4, N2O, SF6, CO, 13C in CO2, 18O in CO2, O2:N2, and in the future 13C in CH4, Ar:N2, NMHCs. Multiple-species analysis will provide key information on processes controlling the CO_2 concentration changes. For instance ^{13}C and O_2/N_2 can be used in models to separate the ocean and the terrestrial components in atmospheric CO_2 and SF_6, CO and CH_4 to characterize air masses exposed to industrial emissions, which thereby serve to filter out local influences when selecting continuous CO_2

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[2] *Given the high variability of concentrations in continental air masses, we acknowledge the fact that bi-weekly CO_2 sampling provides less constraint on regional fluxes than do continuous observations, but the power of flasks data is that they give access to more species*

records. In addition to flask sites operated by European laboratories, flask data from CSIRO-DAR (R. Francey) and NOAA-CMDL (P.P. Tans) air sampling networks will be used in models.

Five European laboratories: LSCE (Fr), MPI-BGC (G), UHEI (G), UNIBE (Sw) and CIO (NL), have capabilities to make high precision multiple species measurements in flask air samples. Those laboratories are well experienced working together within EU programmes since more than 10 years. Common work includes analytical developments, sharing of sampling devices and flasks, and frequent intercomparison procedures. We will collect weekly flask samples analysis at 21 European locations for species CO_2, CH_4, N_2O, ^{13}C, ^{18}O, CO and at a subset of stations for O2:N2 (Table 3) as part of a cooperative effort involving Europe, USA and Australia. All flask data will be reported in a harmonized way to the database. Analytical developments for adding new species high-precision measurements in flask air will be vigorously pursued, focused on Ar:N2 (tracer of transport over land); linear NMHC (tracers of air pollution), and 13C in CH4 (tracer to apportion methane sources).

5.3.9 Vertical profiles of CO_2
(Contact M. Ramonet)

Because the variance of CO_2 peaks near the surface, due to proximate sources and sinks and variable transport patterns within the PBL, near-ground observations must be extended into the vertical domain. Frequent vertical soundings using small aircrafts is a cost effective solution, provided that continuous *in situ* CO_2 profiles are obtained through the entire PBL up to the free troposphere, alongside with information on the atmospheric structure. Aircraft soundings will be combined with *in situ* continuous tall towers observations ensuring the temporal continuity between two airplane soundings. Synergetic sampling at tall towers and aircrafts will assess representation errors and constrain vertical mixing of CO_2 in models, which is a major source of bias in inversions. A network of six aircraft profiles in the lower troposphere between the ground and 3000 metres is now operational on an East-West transect in Europe as part of former projects (Figure 1). These profiles carried out each 20 days with flask sampling at 10 altitudes constrain continental budgets at typical scales of 2000 km, and deliver an error reduction on the order of 30% at the best on inverted fluxes. In addition, our current airplane sampling strategy is likely to be biased towards fair weather conditions, to an unknown extent because we do not have all-weather data. Therefore, we must increase dramatically the sampling frequency of aircraft measurements and extend vertical soundings to all weather conditions to deliver a powerful constraint to inversions.

5.3.10 Quality control of atmospheric measurements
(Contact : A. Manning)

At present up to 15 laboratories contribute to the European atmospheric network, which generates a risk of producing systematic concentration differences among stations, due to differences in standardization and measurement protocols[3]. Specific accuracy objectives have been established by the WMO-Expert CO_2 panel and will be followed for characterizing systematic differences between European laboratories. We established in Europe during FP5 systematic and frequent intercomparisons among stations via the exchange of flask samples, and of low and high pressure cylinders, in close collaboration with CSIRO-DAR (Australia), NIES (Japan) and NOAA-CMDL (USA). Such activities must be pursued with vigour to monitor dynamically the differences between the laboratories, and trace the problems to calibration or instrumental drifts. Intercomparison and calibration work is labour intensive, not often reported in scientific papers, but it is central to the success of this project to ensure that European measurements meet the highest quality requirements and can be merged with other networks of the USA, Japan, and Australia.

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[3] *At the international level, the WMO-Global Atmosphere Watch programme coordinates infrequent round robin exchange of standard material and differences on the order of * ppm have been reported between laboratories, on the order of the atmospheric signals we aim to characterize within Europe.*

5.3.11 Radiocarbon and CO analysis to quantify fossil fuel emissions (Contact I. Levin)

The fossil fuel (^{14}C-free) CO_2 component over Europe can univocally be determined only via $^{14}CO_2$ observations. $^{14}CO_2$ is a difficult measurement, than can be performed with adequate precision either using AMS or "traditional" radioactive counting. European researchers pioneered the use of $^{14}CO_2$ to verify fossil fuel emissions. This requires accurate and precise quasi-continuous measurements of the marine background level, which has to be compared to the respective observations at the continental sites. Carbon Monoxide (CO) can also serve as a proxy for the fossil fuel CO_2 component, but other factors influence the variability of CO, such as oxidation by OH radicals, emissions of CO from other sources than fossil fuel burning. Indeed, investigation of fossil emissions in Europe showed a large temporal and spatial variability of the respective CO/CO_2 ratio in addition to expected systematic trends caused by changing fuel types (i.e. replacing oil by gas). Therefore, "calibration" of the fossil fuel CO/CO_2 ratio is required when CO shall be used successfully as a quantitative proxy. Due to the limited detection level even of high precision (better than 3‰) $^{14}CO_2$ measurements (of ca.1 ppm fossil fuel CO_2 with the background 14CO$_2$ level determined to 1‰) this calibration can accurately be performed only at polluted sites. These „calibration sites" require ongoing parallel (integrated) $^{14}CO_2$ and CO sampling and analysis.

5.3.12 Calibrated CO_2 concentration measurements at selected eddy-covariance towers (Contact B. Kruijt)

In daytime well-mixed conditions, near-surface CO_2 concentrations approaches the middle PBL values, and therefore have a strong potential to constrain regional fluxes in atmospheric inversions. Since CO_2 analyzers are already installed at eddy covariance sites to measure storage components of NEE, it is tempting to improve the calibration of their CO_2 concentration records in order to develop a cost effective extension in spatial coverage of the atmospheric network. First, we will analyze continuous vertical profiles obtained at different heights at tall towers and available scaling information (local meteorology and heat fluxes) in order to determine the „optimal" conditions (time of the day, synoptic conditions, season) under which near-surface CO_2 concentration can be best scaled to the PBL concentration. In parallel, we will extend the testing of cheap but robust and stable infra-red CO_2 analyzers often used at eddy covariance towers to determine whether and how those instruments can be used for obtaining 0.5 ppm accurate records; preliminary results indicate that this is achievable to ± 1 ppm. Then, we will progressively calibrate CO_2 on top of 10 of the existing eddy flux towers of the IP with a target accuracy precision of ± 0.5 ppm for mid afternoon[4] instantaneous concentrations measurements.

5.3.13 Expected results

The primary result expected from the Atmospheric Component of the IP is the establishment of a unified European Atmospheric Observing System to monitor the carbon balance of Europe and its regional distribution. This system will be the European contribution to the global, internationally coordinated effort to enhance the set of in-situ atmospheric observations to diagnose the current distribution of carbon sources and sinks. The European Atmospheric Observing system will reach an unprecedented level of station density and, thanks to stringent intercomparison procedures, will deliver a coherent ensemble of atmospheric CO2 and carbon cycle related tracers to atmospheric transport models. In addition to this European effort, we will benefit from similar efforts being planned over the North American continent, and from the existing lower density networks of European and Japanese aircraft observations over Russia and Siberia to quantify the European carbon balance in the context of Northern Hemisphere and global sinks. We also expect that an ocean carbon Integrated Project centred around the North Atlantic will add systematic atmospheric observations and constraint on the fluxes over that region.

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[4] *Only mid-afternoon selected data can be used in inverse models, because the near ground vertical gradients of CO2 at night-time are entirely influenced by local sources and boundary layer structure.*

We expect that the synergetic use of atmospheric measurements and inverse models in CARBOEUROPE will enable us to downscale the carbon fluxes using atmospheric measurements to the sub-continental level within Europe (e.g. Eastern European countries, Mediterranean area) and to the level of smaller regions of typical size 1000 km over the best sampled areas within North-Western Europe (eg. France, Germany, Benelux Countries). Uncertainties on flux estimates will be assessed by using a suite of different atmospheric transport models, and based on different data selection procedures established for each site. We expect an uncertainty for the overall European carbon balance of 20%, that is about ± 0.2 GtC year-1. We expect an uncertainty for regional fluxes in best sampled Western European regions of 30% each month.

Finally, we expect to attribute the European CO_2 gradients within the atmosphere to different component of the fluxes : oceanic, terrestrial and fossil, based on the analysis of multiple species in flask air samples and at some *in situ* sites. Assessing the fossil fuel CO_2 component will use a unique technique where European laboratories have a strong leadership, that is high precision measurements of $^{14}CO_2$, 222Radon and CO. This approach will provide fossil fuel CO_2 mixing ratio determinations on the order of 20% accuracy in moderately polluted areas and respective emissions estimates with an uncertainty of 25-35%.

Table 1: List of sites in the atmospheric measurement component of CARBOEUROPE.

Ground Level stations continuous

	Site	Code	Latitude	Longitude	Altitude m asl	Country	Species measured
1	Mace Head	MHD	53°19' N	09°53'W	26	IRL	CO_2, ^{222}Rn, CH_4, CO, N_2O, CFCs
2	Zeppelin	ZEP	78°54' N	11°53' E	475	NW	CO_2 , ^{222}Rn (2)
3	Lampedusa	LAM	35°31' N	12°38' E	70	I	CO_2 , ^{222}Rn (2)
4	Puy de Dôme	PUY	45°45' N	03°00' E	1465	FR	CO_2, ^{222}Rn
5	Schauinsland	SCH	47°55' N	07°55' E	1205	D	CO_2, ^{222}Rn, CH_4, N_2O, SF_6, CO
6	Monte Cimone	CMN	44°11' N	10°42' E	2165	I	CO_2, ^{222}Rn
7	Plateau Rosa	PRS	45°56' N	07°42' E	3480	I	CO_2
8	Jungfraujoch	JFJ	46°33' N	07°59' E	3580	CH	CO_2 , ^{222}Rn
9	Lutjewad	LUT	53°23' N	06°22' E	0	NL	CO_2, CH_4, CO, ^{222}Rn (2)
10	Westerland	WES	54°56' N	08°19' E	12	D	CO_2, ^{222}Rn (2)
11	Kasprowy Wierch	KAS	49°14' N	19°56' E	1987	PL	CO_2, CH_4, SF_6, ^{222}Rn
12	Pallas	PAL	67°58' N	24°07' E	560	FIN	CO_2, ^{222}Rn
(13)	Alert (1)	ALT	82°27' N	62°31' W	210	CAN	CO_2, CH_4, CO, ^{222}Rn

Tall towers continuous

	Site	Code	Latitude	Longitude	Altitude	Country	Species measured
1	Cabauw	CBW	51°58' N	04°55' E	213	NL	CO_2, CH_4, CO, N_2O, SF_6, ^{222}Rn
2	Orléans	ORL	47°58' N	02°06' E	203	FR	CO_2, CH_4, CO, N_2O, SF_6, ^{222}Rn
3	Ochsenkopf	OCH	50°09' N	04°52' E	177	D	CO_2, CH_4, CO, N_2O, SF_6, O_2/N_2
4	Bialystok	BIA	53.20°N	22.75°E	330	PL	CO_2, CH_4, CO, N_2O, SF_6, O_2/N_2
5	Griffin	GRI	55°57' N	03°13' W	230	UK	CO_2, CH_4, CO, N_2O, SF_6, ^{222}Rn
6	Hegyhatsal	HUN	46°57' N	16°39' E	135	HUN	CO_2, CH_4, CO, N_2O, SF_6
7	Firenze	FIR	43°48' N	11°12' E	100	I	CO_2, CH_4, CO, N_2O, SF_6
8	Norunda	NOR	60°05' N	17°28' E	103	S	CO_2, CH_4
9	La Muela	MUE	41°35' N	01°50' W	200	ES	CO_2
(10)	Labouheyre (3)	LAB	44°12'41"N	0°54' W	100	FR	CO_2
(11)	Beaumont de Lomagne (3)	BLO	43°54'09"N	0°57' W	250	FR	CO_2

Flasks sampling sites

	Site	Code	Latitude	Longitude	Labs	Country	Species measured
1	Alert	ALT	82°27' N	62°31' W	CMDL,AES	CAN	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
2	Baltic Sea	BAL	55°30' N	16°40' E	CMDL	PL	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
3	Black Sea	BSC	44°10' N	28°41' E	CMDL	RO	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
4	Gozo	GOZ	36°03' N	14°11' E	CMDL	MT	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
5	Hegyhatsal	HUN	46°57' N	16°39' E	CIO, CMDL	HUN	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$, O_2/N_2
6	Iceland	ICE	63°15' N	20°09' W	CMDL	IS	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
7	Izaña	IZO	28°18' N	16°29' W	CMDL	SP	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
8	Mace Head	MHD	53°20' N	09°54' W	LSCE,CIO,CMDL	IE	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$, O_2/N_2
9	Zeppelin	ZEP	78°54' N	11°53' E	CMDL	NW	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
10	Station 'M'	STM	66°00' N	02°00' E	CMDL	NW	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
11	Shetland Islands	SIS	60°17' N	01°17' W	CSIRO	UK	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
12	Lampedusa	LAM	35°31' N	12°38' E	ENEA	I	CO_2, CH_4, N_2O
13	Begur	BGU	41°50' N	03°20' E	LSCE	SP	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
14	Finokalia	FIK	35°19' N	25°40' E	LSCE	GR	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
15	Portsall	BZH	48°35' N	04°40' W	LSCE	FR	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
16	Puy de Dôme	PUY	45°45' N	03°00' E	LSCE,UNIBE	FR	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$, O_2/N_2
17	Pic du Midi	PDM	43°04' N	00°09' E	LSCE	FR	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
18	Lutjewad	LUT	53°23' N	06°22' E	CIO	NL	CO_2, CH_4, CO, $^{13}CO_2$, $CO^{18}O$, O_2/N_2
19	Schauinsland	SCH	47°55' N	07°55' E	UHEI	D	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
20	Jungfraujoch	JFJ	46°33' N	07°59' E	UNIBE	CH	CO_2, $^{13}CO_2$, $CO^{18}O$, O_2/N_2
21	Cabauw (4)	CBW	51°58' N	04°55' E	CIO	NL	CO_2, CH_4, CO, $^{13}CO_2$, $CO^{18}O$
22	Orléans (4)	ORL	47°58' N	02°06' E	LSCE	FR	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
23	Ochsenkopf (4)	OCH	50°09' N	04°52' E	MPI	D	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
24	Griffin (4)	GRI	56°36' N	03°47' W	LSCE,UNIBE	UK	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$, O_2/N_2
25	Norunda (4)	NOR	60°05' N	17°28' E	LUPGEA	S	CO_2, CH_4,
26	Firenze (4)	FIR	43°48' N	11°12' E	UNITUS	I	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$

Vertical aircraft profiles

	Site	Code	Latitude	Longitude	Labs	Country	Species measured
1	Griffin (5), (8)	GRI	56°36' N	03°47' W	LSCE,UNIBE	UK	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$, O_2/N_2
2	Orléans (5), (6)	ORL	48°50' N	02°30' E	LSCE, CIO	FR	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$, O_2/N_2
3	Hungary (5), (8)	HUN	46°57' N	16°39' E	LSCE, CIO, MPI	HUN	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
4	Byalistok (5)	BYA	53°12' N	22°45' E	MPI	D	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
5	Schauinsland (6), (7)	SIL	47°55' N	07°55' E	UHEI, CIO	D	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
6	Thüringen (6)	THU	50°54' N	11°30' E	MPI	D	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
7	Fyodorovskoe (9)	TVE	56°28' N	32°55' E	LSCE, CIO	RU	CO_2, CH_4, CO, N_2O, SF_6, $^{13}CO_2$, $CO^{18}O$
8	La Muela (9)	MUE	41°35' N	1°50' W	UBA	SP	CO_2

(1) *Associated site*

(2) *^{222}Rn monitors that will be added during the IP*

(3) *Tall tower for the Regionalisation workpackage*

(4) *Tall towers*

(5) *Every 20 days until 2006; then every 5 days*

(6) *Every 20 days; discontinued before 2006*

(7) *Continuous CO_2 airborne measurements existing*

(8) *Continuous CO_2 airborne measurements to be installed in 2005*

(9) *Associated aircraft sites funded by other projects*

5.4 Flask Sampling Strategy by MSC for Atmospheric Observations of Greenhouse Gases and CO_2 Isotopes over Canada: Status & Plan

Lin Huang and Doug Worthy

5.4.1 Introduction

A large amount of organic carbon is locked up in the frozen *tundra* and northern *boreal soils* of Canada. These carbon pools are likely sensitive to global climate change and could have a substantial impact on global atmospheric CO_2 levels. It is certain that carbon observations (as one of important components in Earth Observation System http://earthobservations.org; http://www.cgeo-gcot.gc.ca) in Canada, particularly for atmospheric CO_2 related observations, will add valuable information in quantifying the sources/sinks distribution for the Northern Hemisphere (a key region within global carbon cycle).

As part of the global effort in carbon cycle research, the early MSC flask programme (i.e. 1975-1997) initially focused on atmospheric CO_2 measurements at baseline stations (Table 1, Worthy et al, this issue). With the increasing importance of understanding carbon cycle and budgets on the regional and continental scales, particularly in Northern Hemisphere, sampling at continental sites has become indispensable (e.g. Tans, 1996; Wofsy and Harrison, 2002; Bakwin et al., 2003). Because spatial heterogeneity and temporal variation in processes are larger, the development of an adequate flask sampling strategy on continental or regional scales can be challenging. Questions often raised are:

- *How many sites are sufficient to cover the areas of interest?*
- *Where should these sites be located in order to represent geographic identifications (or sources/sinks distribution)?*
- *How frequent of sampling is sufficient to observe important processes?*

As noted in the Recommendation of 12th WMO/IAEA Expert Meeting (this issue), other critical issues to be addressed are: the relative benefit of flask measurements vs. continuous measurements, a few high accuracy measurements versus many somewhat lower accuracy measurements, and vertical profile data vs. dense ground coverage. Theoretically, the results from modelling and data simulation are expected to provide quantitative answers to those types of questions. Unfortunately, these tools are still in development although they may provide some general guidance. In addition, it should be taken into account that the ratio of financial resources versus the surface area in Canada is much smaller than that in United States and that in Western Europe. This requires to use our resources wisely and carefully. One of the low cost and reliable methods is via flask sampling. In this report, we will outline the current status along with a possible future plan of the flask sampling strategy at MSC. A sampling strategy should include: sampling network, sampling frequency and coordinated measurements. A sound sampling strategy should be always based on scientific objectives.

5.4.2 Objectives

As a part of global effort, the objectives of flask-sampling network (MSC) for atmospheric observation of greenhouse gases and CO_2 isotopes over Canada are:

- Quantify spatial-temporal variations of Greenhouse Gases (GHGs) concentrations and CO_2 isotopes, in conjunction with aircraft vertical profile data, flux measurements, and biosphere- atmosphere coupled models, to constrain the sources/sinks distribution in Canada, placed in North American and the global context.
- Understand the controlling processes of the source/sink distributions in various ecosystems in Canada and their response to global climate change

- Provide information/tools to assess the effectiveness of emission of greenhouse gases to national and international policy makers.

5.4.3 Sampling Network

To achieve the objectives, it is important to monitor and quantify the impact of carbon fluxes from all major ecosystems in Canada to the atmosphere and the transport of fluxes through (in and out) the regional boundary layer over Canada. The current location of flask-sampling stations and future plan (as part of components of Canadian EOS) are summarized in Table 1. The geographic representation is shown in Figure 1. It is obvious that two important ecosystems in Canada are missing in the current sampling network, i.e. Tundra, a potential large CO_2 source (Mack et al., 2004), and Hudson Bay, the largest inner-continent water system. The impact from both ecosystems on regional and global carbon cycle is highly uncertainty. The planned flask-sampling network (Figure 1) will focus on the under-sampled area in the current network, including all major ecosystems over Canada (from background stations, boreal forest, tundra, fresh water system to urbanization-encroachment area) and covering a longitudinal range from the Western coast 122°W (Estevan Point) to the Eastern coast 60°W (Sable Island), and a latitudinal range from 44°N (Sable Island) to 82°N (Alert, NU).

Table 1. **Flask Sampling Stations at MSC** (1997- present)

Station	Location	Representation	Frequency	Species	Record	Comments
Alert, NU	82°27'N, 62°31'W	*Global background*	weekly	δ^{13}C & δ^{18}O in CO_2	1997 - present	
GAW baseline station		*especially in Northern*	bi-weekly	δ^{13}C & δ^{18}O in CO_2	1997 - present	ICP (MSC vs. CSIRO)
		Hemisphere	weekly	CO_2, CH_4, CO, N_2O, SF_6	1998 - present	
			bi-weekly	CO_2, CH_4, CO, N_2O, SF_6	2000 - present	ICP (MSC vs. CSIRO)
Estevan Point, BC	49°35'N, 126°22'W	*In-flow from North Parcific*	weekly	δ^{13}C & δ^{18}O in CO_2	1997 - present	
		and long -range transport	bi-weekly	δ^{13}C & δ^{18}O in CO_2	1997 - 2001	ICP (MSC vs. CSIRO)
		from Asian	weekly	CO_2, CH_4, CO, N_2O, SF_6	1998 - present	
Sable Island, NS	43°56'N, 60°01'W	*Out-flow from the eastern part of North American*	weekly	CO2, CH4, CO, N2O, SF6 & δ^{13}C, δ^{18}O in CO_2	2003 - present	Started with COBRA-NA2003
Fraserdale, ON	49°53'N, 81°34'W	*Eastern boreal forest*	campaigns	CO2, CH4, CO, N2O, SF6 & δ^{13}C, δ^{18}O in CO_2	1998 - 2000	Ground and aircraft sampling
			weekly	CO2, CH4, CO, N2O, SF6 & δ^{13}C, δ^{18}O in CO_2	2002 - present	Diurnal two-point sampling
Prince Albert, SK	53°59'N,105°7'W	*Western boreal forest*	weekly	CO2, CH4, CO, N2O, SF6 & δ^{13}C, δ^{18}O in CO_2	2002 - present	
(BERMS-OBS)			campaigns	CO2, CH4, CO, N2O, SF6 & δ^{13}C, δ^{18}O in CO_2	2002, 03 & 04	Aircraft campaigns
Borden, ON	44°17'N,79°53'W	*Urban-encroachment*	weekly	CO2, CH4, CO, N2O, SF6 & δ^{13}C, δ^{18}O in CO_2		Planned
The East of Hadson Bay		*Out-flow from Hudson Bay*	weekly	CO2, CH4, CO, N2O, SF6 & δ^{13}C, δ^{18}O in CO_2		Planned
The West of Hudson Bay		*Tundra area*	weekly	CO2, CH4, CO, N2O, SF6 & δ^{13}C, δ^{18}O in CO_2		Planned

A brief summary of the scientific interest and geographic representation are as follows:

Alert: *the closest accessible land to the North Pole and far from major anthropogenic sources, reflecting average atmospheric compositions of the Northern Hemisphere. It is a GAW baseline station and functions as an international ICP site (a candidate of "super sites" for global carbon cycle measurement community). Currently, there are eight flask-programmes operating at the site, including CMDL/NOAA, CSIRO, SIO, MIP-GB, etc. Those programmes provide a link to permit merging Canadian data (MSC) with international data sets.*

Estevan Point: *located in west coast of Vancouver Island (100m from the beach). It is primarily influenced mainly by the in-flow from the North Pacific and across, which may have impact from long- range transport out of Asian.*

Sable Island: *located ~ 300km off the east coast of Nova Scotia in the Atlantic Ocean, predominantly influenced by the airflow originating from the eastern seaboard of the North American continent.*

Fraserdale: *located in north central Ontario with strong influence by the eastern boreal forest and north wetland regions around Hudson Bay. An inverse modelling exercise has shown that the site plays an important role in reducing the uncertainty of the CO_2 flux estimation in Boreal North America (Yuen et al., 2004). Continuous black carbon (BC) measurements indicate that it is also an idea site for monitoring boreal forest fires and the CO_2 flux from biomass burning can be partitioned.*

Prince Albert: *a Fluxnet Canada site, located in an old black spruce forest, near Prince Albert National Park, SK and as part of BERMS (Boreal Ecosystem Research and Monitoring Sites) research programme. The site is strongly influenced from the western boreal forest as well as from the southern grassland regions.*

Borden: *an associated site of the Fluxnet Canada Research Network, and is the only site situated in the Great Lakes/St. Lawrence region. The site is impacted by continental fresh water (Great Lakes) as well as by urbanization-encroachment activities and where more than 1/3^rd^ of Canada's population resides.*

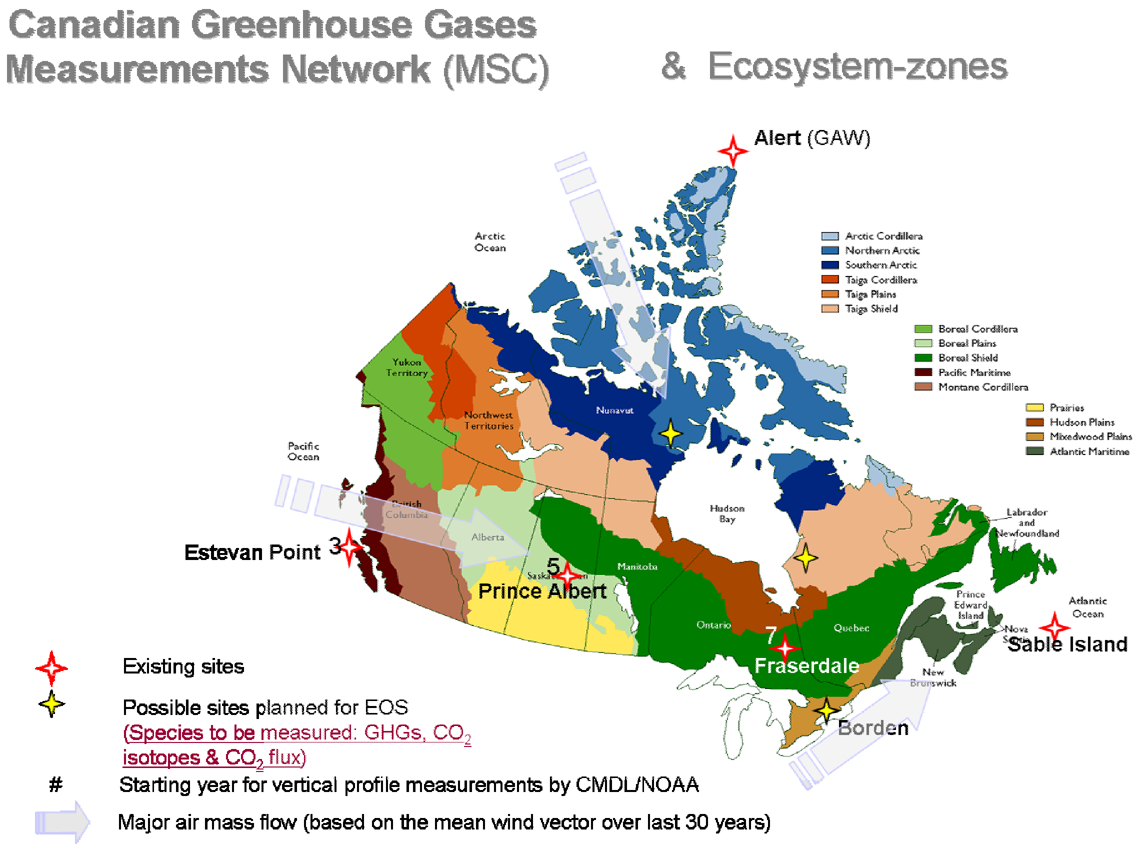

Figure 1: Geographic representation of Canadian GHGs measurement network (flask sampling). The species measured at the existing sites are shown in Table 1.

The Southeast of Hudson Bay: *a site planned in the region of the Southeast of Hudson Bay, which is strongly influenced by the largest continental water system.*

The Northwest of Hudson Bay: *a site planned in the region of the Northwest of Hudson Bay, primarily impacted by the tundra area.*

Amongst the eight sites, only the first three sites are considered as marine boundary sites or baseline stations. The other five sites represent major ecosystems over Canada. Detailed descriptions for the current sites can be found in Canadian Baseline Programme (2002).

5.4.3 Sampling frequency

Ecosystem processes on different time scales contribute to the temporal variation of CO_2 fluxes on regional scales, then ultimately to the variation of atmospheric CO_2 on the global scale. To study processes on a particular time scale, a sampling frequency higher than the time scale of interest is required (i.e. weekly sampling is required for studying monthly or seasonal processes, whereas hourly sampling is required for studying diurnal or synoptic process). While the attention is increasing on high-frequency process studied by continuous measurements, flask-sampling still plays an important role in seasonal variations on regional, continental and global scales, particularly in terms of multi-tracer constraints. Weekly paired-flask sampling is typically conducted at baseline stations to constrain seasonal variations on the global scale. To understand ecosystem processes (e.g. photosynthesis and respiration) on the time scale of interest, diurnal sampling is preferred. Auto-samplers are good candidates for diurnal sampling to make multi-species measurements because:

1) they can be programmed to sample at specific times, e.g. we could remotely choose the time from Toronto;
2) they minimize human-induced errors in sampling;
3) sampling via auto-samplers can be conveniently and efficiently coordinated with other scientific programmes such as COBRA-NA2003 (conducted under North American Carbon Programme) and regular vertical profile measurement studies by CMDL/NOAA (the starting years of those measurements are marked in Figure 1).

A prototype custom built flask auto-sampler was installed at Fraserdale site (Ernst, et al., 2003). Initially, the sampler was used during 8 intensive campaigns for diurnal sampling (i.e. every two hours), between 1998 and 2000 (Huang et al., 2003).). It is currently automated to permit remote control access and permanently installed at Fraserdale for weekly diurnal sampling (one diurnal maximum and one diurnal minimum each week) in order to understand the long-term trend in the amplitude of diurnal changes of CO_2 isotopes and its relationship with correspondent changes of GHGs. Figure 2 shows the inter-comparison results of CO_2 from the flask samples with hourly averaged in- situ measurements during COBRA-NA2003 (http://www.fas.harvard.edu/~cobra). Although the flask CO_2 value does not consistently catch the diurnal maximum or minimum of CO_2 signals, it is certain that the statistical patterns of diurnal variations can be obtained for both greenhouse gases and CO_2 isotopes. The long-term trends of these patterns, especially for $\delta^{13}C$ and $\delta^{18}O$ in CO_2, will provide valuable information for the study of ecosystem processes and regional carbon budget evaluations. Funding permitting, it is hoped to install auto-samplers at as many of these continental sites as possible (Figure.1).

5.4.4 Coordinated Measurements

Multi-Species: Atmospheric levels of the greenhouse gases (CO_2 CH_4, N_2O) and CO_2 isotopes, on regional scales, are primarily impacted by ecosystem processes (i.e. photosynthesis, respiration, bacterial activities), biomass-burning and the combustion of fossil fuels. CO and H_2 are mainly influenced by photochemical processes, biomass-burning and fossil fuel emissions. Microbial uptake in soils is also an important sink for H_2. The $\delta^{13}C$ and $\delta^{18}O$ data contains vital information on many of the controlling processes of carbon cycle (i.e. photosynthesis, respiration as well as interaction with the water cycle), and can provides an effective additional constraint on components of carbon cycle modelling. To understand the distribution of sources/sinks of CO_2 and the controlling mechanisms, *an approach of mutual-constrain via multi-tracer* will be employed. The species measured in the flask samples currently are CO_2, CH_4, N_2O, CO, SF_6, H_2, $\delta^{13}C$ and $\delta^{18}O$ in CO_2. Specific details on our measurement protocols and corresponding traceability can be found in the reports by Worthy et al., (2003) and Huang et al., (2003).

Strategic collocated aerosol sampling at Alert and Fraserdale for black carbon (BC) and its carbon isotope measurements will provide additional constraints on CO_2 flux from biomass-burning and fossil-fuel combustion. It is known that BC is only released from those two high temperature processes, whereas CO are products from biomass-burning and fossil-fuel combustion as well as from photochemical oxidations, particularly in summer time. Thus, using only CO/CO_2 ratio to partition CO_2 flux from biomass-burning and fossil-fuel combustion is not sufficient. The correlation in BC and CO (Figure 3) will provide a direct constraint on CO flux estimation and, in turn, an indirect constrain on CO_2 flux partitioning.

ICP and mutual-constraints:

ICP is a means to detect experimental deficiencies and sampling problems and to evaluate possible biases amongst the data sets obtained from different laboratories or from different methodologies. Flask inter-comparison programmes are strongly encouraged as described in the recommendation from the 12th WMO meeting (this issue) to permit the merging of different data sets into international data archives (e.g. the World Meteorological Organization [WMO] World Data Centre for Greenhouse Gases in Japan and GlobalView in U.S.). As mentioned earlier, Alert is a potential good candidate for a "super sites" for flask ICPs. Amongst the eight flask programmes operating at Alert, MSC is conducting ICP exercises with two other programmes. An ICP with CSIRO (i.e. mutual exchange of air in glass flasks) has been conducted for $\delta^{13}C$ and $\delta^{18}O$ in CO_2 since 1997 and the other GHGs since 2000. The ICP for GHGs with CMDL (NOAA) at Alert was initialized in 1999 and the plans are being made to include $\delta^{13}C$ and $\delta^{18}O$ in CO_2 with CMDL/INSTAAR. Further ICP activities with other programmes (e.g. MPI-BGC and University of Heidelberg, Germany) at Alert will be initialized 2005.

Another category of ICP is conducted between hourly averaged continuous measurements and individual flask measurements for the same sampling time, as a mean of mutual constrains to the precision and accuracy of these measurements. Continuous measurements can avoid potential problems related to sampling procedures (e.g. fractionation or contamination), whereas, flask measurements provides more constraints on the quality of the data because of pair–flask sampling, the closest pathway to the primary standards and multi-species measurements in the same sample. Almost all flask sampling sites in MSC network (except for Estevan Point) are or will be collocated with in situ greenhouse gas measurements to guarantee the quality of these measurements. Previous results are reported in this issue (Worthy et al. this issue).

Coordination with CO_2 Flux Measurement: As recommended by this meeting (the Recommendation, this issue; Davis, this issue), there is a plan to pursue the option of combination of high precision CO_2 concentration measurements and CO_2 flux measurements at tall towers (>100m) through collaboration with Fluxnet Canada and the flux measurement group at MSC, as Canadian contribution to this international effort. This will benefit understanding the carbon exchange process in the planetary boundary layer and help up scaling surface CO_2 fluxes from flux towers to regional scale of Canada.

Coordination with Boundary Layer Measurements Using Aircrafts: Vertical profile measurements are important to understand the processes in atmospheric boundary layer for estimation of the total column CO_2 budget. Aircraft sampling is a crucial component within NACP. As shown in Fig. 1, the MSC flask network will continue the coordination with the regular vertical measurements by CMDL/NOAA, and intensive aircraft campaigns under NACP, the similar activities such as COBRA-NA2003 study. Auto-samplers, which are efficient and flexible, will be employed to coordinate these measurements at our ground stations.

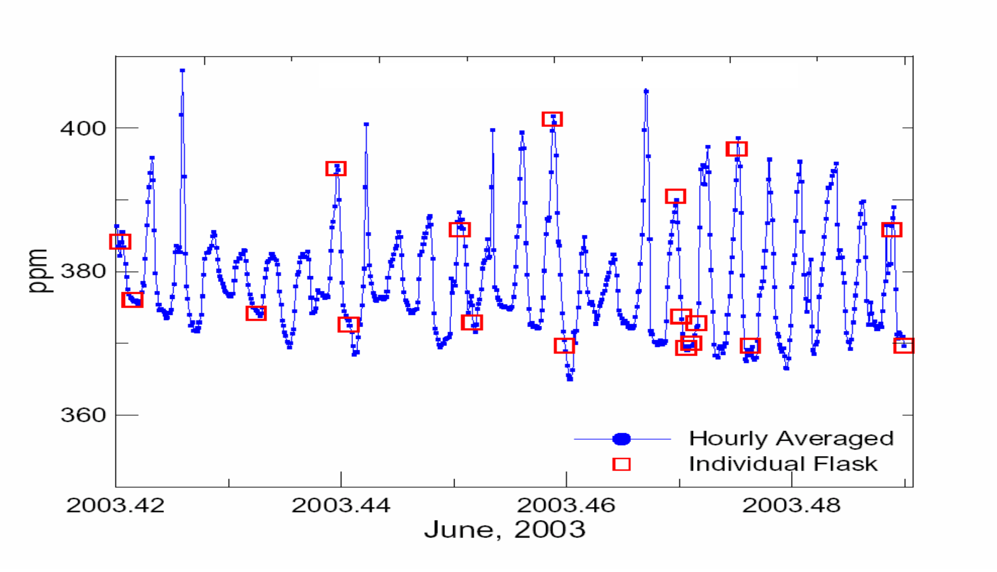

Figure 2: Inter-comparison of CO_2 measurements from flask samples along with in situ hourly averaged measurements during COBRA-NA2003 at Fraserdale. Open square: individual flask; solid dots: hourly average of in situ measurements.

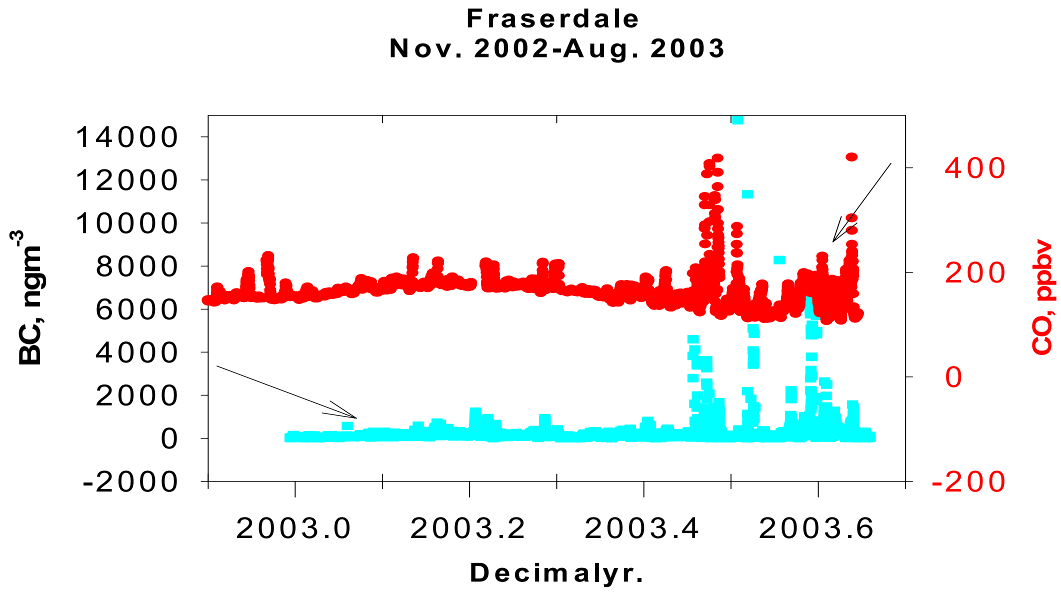

Figure 3: Black carbon and CO concentrations (January-August 2003). Top panel: CO (dots); Bottom panel: BC (squares), showing a positive correlation between BC and CO for the forest fire episodes during June to August (Courtesy of Sangeeta Sharma et al, 2004).

5.4.5 Summary

A flask-sampling strategy for the measurements of atmospheric GHGs and CO_2 isotopes in Canada (by MSC) has been presented. The inter-continental sampling will focus on the unique ecosystems in North America, particularly within the boreal forest and tundra regions. The sampling frequency at continental sites will be conducted on weekly basis. Diurnal sampling will be implemented in order to constrain the seasonal and annual variations of ecosystem processes. The measurements will focus on the integration and coordination of multi-species and vertical vs. ground to provide multi-constraints on the distribution of CO_2 sources and sinks over Canada.

5.4.6 Acknowledgements

We would like to thank Drs. Neil Trivett and Fred Hopper for their enthusiasm and efforts in initializing the flask programme at MSC (for both GHGs measurements and CO_2 isotopes), Dr. C.S. Wong's efforts (Institute of Ocean Sciences, Fisheries and Oceans Canada) are also acknowledged for the CO_2 measurements in the early stages of the programme (prior to 1988). The technical contributions by V. Hudec, D. Ernst, M. Ernst and A. Chivulescu's for maintaining and operating the flask sampling programmes are highly appreciated. We thank Sangeeta Sharma for the use of Figure.3.

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5.5 Well-Calibrated CO_2 Mixing Ratio Measurements at Flux Towers: The Virtual Tall Towers Approach

Kenneth J. Davis

5.5.1 Introduction

The study of the terrestrial carbon cycle is currently data-limited. One approach to increasing the density of data over the continents is to instrument eddy-covariance flux towers with well-calibrated CO_2 mixing ratio measurements. More than two hundred such towers are currently being operated at continental sites around the globe. Most of these towers, however, while measuring CO_2 mixing ratios at high frequency, continuously, and with good relative precision, do not have carefully calibrated long-term mixing ratio measurements. Similarly it has been thought that mixing ratio measurements in the atmospheric surface layer, the lowest portion of the atmospheric boundary layer, would be too close to strong sources and sinks to be useful for studying the carbon cycle via atmospheric budget or inverse studies. Methods exist, however, for both precise calibration of flux tower mixing ratio measurements and careful interpretation of surface layer data.

5.5.2 Instrumentation

Methodology for well-calibrated continuous CO_2 mixing ratio measurements at remote tower locations was established and evaluated by Bakwin *et al.,* (1995; 1998) and Zhao *et al.,* (1997). The technology is relatively inexpensive, and many flux towers already possess the infrared gas analyzers necessary for the measurement. The primary additional needs are for high-quality calibration gases, drying of sample air, pressure and flow control of the analyzers, and site intercalibration methods to be adopted. Information concerning tower-based methodology can be found at http://rflux.psu.edu. Adaptations of Bakwin *et al.,* (1998)'s work to tower-based terrestrial CO_2 networks has been described by Richardson *et al.,* (2003). This discussion will focus on how mixing ratio measurements on flux towers in the atmospheric surface layer can be interpreted in a way that provides data concerning regional to global scale mixing ratio gradients.

5.5.3 Virtual tall towers methodology

An underlying assumption of this approach is that measurements of the CO_2 mixing ratio representative of the continental atmospheric boundary layer (ABL) are beneficial to the study of the terrestrial carbon cycle. It has been argued that the boundary layer is too complex, thus such measurements will be uninterpretable with tools such as atmospheric transport models. Conversely, however, if the continental ABL is not simulated well, the accuracy of the results of transport models is significantly limited (e.g. Gurney *et al*., 2002).

5.5.3.1 Spatial gradients in atmospheric CO_2 mixing ratios

Given this underlying assumption, this method rests primarily upon the fact that at midday over land, the atmospheric boundary layer (ABL) is typically convective, thus well-mixed. As a result, the vertical mixing ratio gradients within the continental ABL are quite small (see, for example Stull, 1988; Moeng and Wyngaard, 1989). This has been carefully documented for CO_2 via the NOAA CMDL tall towers measurement programme (Bakwin *et al.,* 1998). We interpret the 396m measurements at the WLEF tall tower as representative of the well-mixed, continental ABL mixing ratio. The monthly mean difference between this level and surface layer mixing ratio measurements, sub-sampled for midday hours is shown in Table 1.

Table 1: Monthly mean CO_2 mixing ratios at various heights and times of day as observed at the WLEF tower during 1997. Annual mean at Mauna Loa was 366.7 ppm in 1997.

Month	CO_2 (ppm) at 11m, early pm only	CO_2 (ppm) at 396m, early pm only	ΔCO_2 (ppm) 11m – 396m, early pm only	CO_2 (ppm) at 396m, entire day	ΔCO_2 (ppm) 396m pm – 396m entire day,
1	371.4	370.3	1.1	369.7	0.6
2	371.4	371.2	0.2	371.1	0.1
3	371.4	371.0	0.4	371.0	0.0
4	370.4	370.4	0.0	370.4	0.0
5	368.1	368.2	-0.1	368.3	-0.1
6	355.5	357.3	-1.8	359.4	-2.1
7	348.0	350.2	-2.2	351.1	-0.9
8	346.1	348.1	-2.0	349.3	-1.2
9	354.9	356.2	-1.3	358.0	-1.8
10	365.8	365.6	0.2	366.0	-0.4
11	370.3	369.9	0.3	369.6	0.3
12	371.5	370.6	0.9	370.2	0.4
Annual mean	363.7	364.1	-0.4	364.5	-0.4

Table 2, in comparison, shows the magnitude of syntopic, seasonal, and annual gradients that can be used to derive information about terrestrial sources and sinks of CO_2. Figure 2, adapted from Yi *et al.,* (2004) shows the seasonal course of the 1998 mean mixing ratios of CO_2 for the CBL at the WLEF tower in Wisconsin, the marine boundary layer for 44.4N, and the free troposphere as represented by aircraft data at Carr, CO. Figure 3 shows a monthly time series of CO_2 mixing ratios sampled at both 396 m and 30 m from the WLEF tower. The 30 m data are sub-sampled for midday (typically convective) conditions. The fairly large amplitude perturbations in mixing ratio are correlated with synoptic passages. Recent publications (Hurwitz *et al.,* 2004; Yi *et al.,* 2004; Bakwin *et al.,* 2004; and Helliker *et al.,* 2004) provide more detail regarding synoptic and seasonal patterns in continental ABL and free tropospheric mixing ratios and fluxes.

Table 2: Approximate range of magnitudes of CO_2 signals in the earth's atmosphere compared to surface layer – mid-ABL mixing ratio biases observed at the WLEF tower.

Time scale	**Synoptic (days, within continent)**	**Seasonal (amplitude of continental cycle, difference between the marine and continental boundary layers)**	**Annual (marine-continental difference)**
Mixing ratio difference (ppm)	5-20	4-15	2
Bias (midday surface layer to 24-hour mid-ABL, ppm)	1-4	1-4 (peak in summer)	0.4/0.4 (midday-24hr/ surface layer-mid ABL)

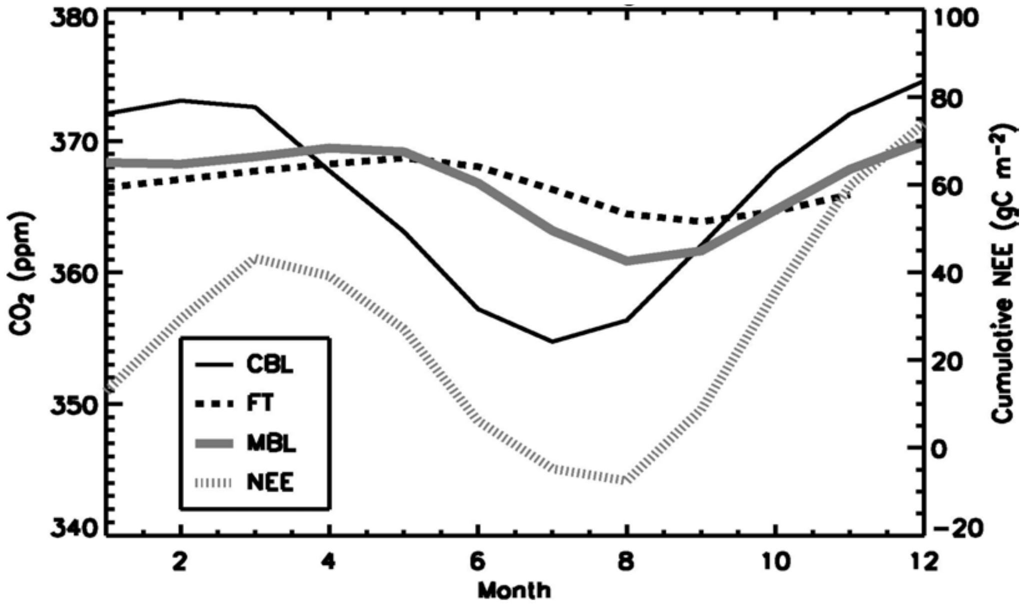

Figure 2: Smoothed seasonal cycles in the continental boundary layer (CBL) at the WLEF tall tower, the free troposphere (FT, as derived from aircraft profiles), and the marine boundary layer (MBL) at the latitude of WLEF (from GlobalView). Cumulative net ecosystem-atmosphere exchange (NEE) of CO_2, observed via eddy covariance at the WLEF tower, is shown for reference. Data are from 1998. After Yi et al., (2004).

It is evident from Tables 1 and 2, and Figure 2 that the difference between monthly mean surface layer mixing ratios and mid-ABL mixing ratios, when sampled during well-mixed conditions, is much smaller than both 1) the amplitude of the seasonal cycle in the continental boundary layer; and 2) the difference between monthly mean marine and continental boundary layer mixing ratios. It is also clear from the Table 2 and Figure 3 that the amplitude of synoptic cycles in CO_2 mixing ratio is much larger than the offset between surface layer and the middle of the well-mixed ABL, sometimes referred to as the mixed-layer (ML). Thus the study of synoptic and seasonal patterns could be accomplished with surface layer flux and mixing ratio data solely via sub-sampling for convective conditions. Surface buoyancy flux is a basic measurement at all CO_2 flux tower sites. Tables 1 and 2 also show that even annually averaged differences between the continental and marine boundary layers can be resolved with this approach, though the systematic offset between 30 m and 396 m, at 0.4 ppm, is about 20% of the annually averaged marine-continental gradient (about 2 ppm).

Selecting midday surface-layer mixing ratio measurements allows for many of these temporal patterns and spatial gradients to be resolved. Since CO_2 flux towers are relatively abundant (see, for example, Baldocchi *et al.,* 2001) and are already equipped to measure CO_2 mixing ratios, calibrating these flux towers following the work of Bakwin *et al.,* (1998) and Richardson *et al.,* (2003) is a straightforward and worthwhile endeavour for the study of synoptic to seasonal scale temporal and spatial gradients in continental ABL CO_2 mixing ratios. A small number of flux towers already follow these or similar procedures, and several publications have recently been published or are in press based on midday subsampling of these mixing ratio data (Bakwin *et al.,* 2004; Yi *et al.,* 2004; Helliker *et al.,* 2004).

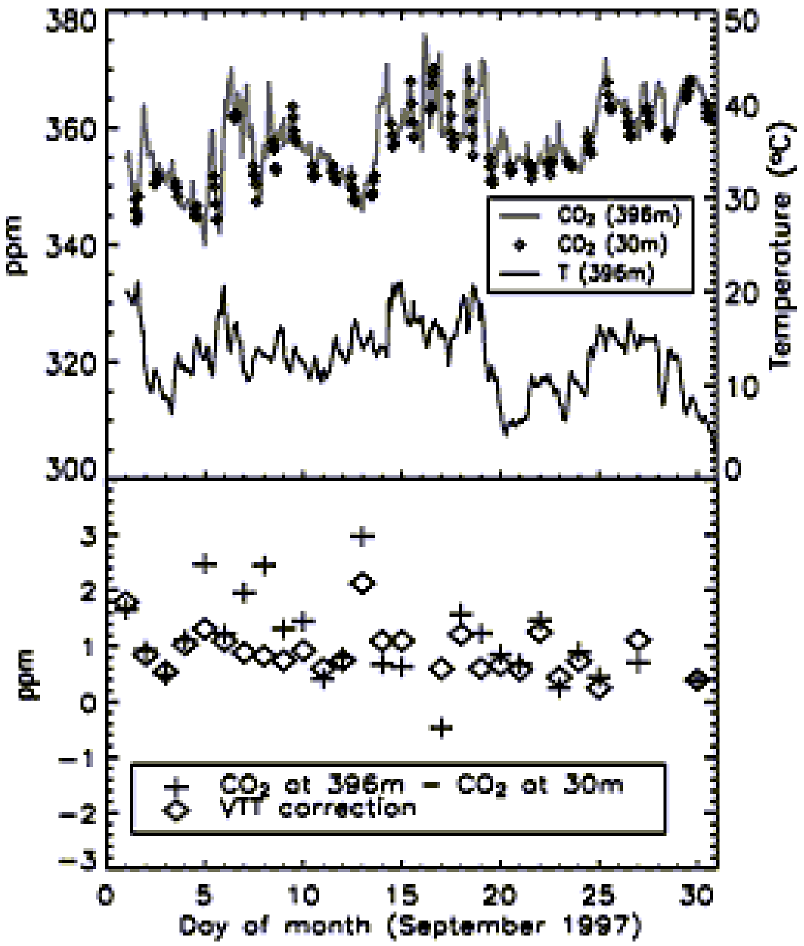

Figure 3: a) CO_2 mixing ratios and temperature as observed from the WLEF tower during September, 1997.

b) Observed and modelled offset between surface layer and mid-ABL CO_2 mixing ratios.

In addition the difference between surface layer and mid-ABL mixing ratios can be predicted in the convective boundary layer by mixed layer (ML) similarity theory (Wyngaard and Brost, 1984; Moeng and Wyngaard, 1989). The difference between the surface layer and mid-ABL mixing ratio in these conditions is proportional to the surface flux of CO_2 and also altered by the surface buoyancy flux, both of which are measured directly by flux towers. This correction, along with the sub-sampling for convective conditions, is the basis of the virtual tall tower (VTT) approach (Davis *et al.,* 1998; Davis *et al.,* in preparation). This approach has been borne out by the empirical success of studies using surface layer mixing ratio data including Potosnak *et al*., (1999), and favourable comparisons of results from tall towers and surface layer towers (Bakwin *et al.,* 2004). Table 1, and the following results (Davis *et al.,* in preparation) quantify this discussion.

5.5.3.2 Mixed-layer gradient correction

Extrapolation to mid-boundary layer mixing ratios can be achieved using mixed-layer similarity theory (Wyngaard and Brost, 1984). This theory states that for a well-mixed boundary layer where solar heating of the earth's surface drives vigorous convection, the mean vertical mixing ratio gradient is governed via the following expression:

$$\frac{\partial C}{\partial z} = -g_b\left({}^{z}\!/_{z_i} \right)\frac{F_0^C}{w_* z_i} - g_t\left({}^{z}\!/_{z_i} \right)\frac{F_{z_i}^C}{w_* z_i} \qquad (1)$$

where C is the scalar mixing ratio (e.g. CO_2), F_0^C and F_{zi}^C are the surface and entrainment fluxes of the scalar, z_i is the depth of the convective boundary layer, w_* is the convective velocity scale (a function of the surface buoyancy flux and z_i), z is altitude above ground (or, for a forest, above the displacement height) and g_b and g_t are dimensionless gradient functions that depend on normalized altitude within the convective layer.

The difference between surface layer and mid-boundary layer mixing ratios can be computed by integrating the flux-gradient relationship across this vertical interval,

$$\Delta C = C\left({}^{z_{ABL}}\!/_{z_i} \right) - C\left({}^{z_0}\!/_{z_i} \right) = -\frac{F_0^C}{w_* z_i} \int_{z0}^{zABL} g_b\left({}^{z}\!/_{z_i} \right) \partial z - \frac{F_{z_i}^C}{w_* z_i} \int_{z0}^{zABL} g_t\left({}^{z}\!/_{z_i} \right) \partial z, \qquad (2)$$

where z_0 is the altitude of the surface layer measurement, and z_{ABL} is an altitude within the well-mixed atmospheric boundary layer. Note that the gradient varies linearly with the magnitude of the surface flux (so that in winter, if fluxes are very small, essentially no correction is required), and that the difference in mixing ratio is proportional to the integral of the gradient functions. Note also that for the lower half of the boundary layer, the top-down gradient function is quite small (Moeng and Wyngaard, 1989).

Moeng and Wyngaard (1989) simulated these gradient functions using large eddy simulations (LES). Davis et al. (1998), using CO_2 flux and mixing ratio data from the WLEF tall tower for one month, calculated the bottom-up gradient function using data limited to convective conditions. Patton et al. (2003) also computed the bottom-up gradient function from a nested forest-boundary layer LES, the first LES study to include explicit forest canopy flow within a convective ABL simulation. Figure 4 shows calculations of the mixed-layer gradient functions from WLEF tall tower data collected over multiple years (Davis et al., in preparation), in addition to the gradient functions computed by Patton et al., (2003) from LES both with and without a forest canopy.

5.5.3.3 Uncertainties in the ML gradient correction

The VTT approach is subject to random and systematic errors. The random uncertainty of the observed bottom-up gradient function, which includes turbulent fluctuations in fluxes and mixing ratios as well as random instrumental errors, all captured in the WLEF observations, are plotted as error bars in the computed gradient functions in Figure 4. These uncertainties, propagated through equation (2), yield a random uncertainty in the monthly mean mid-CBL mixing ratio of 0.15 ppm for midsummer fluxes. The choice of gradient function, g_b, is uncertain as shown by the bottom-up gradient functions plotted in Figure 4. Tower-based gradient function observations over a forest appear to agree more closely to LES simulations of g_b in the absence of a forest canopy. The forest canopy simulations show a significantly smaller bottom-up gradient function. The cause of these differences is not clear, and is a topic for future research. This leads to a systematic uncertainty in the ML gradient correction. The maximum reasonable error that could be made among the choices shown in Figure 1 is about 50% of the total change in CO_2 mixing ratio from surface layer to mid-boundary layer. Table 1 shows that on a monthly mean basis, this amounts to a maximum (mid-summer) systematic bias of 1.0 ppm between the computed and actual mid-CBL mixing ratio. Since the surface layer to boundary layer gradient changes sign seasonally, this potential bias would partly cancel for an annual average. Since WLEF data shows a 0.4 ppm annual bias between surface layer and mid-CBL data, we estimate a maximum annual mean systematic bias after correction of about 0.2 ppm.

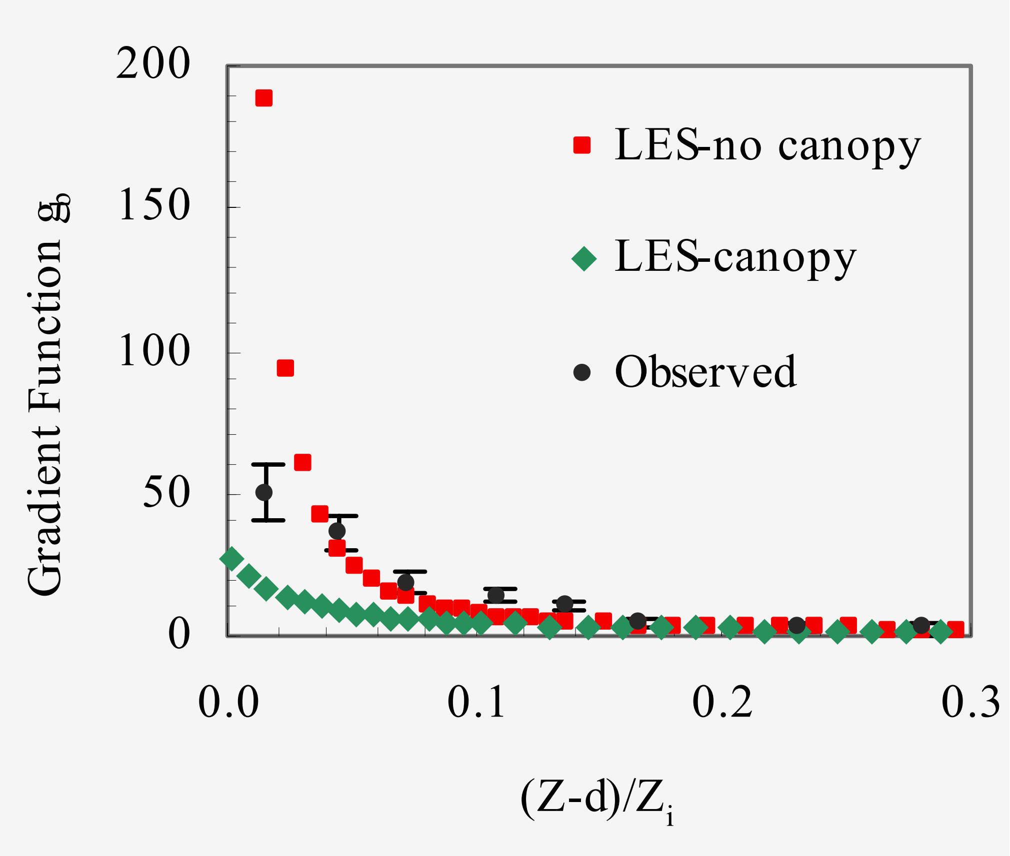

Figure 4: Observed and modelled bottom-up gradient function, g_b, as a function of normalized altitude above the displacement height, d. Altitude is normalized by the ABL depth, z_i. LES results follow Patton et al., (2003).

5.5.3.4 Application of the ML gradient correction

Figure 3 shows an example of this correction, as applied to the WLEF tower. The top panel (Figure 3a) shows hourly CO_2 mixing ratio data from 396m at the WLEF tower, and data from 30m sub-sampled for convective conditions. The lower panel (Figure 3b) shows the difference between midday-mean 396m and 30m mixing ratio data (+'s) which is about 2 ppm early in the month, and decreases later in the month as the deciduous forest senesces. The diamonds represent the 30 m mixing ratio data with a relatively crude ML gradient correction applied, that is, application of equation (2) using the LES-derived gradient functions of Moeng and Wyngaard (1984). Monthly mean values are used for the mixed layer depth (Yi *et al.,* 2001) and the surface fluxes (Davis *et al.,* 2003). The correction results in a monthly mean systematic bias in the VTT estimated CBL mixing ratio of just under –0.2 ppm. The standard deviation of the difference between the 396 m data and the VTT estimate is 0.6 ppm, resulting in a monthly standard error of just over 0.1 ppm, consistent with the error propagation that predicted 0.15 ppm. Thus, both the bias and random error of monthly VTT mixing ratio data are small enough to detect annually averaged continental-to-marine mixing ratio gradients. The bias would change sign summer vs. winter, thus partly cancel if the VTT data were used on an annual average basis.

It is important to note that only the flux and gradient footprints of the tower need to be reasonably homogeneous for this micrometeorological correction to work well. The vertical gradient footprint is similar to the flux footprint (Horst *et al.,* 1999). The much larger region that influences the time rate of change of the ABL mean mixing ratio (e.g. Gloor *et al.,* 1999) does not need to be homogeneous for the ML gradient correction to be valid.   Heterogeneity within the flux and vertical gradient footprints, however, will cause additional uncertainty. Existing flux tower sites are not entirely homogeneous, thus this issue may also need to be evaluated further.

5.5.4 Implementation

Given that the global flux measurement network now includes more than 200 sites, and that terrestrial ABL CO_2 mixing ratio measurements are lacking in all parts of the globe, the VTT approach represents a relatively simple and inexpensive way to expand the global CO_2 mixing ratio network. A number of existing flux towers maintain well-calibrated CO_2 mixing ratio measurements (approximately five in North America and 1-2 in South America, for example). Five to seven additional AmeriFlux towers will be enhanced with these measurements in 2005, roughly doubling the number of flux towers in North America that are able to provide VTT data. We anticipate adding this data stream to the GlobalView data base. Intercalibration activities will, at minimum, include archive CO_2 tanks distributed to these tower sites to provide long-term – roughly 10 year – continuity of calibrations, and co-location of one instrument with NOAA CMDL's WLEF tall tower measurement site.

5.5.5 Acknowledgements

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5.6 A Calibration And Intercomparison Scheme for Continuous, Multi-Species atmospheric Measurements from a Network of Tall Towers in Europe

Andrew Manning

This report outlines the calibration and intercomparison scheme which will be used within the EU *CHIOTTO* project. The scheme is based on a talk given at the 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques, but also includes improvements and modifications based on feedback received at this meeting.

5.6.1 Introduction

In late 2002 the European Union funded a new project under their “Environment and Sustainable Development” section of their “Programme for Research, Technological Development and Demonstration” under the “Fifth Framework Programme”. This project is named *CHIOTTO, Continuous High precisiON Tall Tower Observations of greenhouse gases. CHIOTTO* is a consortium of nine European scientific research institutes and universities operating a network of eight tall towers in Europe. *CHIOTTO* is one component of the much larger *CarboEurope* project which is aimed at quantifying and understanding the terrestrial carbon balance in Europe. From these eight towers we will measure semi-continuously several greenhouse gases and related tracer species. The species measured varies somewhat from tower to tower, but includes CO_2, CH_4, CO, N_2O, SF_6, O_2/N_2, and ^{222}Rn. In addition, weekly flask samples will be collected from some towers, enabling stable isotope measurements of $\delta^{13}C\text{-}CO_2$ and $\delta^{18}O\text{-}CO_2$. The top heights of the towers range from 103 to 310 m above ground level, and sample measurements will be made from several heights at each tower, allowing vertical profiles to be determined. As shown in Figure 1 and Table 1, the *CHIOTTO* tower network spans a longitudinal range from Scotland (03°W) to eastern Poland (23°E), and a latitudinal range from Sweden (60°N) to northern Italy (44°N). The towers used are all pre-existing towers, for the most part owned and operated by telecommunications companies, who have very generously allowed us to collect atmospheric measurements from platforms on their towers.

The primary motivation for obtaining atmospheric data from tall towers is to fill existing measurement gaps in geographic location and on spatial scales. In obtaining “background” atmospheric measurements we wish to observe and quantify relatively small, long term, synoptic-scale changes from within the relatively large “noise” of both localised diurnal cycles and localised anthropogenic emissions. Therefore, such measurements traditionally have been made from coastal or alpine locations. However, such a sampling protocol results in a geographic bias away from mid-continental locations, compromising our ability to accurately quantify the size of, and temporal variability in, the land biotic carbon sink. Additionally, coastal atmospheric measurements sites provide data on approximately hemispheric scales, whereas eddy flux measurements, for which there is a large body of existing data, provide data on scales of the order of 1 km^2. This leaves a significant data gap on spatial scales which tall tower measurements, providing data on scales of 500 km^2 to 100,000 km^2, are able to fill.

In addition to the motivations given above for utilising tall towers for atmospheric sampling, there are three other main strengths in creating a tall tower atmospheric measurement network such as *CHIOTTO.* First, *CHIOTTO* employs a multi-species approach, measuring not only CO_2 concentrations, but a host of other greenhouse gases and related tracers. In this manner, we will have the potential to obtain a much more complete picture of the carbon cycle, the processes and mechanisms controlling and influencing it, and in particular the terrestrial carbon cycle in continental Europe. Second, we will obtain semi-continuous measurements (one sample measurement every 15 minutes or faster), allowing us to observe processes and variability occurring at high temporal frequency. For example, we will be able to accurately determine diurnal variability in the species measured. Finally, although a limited number of tall tower measurements have been made before [*Bakwin et al.*, 1997; *Bakwin et al.*, 1998; *Bakwin et al.*, 1995; *Hurst et al.*, 1997], *CHIOTTO* represents the first-ever network of tall tower atmospheric measurements run by a single consortium. It is this third strength which this paper aims to exploit to full advantage.

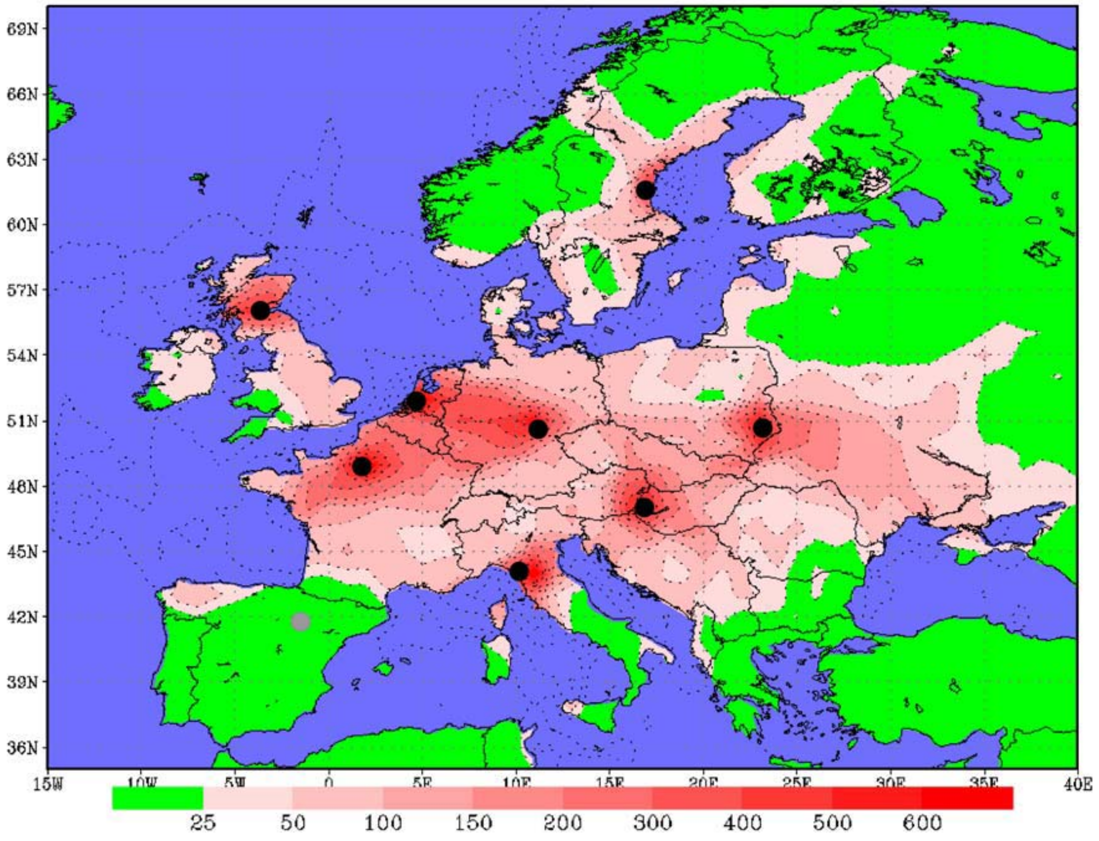

Figure 1: Black dots show the locations of the eight tall towers in the CHIOTTO network. The grey dot in Spain shows the location of an anticipated additional site in 2005. The greyscale shows the "footprint" area of each tower, where values ranging from 0 to 700 represent the contribution of fluxes (in per mil units) to the expected atmospheric CO_2 variability at each tower. These footprints were obtained using a back trajectory analysis similar to Gloor et al. [2001]. The resulting patterns are a measure as to what extent fluxes in Europe are observable by the CHIOTTO tower network. (Figure courtesy of Manuel Gloor.)

Table 1: Coordinates of CHIOTTO towers, and species measured.

Site	Code	Latitude	Longitude	Tower height	Species measured
Angus, Scotland	TTA	55°57'N	3°13'W	220	CO_2, CH_4, N_2O, SF_6, ^{222}Rn
Bialystok, Poland	BIK	53°12'N	22°45'E	310	CO_2, CH_4, CO, N_2O, SF_6, O_2/N_2
Cabauw, Netherlands	CBW	51°58'N	04°55'E	213	CO_2, CH_4, CO, N_2O, SF_6, ^{222}Rn
Firenze, Italy	FIR	43°48'N	11°12'E	210	CO_2, CH_4, N_2O, SF_6
Hegyhatsal, Hungary	HUN	46°57'N	16°39'E	115	CO_2, CH_4, CO, N_2O, SF_6
La Muela, Spain	MUE	41°35'N	1°50'W	200	CO_2
Norunda, Sweden	NOR	60°05'N	17°28'E	103	CO_2, CH_4
Ochsenkopf, Germany	OXK	50°03'N	11°49'E	163	CO_2, CH_4, N_2O, SF_6, O_2/N_2, ^{222}Rn
Orléans, France	ORL	47°58'N	02°06'E	180	CO_2, CH_4, CO, N_2O, SF_6, ^{222}Rn

5.6.2 Calibration and intercomparison methodology

Table 2 shows the precision and accuracy goals we have set ourselves in the *CHIOTTO* project. These goals are based on a consideration of requirements for the data to be scientifically useful, as well as what is considered realistically achievable from an analytical and sampling standpoint. In the case of CO_2 accuracy, this value is the same as the previously established WMO goal for CO_2 accuracy (for northern hemisphere sites). In this table we consider the word "precision" to mean the precision obtained by an individual analyser at an individual tower for the time intervals on which sample data are reported. By "accuracy" we mean the accuracy of intercomparisons between different towers, as well as the intercomparability to accepted, WMO-defined, international calibration scales. Our calibration and intercomparison methodology is thus a vital component towards achieving these ambitious goals.

Table 2: Precision and accuracy goals established for CHIOTTO.

Gas species	**Precision**(1)	**Accuracy**(2)
CO_2	±0.05 ppm	±0.10 ppm
O_2/N_2	±5 per meg	±10 per meg
CH_4	±2.0 ppb	±3.0 ppb
CO	±1.0 ppb	±3.0 ppb
N_2O	±0.1 ppb	±0.2 ppb
SF_6	±0.1 ppt	±0.2 ppt
Rn(3)	0.2 Bq m^{-3} or 10%	10%

(1) *Precision of the continuous analysers at each tower.*
(2) *Accuracy of intercomparisons between different towers.*
(3) *For Radon, these values are detection limit goals.*

The first step towards achieving good intercomparison results was to standardise the equipment and gas handling procedures as much as possible at all towers. The details of these standardisation efforts will not be discussed in this paper. Suffice to say that through frequent communication and establishment of equipment and gas handling procedure guidelines, we were moderately successful in these efforts, within the various and different constraints the different institutes in the consortium were under.

In considering an ideal calibration and intercomparison methodology I realised that the original plan of intercomparisons via flask samples collected at each tower and measured in two or three central laboratories was not the solution. For example, after several years of improvements, "sausage-flask" intercomparisons between several European laboratories are now approaching an intercomparability of about ±0.2 ppm in CO_2 concentration [*Levin et al.*, 2004]. These are from flasks filled simultaneously in a controlled laboratory environment, and yet they are still not able to meet the *CHIOTTO* accuracy requirement of ±0.10 ppm. Flasks are also known to exhibit drifts in concentrations which are dependent on storage time and which contribute to further uncertainty. Finally, the air collected in a flask sample can never be considered as exactly the same air as measured by a continuous analyser at a tower. The size of the air sample is different and typically there may be different sampling pumps, different air drying procedures, and different air intakes.

Thus, in *CHIOTTO,* we will calibrate and intercompare primarily through the use of high pressure gas cylinders containing air of known concentrations. We will also use flask samples as an additional, but secondary level of intercomparison, as defined further below. Each tower will have on-site four Working Secondary Standards (WSSes) and three Long-term Secondary Standards (LSSes), with each standard contained in a Luxfer 50 L aluminium cylinder, initially filled to about 140 bar. All seven cylinders, before being sent to each tower, will have concentration values assigned by Max Planck Institute for Biogeochemistry (MPI-BGC) for each of the gas species that will be measured at that tower.

The WSSes are used for daily calibrations of each analyser at each tower. This means that the same cylinders will be used to calibrate, for example, a LiCor CO_2 analyser as well as to calibrate a GC for other gases such as CH_4, CO, N_2O, and SF_6. Despite such heavy usage, all

WSS cylinders are estimated to last for 18-30 months before being depleted and needing replacement. The four WSSes will span a range in concentration in each gas species measured by the tower. These concentration ranges will depend on the expected conditions present at each tower, taking into account expected diurnal and seasonal variability in each gas measured. In this manner, each analyser will be calibrated daily for the full range of concentration values reported from the tower, with no extrapolation of calibration curves necessary. In addition, by having four cylinders, we are able to account for non-linearities in analyser response functions. I also recommend not to run WSS calibrations on exact 24 hour cycles. This has the potential to introduce biases due to, for example, diurnal temperature fluctuations in the laboratory leading to biases in the analyser calibration. Calibration cycles with a different period, although not directly solving this problem, have at least the potential to identify if such problems exist or not.

The LSSes are analysed on each analyser at each tower on a frequency of once every two weeks. For some towers, where logistical demands preclude such a high frequency of LSS calibration, I have recommended a minimum frequency of once every two months. These LSSes provide a check on the integrity of the WSSes. In particular, they are able to show if one of the WSSes is “out of step” with respect to the others, and they are able to show if there are changes over time in WSS concentrations. For example, in many cases, drift observed in trace gas concentrations in a cylinder can be attributed to the slow decrease in pressure in the cylinder as air is removed from it. Thus, the LSSes, which will last about 20 years before being depleted, will be able to show up any such drift occurring in the WSSes, which are depleted at a rate more than ten times faster than the LSSes. Each time the LSSes are analysed, the WSS calibration scales will be reassessed, and potentially adjusted, if such adjustments are deemed necessary.

In the particular case of calibrating LiCor CO_2 analysers, an additional cylinder is needed, called the “Zero Tank”. A LiCor calibration curve is a quadratic relationship of mV output signal[1] versus CO_2 concentration, of the form:

$$CO_2 \text{ concentration (ppm)} = a\text{mV}^2 + b\text{mV} + c.$$

Each time the four WSSes are analysed on the LiCor (once per day), new values are defined for the parameters *a, b,* and *c* based on a least squares regression fit. Because of the physical characteristics of the LiCor analyser, the *c* parameter in the above equation, the zero coefficient, is particularly susceptible to variability (due in large part to ambient temperature fluctuations). Therefore, each tower should have a Zero Tank, which is analysed on the LiCor at higher frequency than the WSS daily calibration, and which should be used to provide updated values to the *c* parameter in the above equation. The frequency with which this Zero Tank should be run depends on the individual tower setup of their LiCor. For those towers which have no active temperature control of their LiCor analysers, a frequency of at least once every two hours is highly recommended. For those towers which have active temperature control for their LiCor (of the order of ±0.2°C or better), it will probably be sufficient to run a Zero Tank calibration once every 12 hours. Note that “Zero Tank” does not mean that this cylinder should have zero CO_2 concentration, which is a common misperception. On the contrary, much improved precision will be achieved if this cylinder has CO_2 concentration close to ambient levels. Unlike the WSS and LSS cylinders, it is not necessary that the Zero Tank concentration be accurately known before installing on a tower system.

The WSS, LSS, and Zero Tank cylinders discussed thus far are all used to actively define or adjust the calibration scales used at each tower. The next step of the *CHIOTTO* calibration protocol is not concerned with defining the calibration scales, but rather is used as a warning system, to indicate if the analyser system is functioning according to the prescribed precision goals. This involves a cylinder called the “Target Tank”. The Target Tank, which should be used

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[1] *The newer LiCor 7000 does not provide a direct mV output, but rather an analogue “corrected” voltage signal derived from their digital ppm output. Thus, for this analyser, we use the LiCor ppm output signal, but we still apply our own non-linear (quadratic) calibration curve. Thus the concept presented here is still valid, only it is applied to the LiCor ppm output, rather than to mV output.*

with all analysers at the tower, should be analysed at a frequency similar to the frequency of analysis for the LiCor Zero Tank (in other words, this depends somewhat on the field laboratory conditions at each tower). As with the Zero Tank, the lowest frequency of analysis of the Target Tank should be every 12 hours. If the concentration calculated by the system for the Target Tank is outside prescribed limits for any gas species, then a warning flag should be raised indicating that all subsequent data are possibly suspect. As with the Zero Tank, the prescribed Target Tank concentrations need not be accurately known.

Establishing WSS, LSS, Zero Tank and Target Tank cylinders at each tower in the manner described above aims to achieve a very high level of internal consistency of the calibrations of each analyser at each tower. Thus it is directly concerned with achieving the precision goals for *CHIOTTO*, as shown in column two of Table 2 above. To achieve the *CHIOTTO* accuracy goals, shown in column three of Table 2, I have developed the following three-step process.

First, all WSSes and LSSes initially sent to each tower will be assigned concentration values by MPI-BGC. These assignations will be traceable to WMO standards (for the trace gas species where such standards exist). This traceability is achieved because MPI-BGC has a suite of six Primary Secondary Standards (PSSes) which were purchased directly from the WMO-certified standard laboratories (NOAA/CMDL, in the case of CO_2 and CH_4). In addition, Pieter Tans from NOAA/CMDL has given MPI-BGC permission to transfer these WMO scales from our PSSes to the WSSes and LSSes which we supply to each tower (at least for the duration of the *CHIOTTO* project). This is a very generous offer from Pieter for which we are very thankful. Thus, in the beginning of operation, each tower will have a strong link to the official WMO calibration scales. In addition, at the end of a WSS's lifetime, and before all air has been depleted from the cylinder, it will be returned to MPI-BGC and re-analysed against the PSS cylinders. In this manner, any drift in concentrations in the WSS cylinders can be quantified. But it is important to realise that this procedure only provides information about the average drift over the lifetime of a cylinder.

However, such a link to WMO scales via MPI-BGC is not an ideal situation, and therefore it is envisioned that if the *CHIOTTO* tall towers continue atmospheric monitoring beyond the end of the *CHIOTTO* project (November, 2005), then they each should phase in a protocol of obtaining NOAA/CMDL standards directly. As an example, each tower could replace the three LSS cylinders with three NOAA/CMDL cylinders.

The initial calibration of WSSes and LSSes against the NOAA/CMDL PSSes at MPI-BGC provides a link of each tower's calibration scales to the WMO scales at the time when the tower first receives their WSSes and LSSes. In addition to this, we require a methodology to assess possible drift in time of a tower's calibration scales, in particular, relative to the other towers. Another subtle point to realise, is that even though all towers are supplied with WSSes and LSSes from the same central laboratory, this is not sufficient to ensure that each tower is initially reporting concentration data on identical scales. There are analytical artefacts that could be present at a tower, biasing one or more of its calibration scales. Hence the second step towards achieving the required *CHIOTTO* accuracy makes use of an additional set of six cylinders called Travelling Secondary Standards (TSSes). These six cylinders will rotate in two sets of three between all towers and will thus provide a direct comparison of the calibration scales at all towers.

Each tower will only receive these TSS cylinders two times per year, thus it would be dangerous to make adjustments to a tower's calibration scales based on the TSS analyses, simply because these analyses are so infrequent. Instead, data derived from the TSS analyses will be used as diagnostic information about the relative performance of the tower, in comparison to all others. Whenever TSSes are analysed on a tower system, a full WSS/LSS calibration should also be done on the same day.

The third method to assess the *CHIOTTO* intra-tower accuracy addresses the two most serious deficiencies in using TSSes, that is, their relatively infrequent analysis at a given tower, and the fact that ambient air sampled at a tower is not treated in exactly the same way as air derived from a calibration gas cylinder. For example, drying methods may be different between air derived from the tower inlets versus cylinders, and typically, tower air is brought to the analysers via small diaphragm pumps, whereas high pressure cylinders deliver their air via cylinder regulators. Thus, we plan to collect periodic flask samples from as many towers as possible, analysing them in two or three central laboratories. One must keep in mind the caveats of interpreting data from flask analyses as mentioned above. Nevertheless, I hope that a methodology which combines both infrequent analyses of TSS cylinders and higher frequency collection of flask samples will allow us to achieve the *CHIOTTO* intra-tower accuracy goals as specified in Table 2.

5.6.3 Summary

CHIOTTO is an ambitious project aimed at providing data which will aid in quantifying the European terrestrial carbon sources and sinks on a regional to continental scale. We hope to fill a measurement and information gap on geographic and spatial scales by measuring multiple species continuously from platforms on eight tall towers in Europe. One strength of our project is the potential to calibrate and intercompare our field analysers, because we are a single operating consortium. This paper has outlined the calibration and intercomparison methodology we plan to adopt at each tower, and the precision and accuracy goals which we have set for ourselves.

Each tower will have four Working Secondary Standards (WSSes) with which all analysers at the tower will be calibrated at approximately daily frequency. Three Long-term Secondary Standards (LSSes) will be used as cross-checks for drift in the preliminary WSS calibration scales, and will be analysed against the WSSes at a frequency of approximately once every two weeks. In the case of the LiCor CO_2 analyser, an additional Zero Tank cylinder will be used to calibrate the LiCor zero coefficient, which is particularly susceptible to short term drift. Finally, a Target Tank cylinder, measured by all analysers at greater than daily frequency, will be used to check the internal calibrations, and will provide a warning flag if anything is going wrong.

The steps above should result in a high degree of internal consistency of the calibration scales at a given tower. Equally important is the accuracy of the calibration scales, in particular the accuracy of one tower when compared to another. To achieve the stated *CHIOTTO* accuracy goals, we will, at the beginning of operations, link each tower's calibration scales to the official WMO calibration scales by calibrating all WSS and LSS cylinders against a set of Primary Secondary Standards (PSSes) obtained directly from NOAA/CMDL. To assess potential drifts in WSS/LSS calibration scales over time at a tower, we will have six Travelling Secondary Standards (TSSes) which will rotate between all towers in two sets of three. These TSSes will also serve a vital role in comparing the calibration scales between all towers. Finally, because of the relatively infrequent analyses of TSSes at a tower (approximately twice a year), we hope to collect flask samples from the towers which will be analysed in two or three central laboratories.

5.6.4 Acknowledgements

Discussions with the following people greatly assisted me in formulating the calibration and intercomparison scheme presented here: Ingeborg Levin, Ralph Keeling, Armin Jordan, Doug Worthy, Manuel Gloor, and Pieter Tans. I also acknowledge the European Union which is providing financial support for the *CHIOTTO* project under their Fifth Framework Programme, contract number EVK2-CT-2002-00163.

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5.7 Usefulness of Air CO_2 Measurements at a Continental Site: Carbon Cycle Information at the Landscape Level Near Fraserdale, Ontario

Jing M. Chen, Baozhang Chen, Kaz Higuchi, Douglas Chan, Lin Huang, Doug Worthy and Alex Shashkov

Abstract

An 11-year long (1990-1996, 1999-2002), hourly air CO_2 concentration record measured on a 40-m tower near Fraserdale, northern Ontario, is analyzed for the purpose of retrieving carbon cycle information for the underlying surface. As the tower concentration measurements integrated the effects of the surface up to 10^2~10^4 km in distance, the information retrieved allows for the evaluation of the collective response of boreal ecosystems to climate change at the landscape level consisting of forests of different ages, species and densities as well as non-forest cover types. Using the Boreal Ecosystem Productivity Simulator (BEPS) and the Vertical Diffusion Scheme (VDS, 1-dimensional, Chen et al., 2004), the hourly CO_2 concentration is simulated (r^2=0.62, $n = 91558$ for hourly values and r^2=0.76, n=9155 for10-day averaged hourly values when compared with observations). A novel method is developed to separate the effects of ecosystem metabolism and atmospheric diffusion on the measured air CO_2 concentration. After the separation, the daily gross primary productivity (GPP) is estimated entirely from the CO_2 diurnal variation pattern and meteorology affecting the vertical diffusion, rather than from model simulations. In the 11-year period, the mean air temperature in the growing season (mid-April to end of October) varied from 9.1 to 12.9 ºC. The annual total GPP derived from the concentration varied from 915 to 1168 gC m^{-2}, and in the mean time the modelled ecosystem respiration (R_e) varied from 842 to 1036 gC m^{-2}. The results suggest that the boreal ecosystems near the Fraserdale were a carbon sink. The 11-year record is not yet long enough to have high confidence in this suggestion but as the record gets longer, the confidence will greatly increase.

5.7.1 Introduction

Air CO_2 measurements at continental sites may serve for at least two purposes: (1) to be used together with global baseline CO_2 network measurements for global and regional atmospheric inversion; and (2) to retrieve the carbon cycle information for the local areas upwind of the sites. Since the footprint area of tower concentration measurements is of the order of 10^2-10^4 km^2 (Gloor et al.,1999; Lin et al., 2003; Chan et al., 2004), this information is critically useful for scaling from flux towers (having a footprint area of about 1 km^2) to large regions. However, retrieving quantitative surface information from atmospheric measurements, i.e., estimating fluxes from concentration, is methodologically challenging. In this report, we outline the methods that we developed for this purpose and some preliminary results.

5.7.2 Data Used

An 11-year (1990-1996, 1999-2002), hourly averaged air CO_2 concentration record measured on a 40-m tower at Fraserdale, northern Ontario, Canada ($49^0$52'29.9''N, $81^0$34'12.3''W) is used in this investigation. The measurements were made according to the WMO (World Atmospheric Watch) guidelines, with an accuracy of 0.1 ppm (Higuchi et al., 2003).). Meteorological variables, such as wind speed, air temperature, and relative humidity were measured at 20 m and 40 m on the tower. According to a Landsat TM image (1994) at a 30 m resolution, the landscape (3600 km^2 around the tower) consists of 66% of black spruce (*Picea mariana*) and Jack pine (*Pinus banksiana*), 20% open land after forest fires and logging, 11% aspen (*Populus tremuloides*) and paper birch (*Betula papyrifera*), and 3% open water.

5.7.3 Methodology

5.7.3.1. Forward modelling using a coupled ecosystem and boundary layer model

To estimate the surface information inversely from the atmospheric measurements, we first need a modelling system that allows for forward modelling of atmosphere constituents as affected by the surface fluxes. For this purpose, an ecosystem model named Boreal Ecosystem Productivity Simulator (BEPS, Chen et al., 1999, Liu et al., 2002) is coupled with a Vertical Diffusion Scheme (VDS, Chen et al., 2004) to simulate the CO_2 concentration at various heights within the planetary boundary layer (PBL) at both daytime and night time. BEPS simulates CO_2 and energy fluxes to and from the surface, and VDS simulates the mixed layer (ML) dynamics and the vertical heat, moisture and mass fluxes. Both are one-dimensional models assuming horizontal homogeneity. The mean leaf area index within 60 km of the tower was 3.1 (with a seasonal variation ranging from 2.8 to 3.5) obtained from remote sensing (derived from Landsat TM and AVHRR images).

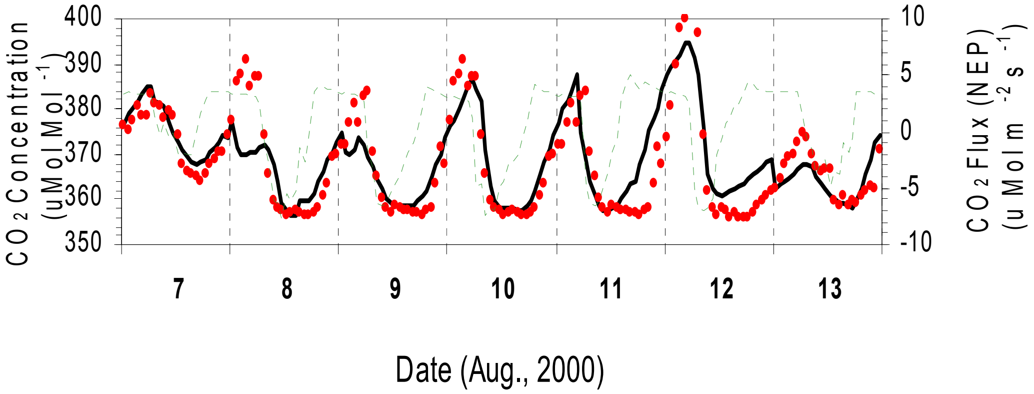

Figure 1: Modelled hourly CO_2 concentration at 40 m (solid black line) compared with measured values at the same height (dots) on 7-13 August 2000, shown as examples. Modelled ecosystem carbon flux (NEP) is also shown (dashed line).

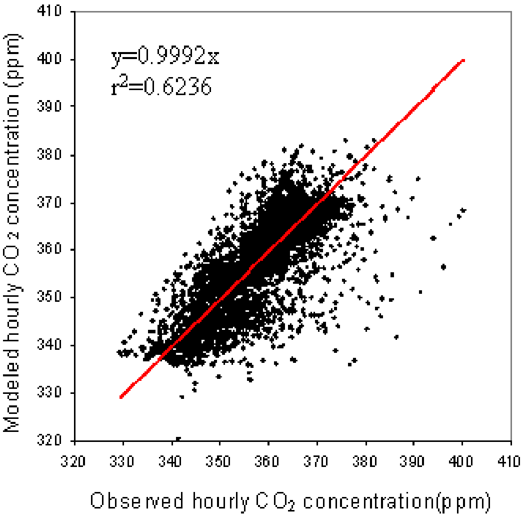

Figure 2: Comparison between modelled and measured hourly CO_2 concentrations at 40 m height for the whole year of 1992 near Fraserdale, Ontario, Canada.

Examples of BEPS-VDS performance in terms of capturing the hour-to-hour variations in CO_2 measured at 40 m height are shown in Figure 1. The modelled value follows closely the measured values in most cases as a combined result of the surface carbon flux simulated by BEPS and the vertical diffusion simulated by VDS. Over the course of the year, the model performs with a similar accuracy, and the results are summarized in Figure 2, where modelled and measured hourly values are compared for an entire year (r^2=0.62). There are a number of hourly values that are considerably underestimated by the model, showing as large departures from the 1:1 line. These large departures are mostly on days with strong vertical convection associated with frontal passages. This condition cannot be well represented by the 1-dimensional model. However, after we performed 10-day averaging for hourly values (i.e., producing 24 hourly averages for a 10-day period), the one-to-one comparison is much improved (r^2=0.76), suggesting that this 1-d model would at least be adequate for estimating 10-day averaged surface and atmospheric processes. Figure 3 shows modelled and measured 10-day averages of CO_2 concentration for the entire measurement periods (1990-1996, 1998-2002), illustrating the ability of the model to track atmospheric CO_2 seasonal variation patterns. In this modelling, the marine boundary layer CO_2 measurements at Cold Bay are used as the top boundary condition in the free troposphere above the local PBL.

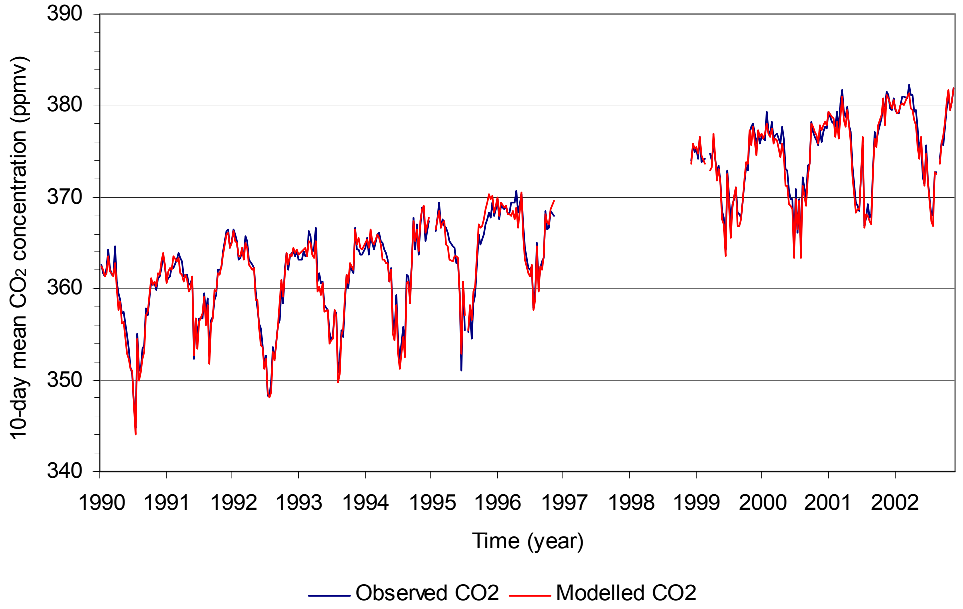

Figure 3: Comparison of modelled and measured 10-day averages of CO_2 concentrations at 40 m for the whole periods (1990-96, 1998-2002) near Fraserdale, Ontario, Canada.

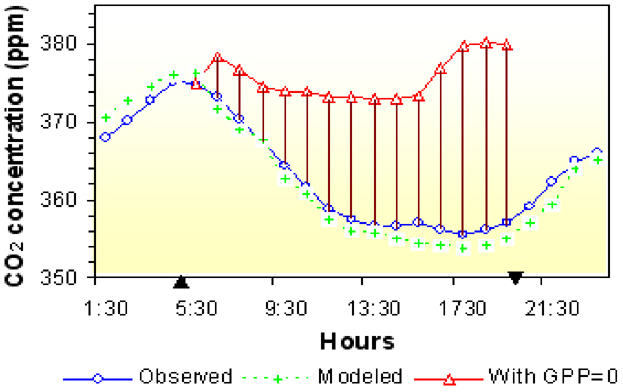

Figure 4: An example of modelled and measured hourly values of atmospheric CO_2 on 11 July 1996 at 40 m at Fraserdale. The agreement indicates that both ecosystem metabolism (photosynthesis and respiration) and atmospheric diffusion are well modelled. A new series is obtained from sunrise to sunset (indicated by triangles) after turning off the gross primary productivity (GPP) in the model. In the absence of GPP, the concentration remained higher than the corresponding measured values. The vertical line is the difference between measured and simulated (with GPP=0) CO_2, i.e., ΔC_i used for estimating the cumulative difference resulting from GPP since sunrise.

5.7.3.2 Inverse GPP estimation based on the diurnal CO_2 variation pattern

The diurnal variation in CO_2 concentration above vegetation canopy depends on the magnitudes of night time ecosystem respiration and daytime photosynthesis. Atmospheric diffusion also contributes to the diurnal variation because the strength of vertical mixing varies greatly from night time to daytime. In order to gain information on ecosystem behaviour, we separated the effects of atmospheric diffusion and ecosystem metabolism on the CO_2 concentration measurements. Figure 4 shows an example of measured and simulated hourly CO_2 concentrations on 11 July 1996. The simulated values generally follow closely the measured values in the diurnal cycle, suggesting that ecosystem respiration and photosynthesis as well as atmospheric diffusion are well simulated. To investigate the effect of daytime photosynthesis on the measured CO_2, we turned off photosynthesis (GPP) in BEPS from sunrise to sunset. As shown in Figure 4, the simulated CO_2 with GPP=0 increases considerably from the measured CO_2. The increase is expected as the carbon uptake by photosynthesis is artificially terminated while the total ecosystem respiration (both heterotrophic and autotrophic) remains unchanged. As atmospheric diffusion is unchanged in both simulations and has the same effect on the measured and modelled CO_2, the difference between the simulated and measured values is therefore solely due to photosynthesis. In this way, the signal of photosynthesis is extracted from the CO_2 time series.

Physically, the hourly difference in CO_2 (ΔC_i, in ppm h^{-1}or 0.0224×10^{-6} mol m^{-3} h^{-1}) between the measured and simulated (with GPP=0) cases is the reduction of CO_2 by GPP per unit air volume in the ML. Assuming that this reduction is uniform in the ML, the simulated ML height z_i can then be used to estimate the GPP per unit surface area as $\Delta C_i\ z_i$ (mol m^{-2} h^{-1}). As the air moves across the landscape, this effect of GPP on air CO_2 gradually accumulates. For hour *i* after sunrise, the total accumulated effect is $\Delta C_i\ z_i$, and GPP in this hour is ($\Delta C_i\ z_i - \Delta C_{i-1}\ z_{i-1}$). The daily total GPP then equals $\sum_{i=SR+1}^{SS}(\Delta C_i z_i - \Delta C_{i-1} z_{i-1})$, where SR is the hour of sunrise and SS is that of sunset. The accumulation of this photosynthesis effect starts at sunrise and moves with the air from sunrise to sunset, and the tower CO_2 measurements therefore integrate the influence of the land surface of daily air travel length upwind of the tower. The methodology has been validated at the BOREAS SSA-Old Black Spruce site (r^2=0.82 and 0.95 for daily and 10-day fluxes, respectively) and the Wisconsin Tall tower site (r^2=0.61 and 0.92 for daily and 10-day fluxes, respectively) where simultaneous concentration and eddy-covariance flux measurements are available.

5.7.4 Results

Using the methodology shown above, daily GPP values were derived for the entire periods (1990-1996, 1998-2002). The daily total ecosystem respiration (ER), the sum of autotrophic respiration and heterotrophic respiration, was also modelled at hourly time steps, as functions of total biomass, soil carbon, temperature, and soil moisture. The accuracy of the daily GPP values derived from the diurnal variation in air CO_2 concentration depends mostly on the vertical diffusion efficiency and does not involve ecosystem modelling (so it is free from conventional GPP modelling errors due to stomatal and leaf biochemistry parameterizations), although the accuracy in ER modelling still has an effect on the daytime GPP derivation. The accuracy in ER modelling is well constrained by the CO_2 concentration data at night time (Figures 1 and 2). Key to these parameter retrievals is the accuracy in the vertical diffusion coefficients at both night time and daytime. As the actual temperature and wind speed gradients measured at 20 m and 40 m heights are used in the diffusion calculation, and the modelling of the maximum daily ML height is constrained using available climatological monthly mean values (Chen et al., 2004), the errors in ER and GPP calculations due to diffusion estimation are minimized. The daily net ecosystem productivity (NEP) is calculated as the difference between GPP and ER. NEP>0 indicates a sink, meaning the surface absorbs carbon from the atmosphere, and vice versa. These daily values are averaged to 10-day values and are shown in Figure 5. The concentration-derived GPP exhibits large seasonal and inter-annual variation patterns (Figure 5a). The values in the winter are missing because the methodology is unreliable in winter when GPP is close to zero. These missing values (mostly zero) are filled from ecosystem modelling results for NEP calculation. The seasonal amplitude in ER is considerably smaller than that of GPP, and the interannual variation is also smaller (Figure 5b). From GPP and ER, NEP for these periods is obtained. It is generally positive (sink) in the growing season and negative (source) in the dormant period. The annual means are close to zero when shown at the same scale as GPP, but are significantly larger than zero in many years, suggesting that the area near Fraserdale was a carbon sink on average. However, the error in NEP estimation at the landscape scale on the basis of air CO_2 concentration measurements has about the same order of magnitude as the averaged carbon sink size (30 g C m^{-2} y^{-1}). As the time series gets longer, the ER simulation can be better constrained, and a greater confidence can be gained in determining the carbon balance.

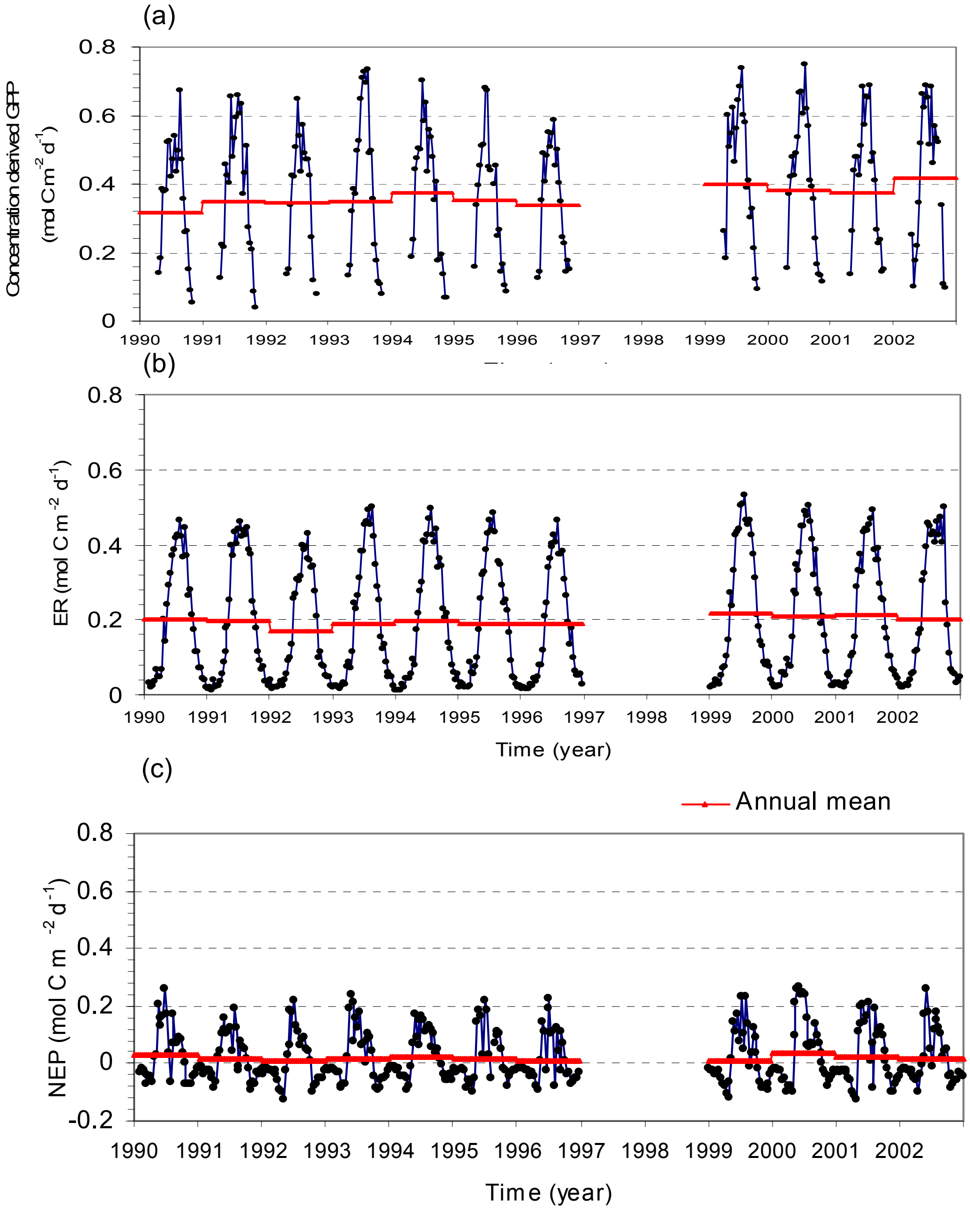

Figure 5: 10-day averaged GPP, ER, and NEP on panels (a), (b), and (c), respectively, retrieved from the CO_2 concentration measurements over the 11 year period (1990-1996, 1998-2002).

5.7.5 Conclusions

Our research suggests that it is possible to retrieve carbon cycle information at landscape scale from tower CO_2 concentration measurements. The information derived from an 11-year CO_2 record shows reliable seasonal and inter-annual variation patterns of photosynthetic and respiratory fluxes. The results suggest that boreal ecosystems near the Fraserdale tower were a carbon sink during the study periods (1990-1996, 1998-2002). Information derived in this way represents a large upwind area up to 10^4 km^2 at the landscape level and is powerful for upscaling from forest stands to regions. Based on our modelling experience, we suggest the following measurement strategies at continental sites:

- High-frequency (hourly) CO_2 measurements are essential for separating photosynthetic and respiratory fluxes and for retrieving reliable daily carbon balance information.
- The accuracy in vertical diffusion modelling is most important for deriving fluxes from concentration. Temperature and wind speed gradients are, therefore, critical and should be measured simultaneously with CO_2 and well calibrated regularly.
- The accuracy for determining the local carbon balance using air CO_2 measurements depends greatly on the record length. Continuous measurements over a decade and longer can be used alone to determine the local carbon balance information.

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5.8 Aircraft Vertical Profiling for the Study of the Synoptic CO_2 Variability in the Atmospheric Boundary Layer.

A.Shashkov, D. Chan and K. Higuchi

Abstract

Atmospheric CO_2 concentration at a boreal forest site in Canada (BERMS, Prince Albert National Park, Saskatchewan) was measured continuously at the surface above the canopy and by aircraft campaign measurements from ~150 m above surface to about 3km height. The data from the July 2002 aircraft campaign was analyzed. The data showed the typical diurnal variation of about 20ppm; which is confined to the surface layer of the planetary boundary layer. However, the data also revealed the complex and variable nature of the CO_2 concentration in the spatial and temporal domains. On the mesoscale and synoptic scale, the variations were typically 5-10ppm, occurring sometimes in the whole planetary boundary layer and above. The change of the columnar CO_2 in the planetary boundary layer was estimated from the profile measurements. The results showed comparable contributions to the CO_2 columnar budget from local surface fluxes and CO_2 transport, with CO_2 transport becoming dominant during a frontal event. The interactions between the biosphere and the atmosphere were examined with a coupled biosphere-atmosphere regional model. The mesoscale and synoptic scale interactions and atmospheric transport produced CO_2 variations comparable to the observations. Since these mesoscale and synoptic scale CO_2 variations were significant and apparently common, a better understanding and quantification of these processes should lead to reduced uncertainties in the relationship of atmospheric CO_2 concentrations to fluxes at the regional scale.

5.8.1 Introduction

Better characterization of the terrestrial sources and sinks of CO_2 is necessary to balance the global carbon cycle (IPCC, 2001). Approaches used to generate estimates of the terrestrial sources and sinks of CO_2 can be generally divided into two groups: (1) inversion of atmospheric CO_2 concentration, isotopic fraction and other measurements through the use of atmospheric transport models, (e.g. Gurney et al. 2002, Fan et al. 1998) and (2) ecosystem methods such as inventories, flux measurements and ecosystem models (e.g. Phillips et al. 1998, Running et al., 1999). These two approaches are often referred as “top-down” and “bottom-up” respectively.

There are large discrepancies in the source/sink estimates between the above two approaches (e.g. Pacala et al., 2001). The key problem behind this discrepancy is the difference in scales the data are representing in each of these approaches. Due to the scarcity of monitoring stations and the specific choice of station locations, the inversion of global CO_2 concentration is currently limited to low-resolution distribution of CO_2 sources/sinks (about 20 source/sink regions globally, Gurney et al. 2002). On the other hand, data obtained from such direct measurements as the CO_2 flux exchange are representative of quite local scale on the order of 1 km^2 (e.g. Baldocchi et al. 2000). In between these two scales, many important atmospheric processes take place, associated primarily with the dynamics in the planetary boundary layer (PBL) (Stull, 1993).

The PBL plays an important role in the global carbon cycle as it governs all exchanges of CO_2 between the land ecosystem and the free troposphere. Denning et al. (1995, 1996a and 1996b) have considered the role of the PBL on the diurnal and seasonal time scales. However, there has not been much research on the CO_2 exchange processes on the time scales between diurnal and seasonal, e.g. mesoscale (with time scale τ~1 day and length scale Lx~100km) and synoptic scale (with time scale τ~5 days and length scale Lx~1000km) processes. The mesoscale and synoptic scale processes are important on the global energy and hydrological cycles (Holton, 1992; Gill, 1982). The aim of this work is to study the role of the PBL mesoscale and synoptic scale processes in the exchange of CO_2 between the biosphere and the atmosphere.

In this report, we briefly describe the observations of CO_2 and meteorological parameters measured by an aircraft over a boreal forest site. Then we characterize and interpret the measurements with a coupled atmosphere-biosphere model. The temporal/spatial scales of our research focus on the atmospheric processes in the 1 to 5 days, 100 to 1000 km domains.

5.8.2 Data and Model

In 2002, to supplement the existing CO_2 flux measurement programme Boreal Ecosystem Research and Monitoring Sites (BERMS) in Prince Albert, Saskatchewan, Canada (54ºN, 105ºW), *in-situ* measurements of atmospheric CO_2 concentration on the eddy-covariance CO_2 flux tower at the old black spruce (OBS) site was initiated. An aircraft intensive campaign in July 2002 was performed over the BERMS site. One of the priority objectives for the intensive aircraft campaign was to collect data frequent enough to resolve mesoscale and synoptic scale variability in CO_2 exchange through the PBL. Weather permitting, the aircraft programme included daily morning and afternoon measurements of vertical profiles, up to ~3 km, of CO_2 concentration and meteorological parameters.

To interpret the measurements, we used a coupled atmosphere-biosphere model. The atmospheric model is the regional model Mesoscale Compressible Community (MC2) model (Benoit et al., 1997). MC2 is a full-elastic non-hydrostatic model and solves a full set of Euler equations on a limited area domain. Current domain covers North America. Horizontal resolution is 20km, and there are 25 vertical levels with 9 levels in the first kilometre above the surface at 15m, 60m, 130m, 215m, 320m, 440m, 585m, 755m and 965m. Time step is 6 minutes. Initial conditions and horizontal boundary conditions were supplied from the Canadian Meteorological Centre (CMC) analysis. The atmospheric model was initialized with uniform CO_2 concentration and the model horizontal boundaries were maintained at the same concentration. The simulation results of CO_2 concentration will be presented as deviations from the uniform value. The biospheric model is the Boreal Ecosystem Productivity Simulator (BEPS) model (Liu et al., 1997). BEPS is a process model driven by remote sensing data of leaf area index (LAI) and land cover type. Meteorological forcing came from MC2 model air temperature, incoming short-wave radiation, humidity and precipitation. BEPS domain is Canada. Time step is 1 hour and resolution is 1km.

The results of the measurements and model simulations for the July 2002 campaign clearly illustrate the potential of the short-term transport processes to contribute significantly to the CO_2 exchange between land surface and the global free troposphere.

5.8.3 Results and Discussion

5.8.3.1 Observations

The intensive campaign period in 2002 was from July 5 to July 15, including flights over the BERMS OBS site from July 8 to 11. The atmospheric conditions (surface pressure, humidity, air temperature, downward solar radiation, wind speed and direction) for this period at the BERMS OBS site are shown in Figure 1. Also shown in Figure 1 are the CO_2 concentration and CO_2 flux measured with eddy covariance (EC) technique at the top of the tower. One may note the simultaneous changes in the surface pressure, air humidity, wind direction that happened between July 9 and 10. These changes corresponded to a weak warm frontal passage and will be discussed later. Normally (e.g. July 8 and 10), a large buildup of CO_2 concentration (typically 20-40ppm) occurs overnight as a result of the formation of shallow stable nocturnal boundary layer and the steady flux of respired CO_2 from plants and soil. The buildup of CO_2 is terminated near sunrise by two factors: (1) destruction of the stable nighttime layer by daytime surface heating, and (2) the commencement of photosynthetic uptake. This results in a rapid collapse of the nighttime CO_2 peak. The daytime concentration changes slowly from one day to another (e.g. July 8 and 9). Such typical diurnal cycle of CO_2 concentration is easily understood in terms of the coupling of the CO_2 flux and the PBL dynamics. For the case under consideration, there is good correspondence between the time period of photosynthesis and the period of the quasi-constant daytime CO_2 minimum concentration (e.g. July 9).

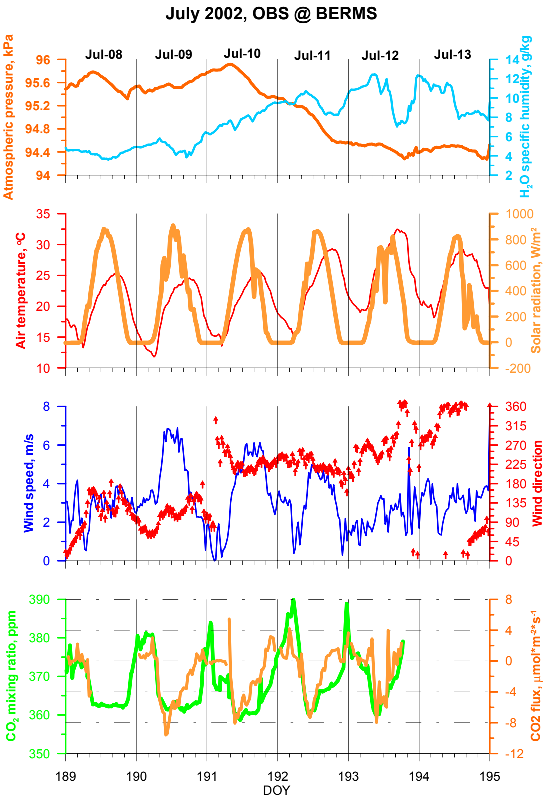

Figure 1: Meteorology and CO_2 at the BERMS Old Black Spruce tower during the July 2002 aircraft campaign. The plots are colour-coordinated with the corresponding Y-axes.

During the intensive campaign over BERMS, however, there were some deviations from this typical picture. During the night of July 9-10, the typical CO_2 buildup was disturbed by the passage of a weak warm front. This is evident in the decreasing pressure and wind direction shift from east to south-west (Figure 1). Furthermore, in the following morning (July 10) the CO_2 concentration was about 5 ppm lower than in the previous afternoon, a significant decrease brought about by a change in the air mass. This is an indication of the effects of the transport associated with synoptic scale forcing (the warm front).

Besides the synoptic scale transport processes, there are indications of other transport processes. In the afternoons of July 10 to July 12, the CO_2 concentration growth started earlier than the timing of sign change in measured flux from sink to source. This is indicative of significant mesoscale transport processes active at these times. These transport processes were not confined to the surface layer from where the tower measurements were obtained. The vertical structures of these transport events are shown in the vertical aircraft profiles of CO_2 evolution shown in Figure 2.

Although the large number of profiles makes the diagram complicated, it clearly presents the overall variability during this 4-day period. Note the variation of ~6ppm over this period at the 700mb level is approximately 40% of the marine boundary layer seasonal cycle at this latitude (GLOBALVIEW-CO_2, 2004). Thus there are large synoptic scale variations in CO_2 in the free troposphere at a continental site.

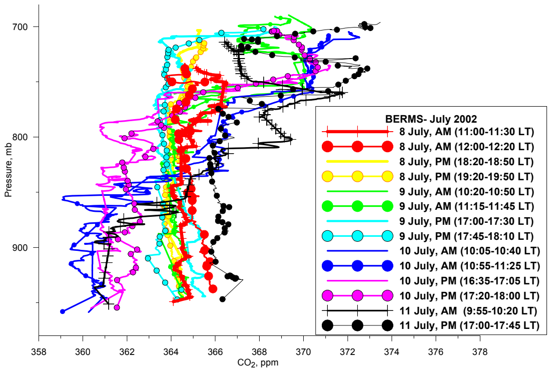

Figure 2: CO_2 vertical profiles, measured over BERMS Old Black Spruce site in July 2002.

The morning CO_2 profiles were more vertically well-mixed before the frontal passage (July 8 and 9) than after. After the frontal passage (July 10 and 11), the morning vertical profiles exhibited layered structures with significant gradients between layers. Also a notable decrease in the CO_2 concentration through night time was observed between July 9 and 10, and between afternoon of July 10 and morning of July 11 followed by a concentration increase in the lower PBL through the daytime of July 11.

During the same time period, the EC measurements above the canopy showed the same typical pattern of CO_2 flux, with net flux to biosphere in the daytime and vice versa at night (see lower panel of Figure 1). Thus, the observed variations in the CO_2 concentration which do not correlate with those of the surface flux are most likely due to horizontal transport in the PBL. The first decrease (July 9 and 10) in the CO_2 concentration through night time was probably associated with the frontal passage, as noted above. However, the change during the night between July 10 and 11 shows that smaller scale processes (mesoscale) can cause a similar change in the CO_2 concentration. These features show that the mesoscale transport processes can extend beyond the surface layer. In this sequence of vertical profiles, the mesoscale features exhibited very complex vertical structures.

The measured vertical profiles of CO_2 concentration provide an opportunity to evaluate carbon dioxide amount in a “pre-selected” column of lower troposphere (including PBL) through the integration of the profiles over height, enabling estimates of the relative contributions of the local CO_2 fluxes and CO_2 transport. By integrating the area between the morning and afternoon CO_2 profiles, we can get an estimate of the daytime total flux into selected column of air, including contributions from surface flux and horizontal transport. Calculation of the difference between integrated afternoon profiles for two sequential days yields an estimate for average 24 hour flux into the air column.

The upper boundary of selected atmospheric column was always chosen at the same isobaric surface in the free troposphere above the PBL. Accepting hydrostatic approximation for the free troposphere we assumed that vertical transport through the top of the selected column is small in comparison with other flux components and could be neglected in our preliminary estimates.

Figure 3 provides a comparison of the PBL flux estimates from the aircraft profiles with EC and BEPS flux estimates averaged over the same corresponding time period. The difference between the integrated PBL CO_2 budget and the surface fluxes (from EC or BEPS) is an estimate of the CO_2 transport. For the daytime flux (Figure 3a) a reasonable agreement is observed for all three different types of estimate with the exception of day 192 (July 11), when the integrated flux estimate show much larger value and the opposite flux sign than the EC and BEPS fluxes.

Similar pattern is observed on Figure 3b, where 24-hour average flux values are plotted. These results indicate a large contribution of synoptic and mesoscale CO_2 transport to the columnar CO_2 budget.

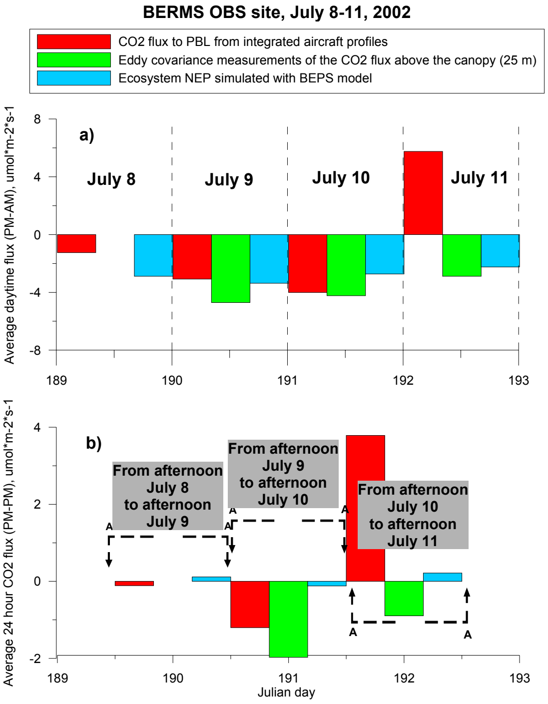

Figure 3: CO_2 flux estimates for BERMS July 2002 campaign, averaged over time between aircraft flights: (a) average daytime flux, (b) average 24-hour flux.

5.8.3.2 Model simulations

To get an insight into the transport processes, which distribute surface CO_2 source/sink signal through troposphere we performed model simulations of the intensive campaign period with the coupled MC2-BEPS model. Since the detailed results of this model study are presented in Chan et al., 2004, here we just briefly outline the modelling results for the weak warm front case (July 2002, BERMS).

Figure 4 shows the MC2 model domain and the 800 km line indicating the location of the model vertical cross-section to be discussed here. The evolution of the frontal passage and its effects on the CO_2 field can be seen in the time evolution of the model output. We will show the evolution of the interaction and transport by presenting the model results for before and after the frontal passage over the BERMS site (Figure 5). The BERMS OBS site is located at the 540 km point, marked with an arrow in each of the panels in Figure 5. The passage of the weak warm front was observed during July 2002 aircraft campaign in the early morning (local time) of July 10 (Julian day 191).

Figure 4: MC2 tranport model domain. Domain of BEPS is Canada. Arrow denotes the location of the vertical cross-section in Figure 5.

The upper panel of Figure 5 shows that, at the 150 km point a band of air with a higher CO_2 concentration associated with the warm front reached 500mb level. The band structure shows sloping transport by frontal lifting from the surface and nearly vertical transport by an enhanced diabatic circulation induced by the frontal cloud band (heating from condensation enhances the upward flow of CO_2). Also clouds associated with the diabatic heating reduced solar radiation at the surface and consequently reduced photosynthesis. This led to higher concentration of CO_2 under the frontal cloud band. This is an example of the interaction of biosphere with frontal cloud bands. In the warm sector slightly behind the frontal band, the CO_2 field shows features of mesoscale vertical transport. The CO_2 was mixed to about 650mb level. While in the cold sector, the PBL at BERMS reached about 750mb. The PBL height in the cold sector was almost uniform, indicating the weakness of the mesoscale vertical motion between the PBL and the free troposphere.

The lower panel of Figure 5 shows the CO_2 concentration in the warm sector after the passage of the weak warm front. In contrast to the cold sector, the CO_2 from the PBL is clearly mixing slantwise into the free troposphere up to about 600 mb level. The strongly sloped transport, coupled with the mesoscale variations in CO_2 concentration, results in a complex layered structure in the free troposphere. Also there are significant horizontal variations in the CO_2 concentration on the order of 5-10 ppm over a distance of about 100 km.

The model results can be compared qualitatively with the aircraft vertical profiles of CO_2 concentration at BERMS shown in Figure 2. Although the sequence of measured vertical profiles contains a great deal of details, it is possible to delineate certain prominent features. A comparison of the afternoon profiles on 9 July (day 190, before the frontal passage) to the morning profiles on 10 July (day 191, after the frontal passage) shows that the front transported air with a lower CO_2 concentration below 850 mb and air with a higher CO_2 concentration above 800 mb to BERMS. These changes in the CO_2concentration of about 5 ppm are comparable to the modelled CO_2 variations near the front. Away from the warm front, the July 10 (day 191) afternoon aircraft profiles show the CO_2 concentration in the whole PBL to be increasing with time. This was the result of an advection of air in the warm sector with a horizontal CO_2 gradient of about 4 ppm over a distance of about 100 km (for a typical wind speed of 10 m s^{-1}). Another example of advection in the warm sector is the difference in the vertical profiles between the afternoon of 10 July (day 191) and the morning of 11 July (day 192). The morning profiles indicate air with a lower CO_2 concentration below 850mb as well as above 750mb, compared with the previous afternoon profiles. These results are consistent with the modelled CO_2 field with horizontal mesoscale (~100 km) variations and vertically complex layered structures above the PBL. The layered structures are again evident in the afternoon profile on 11 July (day 192).

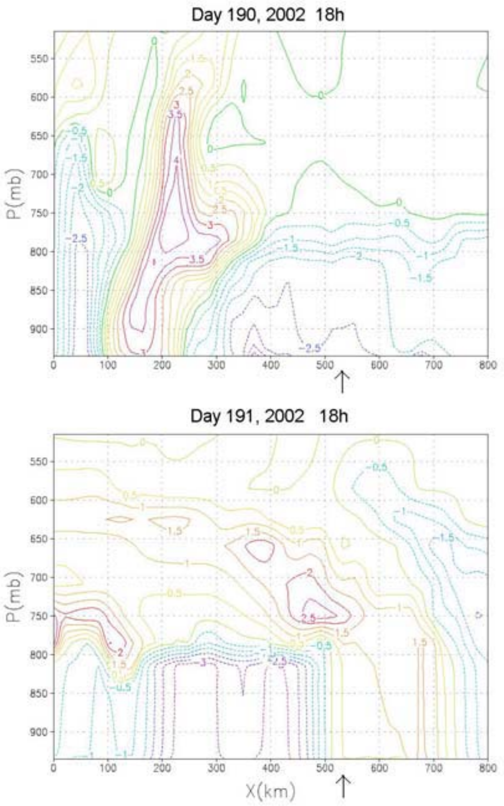

Figure 5: Vertical cross-sections of the modelled CO_2 field for before (upper panel) and after (lower panel) weak warm front passage over BERMS OBS site. The location of the site at 540 km point is denoted with arrows. CO_2 concentrations are given in ppm as deviation from initializing 0 ppm level.

5.8.4 Conclusions

Vertical CO_2 concentration profiles in a near-front zone have a complex structure, defined by synoptic and mesoscale atmosphere-biophere interaction and transport. Mesoscale and synoptic scale advections transport CO_2 from the PBL to the free troposphere.

Estimates from model and aircraft profiles show that in fair weather conditions, the local surface CO_2 flux may be in a reasonable agreement with the CO_2 concentration change in the PBL. But in a near-front zone, synoptic and mesoscale advection may dominate in building the PBL CO_2 budget, resulting in a difference of 100% or more, and even opposite in sign, between near-surface flux measurements and integrated flux into the PBL air column.

Significant irregularities in the vertical profiles were observed and simulated at elevated levels above 900mb and, therefore could not be monitored even using measurements at very tall towers. This illustrates the value of aircraft profile measurements in extending the tall tower measurements (and virtual tall tower estimates) for estimating changes in the PBL CO_2 budget.

The evidence presented in this paper of the complex structures in the meteorological and CO_2 fields brings into question some of the assumptions used in the 1-d virtual tall tower methodology.

5.8.5 Acknowledgements

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6. OTHER TRACERS (O_2/N_2, CO,CH_4 AND N_20) AND OTHER MEASUREMENT TECHNIQUES

6.1 On the long-term stability of O_2/N_2 reference gases

Ralph F. Keeling, Andrew C. Manning, Bill Paplawsky and Adam Cox

6.1.1 *Introduction*

The Atmospheric Oxygen Programme at the Scripps Institution of Oceanography and its predecessor at the National Centre for Atmospheric Research (Keeling and Shertz 1992) has produced records of changes in atmospheric O_2/N_2 ratios that are relevant for estimating sources and sinks of atmospheric carbon dioxide in relation to global change (Keeling et al. 1996; Stephens et al. 1998; Manning 2001). The principle records of this programme are time series for O_2/N_2 ratios analyzed in flasks collected at background air monitoring stations and analyzed at Scripps.

Our air samples are analyzed using an interferometric method that compares the O_2/N_2 ratios of samples with the O_2/N_2 ratio of reference gas delivered from high-pressure gas tanks. The integrity of our O_2/N_2 time series is as dependent on the stability of these reference gases as on any other aspect of the sampling or analysis. Keeling et al. (1998) discussed details of our methods and of the stability of the reference gases from the beginning of the programme in 1989 through 1996. Here we update that work by presenting results on reference gas stability until 2003 and by presenting a more exhaustive discussion of possible sources of instability.

6.1.2 *Methods*

Our calibration procedures can be conceptually divided into two steps, the first of which is designed to provide a stable reference for O_2/N_2 over time scales from days to months, and the second of which is designed to provide a stable reference from years to decades. In the first step, flasks are referenced to air delivered from a pair of high-pressure tanks, known as secondary reference gases or "secondaries". The secondaries are analyzed on each day that flasks are analyzed, and hence have a fairly short lifetime of ~2 years. The replacements are staggered so that only one of the two secondaries is replaced at any given point in time. A replacement is carried out only after exhaustively comparing the new tank against the existing secondaries to establish precisely the concentration of the new tank relative to the existing secondaries. The new tank is assigned a fixed concentration on the basis of these comparisons. The sequence of secondary gases forms the basis of a preliminary scale, known as the “S1” scale, that can be propagated forwards in time indefinitely.

We expect that the “zero” of the S1 scale may drift slowly in absolute terms due to drift in the secondary gases or because of random errors in the assigned concentrations. To eliminate this drift we apply a correction function of the form S2 = S1 + C(t), where S2 is the value on the corrected scale, and C(t) is a time varying additive offset. This same drift correction function is also applied to all of our flask analyses. The correction function C(t) is estimated based on several sources of information, the most important of which is comparisons with a suite of additional reference gases, known as primary reference gases, or "primaries". As new information becomes available, the drift correction function is subject to retrospective revision, with each revision yielding a slightly different version of the S2 scale.

Our primaries consist of twelve tanks prepared between 1986 and 1989, and an additional set of six prepared between 1993 and 1994. As summarized in Table 1, four of the original twelve are 265 standard cubic foot (SCF) aluminium tanks, two are 150 SCF aluminium tanks, and six are 265 SCF chrome-molybdenum steel tanks. The steel tanks have served as primary reference gases for our CO_2 measurements, and were obtained during a period in 1989 when 265 SCF aluminium tanks were unavailable from the manufacturer (Luxfer). The steel tanks were not discussed in Keeling et al. (1998) because it was assumed that they were ill-suited for storing O_2/N_2 reference gases over the long-term due to their potential for corrosion. Here we include them in our discussion because, in retrospect, they provide additional useful constraints.

All reference gases were prepared using the air pumping facility at Scripps, which uses a RIX Industries (Model 3K3B-17.5) water-cooled piston pump and uses molecular sieves for drying. At the time of filling, our primaries had water vapour contents between 0.7 to 2.2 µmole mol^{-1}, depending on the tank. The O_2/N_2 ratio of the air in these 18 tanks spans a range from −350 to +50 per meg on our S2 scale. Every three months, a subset of the primaries is analyzed against the secondaries, and these analyses are staggered such that every primary is analyzed at least every two years. The resulting S1 values of individual primary tanks have a precision of about ±3.0 per meg, based on the reproducibility from one analysis date to the next.

Early in the programme all reference tanks were stored upright in the laboratory during normal usage. By 1991 it had become evident, however, that the O_2/N_2 ratios delivered from tanks were sensitive to the tank's thermal environment. Over the course of the next year, tanks were therefore moved into a horizontal position within an insulated enclosure. For tanks in the enclosure, the gas regulators were separated from the tank with 1/16" O.D. nickel lines, which allowed the pressure gauges on the regulators to be read without opening the enclosure. The relocation of tanks to the enclosure was conducted in stages, to help quantify any shift associated with the move.

Our protocol for delivering references gases were described in (Keeling et al. 1998) and have not changed since that description. The protocol involves the following steps: (1) tanks are stored horizontally in the insulated enclosure for at least 10 hours, (2) the high-pressure lines are pressurized and vented at least 3 times before they are left open to the tank, (3) the high-pressure lines are left open to the tank for at least 2 hours, and (4) the high-pressure lines, still at tank pressure, are swept out at a flow of 5 STP cm^3 s^{-1} for ~20 minutes to minimize artifacts associated with conditioning the regulators and high-pressure lines connecting the tank and regulator. During analysis, we deliver gases at ~5 STP cm^3 s^{-1}, and when alternating between tanks during analysis, a flow 0.8 STP cm^3 s^{-1} is maintained from the "idle" tank, to reduce artifacts associated with preferential permeation of O_2 and CO_2 through O-rings in the regulators. We have exclusively used Model 14 regulators from Scott Specialty Gases (equivalent to Model 1002 from Air Liquide). With these measures we have reduced any systematic line and regulator effects to below 1 per meg (Keeling et al. 1998).

6.1.3 Results On Relative Stability

Figure 1 shows the time histories of the primaries on the S2 scale (2 June 2003 revision) as well as the drift correction function C(t) relating the S2 and S1 scales. To overlay the histories of different tanks, a time-invariant offset has been subtracted from each tank before plotting. In Figure 1, the tanks are divided into three cohorts based on material types (see Table 1).

The drift correction function was designed to eliminate drift in the S1 scale, which would manifest itself as simultaneous parallel drift in all the primaries. The drift correction function is based on a fit that minimizes long-term trends in the average concentration of the ensemble of primaries, although the function also takes account of a few exceptional situations, as discussed below.

In fact, the drift correction function is virtually flat after 1991 and never exceeds the bounds of +5 and +10 per meg over the full period. Although our procedures allow for a significant long-term drift in the S1 scale, the actual drift has been small. In 1992 the primaries all shift upwards on the S1 scale by an average of ~10 per meg. The drift correction function intentionally does not eliminate this shift because it is clear, based on several lines of evidence, that this shift resulted from changes in the air delivered from the primaries rather than from drift in the S1 scale. The shift coincides with the period when primary tanks were moved from an upright position in the laboratory to a horizontal position in the enclosure, which reduced the thermal and gravimetric fractionation associated with delivering air from the tanks. The secondaries were moved into the enclosure in 1991, before the primaries were moved, and the corresponding shift in the gas delivered from the secondaries is compensated by the 10 per meg jump in the drift correction function at that time. In this case, the correction function does serve to eliminate variations in the S1 values of the primaries, which is appropriate because it was the secondaries, not the primaries, that were perturbed. The period before 1992, when all these changes occurred, is discussed in more detail in Keeling et al. (1998), and we have not subsequently revised the drift correction function for this earlier period.

After 1992, nearly all of the primaries show a high level of stability (on either the S1 or S2 scale), to the level of ±5 per meg or better. There are a few exceptional tanks, however, that show slight upwards drift. This drift was sufficiently slow that it escaped our attention until recently. In searching for a cause of this drift, we inspected all our primary tanks and discovered that all of the drifting tanks were leaking through faulty seals at the burst disks on the head valves. We found no leaks on the other tanks. Based on the tank pressure histories we verified that the leakage has occurred steadily for years. Once we realized these tanks were faulty, we excluded them from the fitting procedure used to construct the drift correction function.

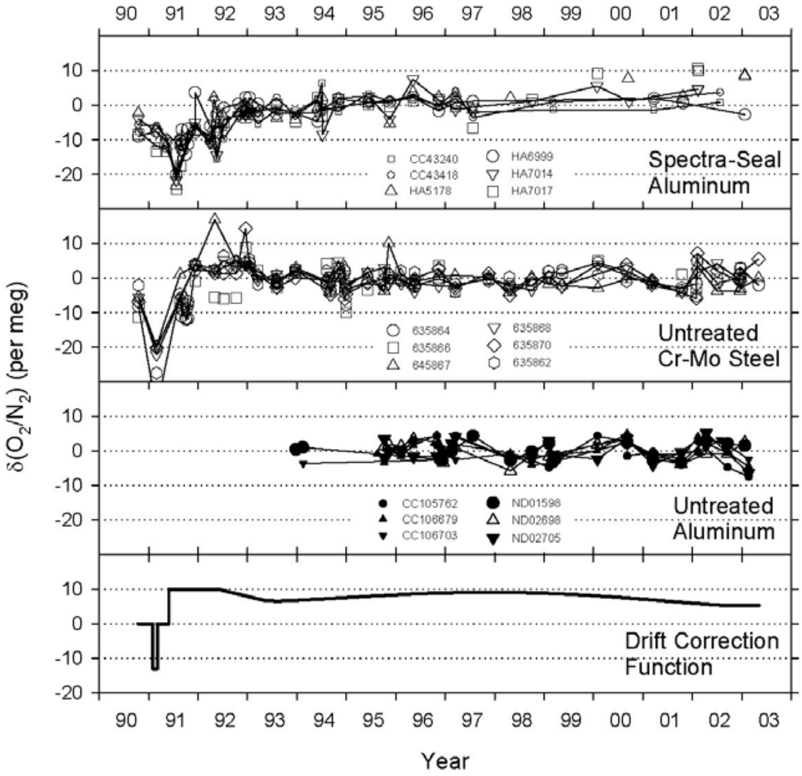

Figure 1: O_2/N_2 ratios of primary reference tanks on the adjusted S2 scale by tank material type (top three panels) and the drift correction function (bottom panel) which has been applied to all tanks (see text). For each tank the mean value since Oct 1992 has been subtracted, thus showing only the residuals from this mean. Small symbols: 150 SCF tanks; Large symbols: 265 SCF tanks. Solid symbols: tanks with dip tubes; hollow symbols: tanks without dip tubes. Lines connect points for an individual tank. Tanks that are known to have leaked are shown without connecting lines.

Table 1: Reference tank characteristics.

Tank ID #	Manufacturer[1]	Cyl. Mat.[2]	Dimensional internal Vol. (l)	Capacity (SCF)[3]	Surface[4]	Valve[5]	Valve connection	dip-tube	Fill date	leakage	Pressure (MPa)		
											Jan. 1990	Jan. 1996	Jan. 2002
CC43230	L	Al	29	150	SP	B	pipe	no	Dec 85	no	10.4	9.8	8.7
CC43418	L	Al	29	150	SP	B	pipe	no	Dec 85	no	9.8	9.1	7.8
HA5178	L	Al	47	265	SP	SS	pipe	no	Sep 86	yes	9.8	8.0	5.6
HA6999	L	Al	47	265	SP	SS	pipe	no	Sep 86	no	12.5	11.8	11.1
HA7014	L	Al	47	265	SP	SS	pipe	no	Sep 86	no	4.9	4.0	3.7
HA7017	L	Al	47	265	SP	SS	pipe	no	Sep 86	yes	8.4	5.3	4.2
635862	TW	S	49	300		SS	pipe	no	Jan 90	yes	16.0	14.6	13.2
635864	TW	S	49	300		SS	pipe	no	Jan 90	no	16.0	14.9	13.5
635866	TW	S	49	300		SS	pipe	no	Jan 90	yes	17.3	11.8	10.6
635867	TW	S	49	300		SS	pipe	no	Nov 89	no	16.0	13.9	12.5
635868	TW	S	49	300		SS	pipe	no	Jan 90	no	16.7	14.6	13.5
635870	TW	S	49	300		SS	pipe	no	Jan 90	no	16.7	15.3	12.9
CC105762	L	Al	29	150		B	flange	yes	Aug 94	no		11.8	10.9
CC106697	L	Al	29	150		B	pipe	yes	Aug 94	no		12.0	10.9
CC106703	L	Al	29	150		B	pipe	yes	Aug 94	no		13.2	11.8
ND01598	L	Al	46	265		B	flange	yes	Dec 93	no		11.3	10.3
ND02698	L	Al	46	265		B	pipe	no	Jan 95	no		14.2	13.2
ND02705	L	Al	46	265		B	pipe	yes	Jul 94	no		14.2	13.5

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[1] *Luxfur (L); Taylor-Wharton (TW)*

[2] *Aluminum (Al); chrome-molybdenum steel (S)*

[3] *Rated fill capacity in standard cubic feet (SCF). 1 SCF = 28.32 STP l.*

[4] *Spectra-seal (SP); a blank denotes no treatment other than standard cleaning. Spectra-seal is a proprietary treatment provided by Airco.*

[5] *Brass (B); Stainless-Steel (SS). All our cylinder valves have PCTFE seats. The valves were supplied either by Ceudeux (CC and ND series tanks) or by Superior Valve Company (all other tanks). Valves connected with pipe thread were sealed with standard Teflon tape. Valves connected with flanges were sealed with a spring-loaded, silver-coated, stainless-steel "C" ring, manufactured by Helicoflex.*

6.1.4 Constraints on Absolute Stability

The records show that our primary and secondary gases (excepting the tanks that leaked) have all maintained a high degree of stability relative to each other over the duration of our programme. High relative stability presumably places constraints on the absolute stability of the tanks, but how strong are these constraints? To answer this question, we consider a range of possible drift mechanism, and use experimental constraints to place bounds on their magnitude.

Tank Corrosion

One possible drift mechanism involves the loss of O_2 by slow oxidative corrosion of the inner walls of the tank. As summarized in Table 1, our primaries have one of three inner surface types: aluminium treated with proprietary treatment by Airco, untreated aluminium, and untreated chrome-molybdenum steel. To examine if surface type influences tank stability, as we would expect if corrosion were important, we have grouped the tank data (shown in Figure 1) by tank material type and we have fit linear trends (not shown in the Figure) through the grouped results to infer linear drift rates, as summarized in Table 2. Because several of the untreated aluminium tanks were not brought into use until 1995, we report rates over two periods: (1) from Aug., 1992 through Apr., 2003, allowing steel and treated aluminium tanks to be compared, and from (2) and Jan. 1995 through April 2003, allowing all three types to be compared.

Table 2: Summary of tank drift in per meg yr^{-1} (relative to S2 scale).

	Drift rate		
Tank type	**8/92-4/03**	**8/92-1/95**	**1/95-4/03**
By material			
Aluminium(Al), treated with spectra-seal (SP)	0.34±0.10	0.41±0.53	0.07±0.16
Steel (S)	-0.13±0.08	-1.89±0.48	0.08±0.11
Aluminium (Al), untreated			-0.09±0.11
By size			
150 SCF tanks	0.04±0.09	1.06±0.72	-0.12±0.12
all other tanks	-0.05±0.06	-1.56±0.46	0.00±0.09

Focusing on results from 1/95-4/03 period, we find no evidence of systematic drift in any tank type on the S2 scale, and the relative drift between tank types is also small: the relative drift between the treated aluminium and steel tanks is estimated at 0.01±0.19 per meg yr^{-1}, while that between untreated aluminium tanks and the steel tanks is -0.17 ± 0.16 per meg yr^{-1}.

To translate these constraints on relative drift into a constraint on absolute drift, we must make an assumption about the degree to which the absolute drift rates of the different tanks types might be matched with one another. For the sake of discussion, we assume that the absolute drift rates of the different tank types might be matched to, at best, a factor of 2. Scenarios can then be constructed that are consistent both with the bounds on relative drift from the fits as well as the matching constraint factor of two. By trial and error, we find a worst-case scenario in which the untreated aluminium tanks are drifting by -0.3 to -0.4 per meg yr^{-1} and remaining tanks are drifting at rates between -0.1 to -0.2 per meg yr^{-1}. This worst-case scenario has the S2 scale drifting (undetectably) at a rate of 0.1 to 0.3 per meg yr^{-1}. The constraints are also compatible, of course, with a best-case scenario in which the drift in the S2 scale is zero.

Scenarios that allow for greater drift in the S2 scale are possible if we assume the matching factor is not 2, but rather 1.5, etc. But there are clearly bounds on what is reasonable. For example, it would seem a remarkable coincidence if the corrosion rates of tanks with very different surfaces were matched to within 10% (matching factor = 1.1), but not remarkable if the corrosion rates of different tank types were matched to within a factor of 10. The factor of 2 is near the low end of the reasonable range, and thus defensible for our purposes. We thus conclude that the value of ~0.3 per meg yr^{-1} is reasonable bound for the drift rate in the S2 scale due to corrosion.

From 8/92 to 1/95, the steel tanks drifted downwards relative to the treated aluminium tanks by ~5 per meg, as can be seen visually in Figure 1 and as is reflected in the fitted trends in Table 2. If this 1992-1995 trend were a corrosion effect, we would expect an even steeper drift rate before 1992, consistent with a conditioning reaction that is largest near the beginning of the tank history and reduced by aging. The data, however, do not show such an effect, thus probably ruling out corrosion as the cause of the 8/92-1/95 relative drift.

In summary, we see no evidence of detectible corrosion effects on our tanks at any point in their history. Any systematic effect on our S2 scale is likely less than 0.3 per meg yr^{-1} over the past eight years, and we see no evidence for larger effects earlier in our programme. If there is general tendency for tanks to take up O_2 by oxidation, the effect must eventually saturate, leaving a largely passive inner surface. This holds for both steel and aluminium tanks.

Leakage

The composition of tank air can potentially be influenced by undetected leakage through small orifices or by permeation through elastomeric seals in the head valves. Our primaries have several different head valve types, some joined to the tank with pipe fittings sealed with Teflon tape, some sealed with metallic C-rings (see Table 1). All the head valves used have seats made from poly-chloro-tri-fluoro-ethylene (PCTFE), a material with low but non-zero permeability to gases (Sturm et al. 2004).

Because N_2 has a higher kinetic velocity than O_2, orifice leakage will enrich the O_2/N_2 ratio in the tank, as observed in our laboratory for leaking tanks, and as described above. In contrast, permeation loss will cause tanks to become depleted in O_2 relative to N_2 because O_2 has higher permeability than N_2 through most elastomers, including PCTFE (Sturm et al. 2004). A downward drift in O_2/N_2 ratio has been observed in pressurized gas flasks with elastomeric seals on the stopcocks (Sturm et al. 2004). A downward drift has also been observed in high pressure tanks in our laboratory that employed Viton O-rings as opposed to metallic C-rings at the valve base. These tanks were not part of our suite of primaries, however.

We can constrain the combined effects of orifice leakage and permeation in our primaries by examining relative drift of tanks of different sizes. If permeation through valve seats were uniformly influencing our tanks, it would cause the O_2/N_2 ratio of our smaller tanks to drift slowly downwards relative to our larger tanks. Similarly, if orifice leakage were uniformly influencing our tanks, it would also cause the O_2/N_2 ratio of our smaller tanks to drift slowly upwards relative to our larger tanks.

From the results summarized in Table 2, the differential drift rate of the smaller (150 SCF) tanks relative to our larger (265 or300 SCF) tanks over the longest period (8/92-4/03) is estimated at 0.09 ± 0.11 per meg yr^{-1}, a result which is not significantly different from zero but more consistent with a small orifice effect than a permeation effect. Assuming the differential drift resulted from absolute drift that is inversely proportional to tank volume, the differential drift of 0.09 ± 0.11 per meg yr^{-1} implies absolute drift rates of 0.23 ± 0.27 per meg yr^{-1} for our smaller tanks and 0.14 ± 0.17 per meg yr^{-1} for our larger tanks. Based on these results and the distribution of small and large tanks in our full ensemble of primaries, we estimate that any effect of permeation or leakage on our S2 scale is bounded at the level of ±0.2 per meg yr^{-1}.

The results in Table 2 also indicate a possibly significant trend with tank size over the limited period 8/92-1/95. However, this apparent trend could be attributed to material type, since the smaller tanks involved are untreated aluminium and the larger tanks are predominantly steel. Also, the lack of a size-dependant trend over the longer period 8/92-4/03, discussed earlier, is sufficient to rule out significant leakage or permeation effects.

Thermal fractionation

Another potential source of parallel drift is thermal fractionation within the cylinder, especially near the tank outlet, which could alter the composition of the air withdrawn from the tank relative to the original (average) composition in the tank. As mentioned above, we believe an effect of this sort influenced our tanks before 1992 and we attempted to minimize the effect by moving the tanks into a thermally insulated enclosure where the tanks were laid horizontally. However, even with these improvements, thermal fractionation might still be important at a smaller level. Since all of our tanks are mounted with the same orientation in the enclosure, a component of the thermal variability may influence all our tanks similarly, and hence go undetected in our normal tank comparisons.

One constraint we have on thermal fractionation is that the head valves on five of our primary tanks (indicated by solid symbols in Figure 1, third panel) were equipped with internal “dip-tubes”, in order to force the withdrawn air to come from a depth in the tank some 15 to 23 cm (depending on the tank) below the base of the valve. We would expect the air delivered from these tanks to be less sensitivity to ambient temperature gradients because the air is withdrawn from deeper in the tank. From Figure 1, it seems possible that these tanks have exhibited slight upward and downward excursions relative to the other tanks, but the effects are bounded at the level of ±3 per meg (1σ) on a short-term basis and the level of ± 1 per meg when averaged over yearly time scales. A reasonable interpretation might be that the tanks with dip tubes remained more stable while the others drifted up or down. We have not attempted to correct for these small effects.

Another constraint on thermal fractionation can be developed based on mass balance. If the air withdrawn from a tank is altered by thermal fractionation (or any other fractionation mechanism), there must be a reciprocal effect on the air remaining in the tank, with the effects accumulating as the tank is progressively depleted, as for a Raleigh-type distillation. Although the accumulation effect will be small for our primaries, because they have experienced only modest depletion, the effect is potentially much larger for our "working tanks", which are tanks that are depleted rapidly but analyzed frequently against our secondaries. The drift in the working tanks can be translated into a constraint on the fractionation associated with withdrawing air, and this constraint is presumably also relevant to our primary and secondary reference gases, which are stored in the enclosure with the same orientation as the working tanks. For example, if at some point in time our working tanks were to start exhibiting greater drift, this could indicate that the fractionation associated with withdrawing air from our other tanks had also increased.

The drift in the O_2/N_2 ratio of the gas delivered from each of our working tanks since the initiation of our programme (reported here on the S1 scale) is shown in Figure 2. Each working tank is denoted by a single point, plotted at the midpoint of the time interval when the tank was in use. The drift was computed as the difference in O_2/N_2 ratio between the full tank (~14 MPa) and the tank at the point 25% of the original gas remained (~3.5 MPa). Since individual working tanks show different drift patterns as a function of time, this method of computing drift is admittedly somewhat arbitrary, but the method nevertheless provides a useful perspective.

According to the Raleigh model, the working-tank drift values in Figure 2 can be converted into a fractionation factor ε by dividing by ln(0.25), where 0.25 is the fraction of the tank remaining at the defined end point. Here ε measures the difference in per meg units between air withdrawn from the tank relative to the remaining air. The estimates of ε, shown on the right axis of Figure 2 exhibit a mean of 1.1 per meg, a standard deviation of ±3 per meg, and a range from -5 to +7 per meg over the full programme record. While these estimates of ε were derived from working tanks alone, they are presumably applicable also to other tanks in the enclosure.

Our laboratory has been located in three different buildings, with moves in Jan, 1993 and April, 1999. One of our principle concerns is that differences in the thermal environment of the buildings may have caused systematic shifts in the air delivered from our primaries from one laboratory to the next. From the results in Figure 2, we estimate the mean and standard error of ε for the three setups, in consecutive order, are 1.0±2.1, 0.2±0.7, and 2.5±0.6 per meg, with the change from the second to third setup being apparently significant. In the first and third setup, there was no significant difference between working tanks with and without dip tubes, while in the second setup there were apparently significant differences: mean and standard error of tanks with and without dip tubes are 2.1±0.8 and -3.5±1.2 per meg, respectively. The results also show possibly larger variations in ε for the steel working tanks, which were used before April 1994, versus aluminium tanks (with or without dip tubes), which were used both before and after April 1994. Larger variability for steel tanks is not unexpected, because steel has a thermal conductivity several times smaller than aluminium, which will cause steel tanks to be generally less uniform in temperature than aluminium tanks.

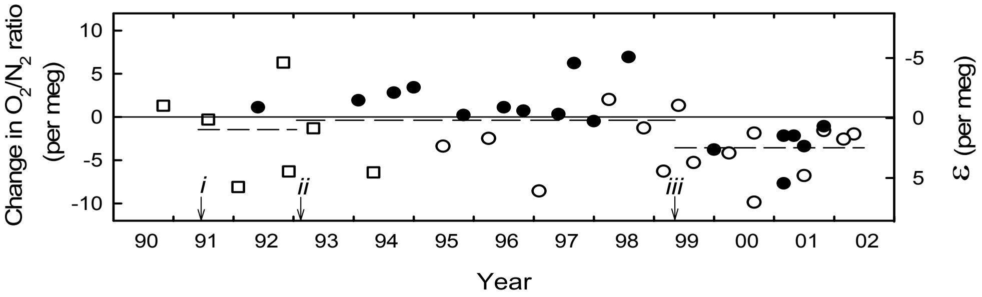

Figure 2: Drifts in working tanks as a function of time. Each working tank is denoted by a single point, plotted at the central time when the tank was in use. The left axis shows change in O_2/N_2 ratio between the full tank and the tank with 25% remaining; the right axis shows the corresponding fractionation factor (see text). Solid circles: aluminium tanks with dip-tubes; hollow circles: aluminium tanks without dip-tubes; hollow squares: steel tanks without dip-tubes. The dashed lines denote time averages over periods bounded by specific events: i) working tanks and secondaries moved into the insulated enclosure, ii) first laboratory move, iii) second laboratory move.

In our current laboratory setup, two lines of evidence suggest that the small observed drift of the working tanks may indeed be due to thermal fractionation. First, over the past few years, we have shown that the changes in O_2/N_2 in our working tank are accompanied by changes in Ar/N_2 that are ~2.5 times larger, consistent with thermal fractionation at high pressures (Keeling et al. 2004). Second, we have observed persistent horizontal gradients within the enclosure of the order of 0.02ºC, with the tank outlets being at the colder end. This gradient is the correct sign to cause O_2/N_2 delivered from the tanks to be enriched, thus causing the O_2/N_2 ratio remaining in the tank to decrease with time, consistent with the observations in Figure 2 for our current setup.

For the move in 1993, the results in Figure 2 do not show any systematic change in ε. The bracketing working tank data effectively constrain the fractionation for steel tanks, for which the estimated change in ε is +1.3±3.2 per meg (average of ε after move minus average of ε before). The change for aluminium tanks, though not constrained by working tank drift, is presumably smaller than this, due to the lower sensitivity to thermal fractionation of aluminium tanks. Thus any offset in our S2 scale associated with the 1993 move is probably at the level of 2 per meg or smaller.

For the laboratory move in 1999, the results from Figure 2 suggest that the air delivered from our primaries with dip tubes may have shifted upwards by 4.0±0.9 per meg, while those without dip tubes should have drifted upwards by around 0.1±1.2 per meg. If correct, we would need to adjust our O_2/N_2 data after the move upwards by ~1.5 per meg relative to data before the move, based on the relative number of primaries with and without dip tubes. We have resisted making this small adjustment for several reasons, however. First, the actual results for the primaries in Figure 1 do not show any significant change between tanks with dip tubes relative to those without dip tubes when the laboratory was moved in 1999. The relative change is estimated to be 0.1±0.8 per meg, whereas the working-tank drift results indicate a relative change of 3.9±1.5 per meg. Evidently, the working tank drift results are giving an exaggerated impression of the actual change in the primaries. Second, as discussed above, we would have expected the dip tubes to reduce, not enhance, the potential for thermal fractionation, in contradiction to the results from Figure 2, again suggesting that the ε values based on working-tanks may be somewhat exaggerated. This could be explained if some of the drift in the working tanks was caused by processes other than thermal fractionation, e.g. wall desorption (see below).

Figure 2 indicates that ε may have varied, not only systematically for different configurations of our laboratory, but also quasi-randomly on shorter time scales. The possibility of shorter-term variability in fractionation was also suggested by comparing the history of tanks with and without dip-tubes (shown in Figure 1). The results from Figure 1 and 2 are consistent in indicating that tanks without dip tubes exhibit short-term variability of the order of ~ ±3 per meg, and that tanks with dip tubes likely exhibit less variability. This variability presumably applies on time scales of hours to months, with smaller effects on annual averages.

In summary, since 1992 it is possible that the air from our reference tanks have fluctuated in parallel by around ±3 per meg on short time scales and ±1 per meg on annual time scales due to variations in thermal fractionation. Our S2 scale may thus have short-term random biases of this magnitude. Based on working-tank drift rates, we estimate that the laboratory moves in 1993 and 1999 induced additional systematic biases in our S2 scale of ±2 per meg or less. Before 1992, when our tanks were stored upright in the laboratory, we have documented and corrected for larger shifts, as described in (Keeling et al. 1998). We estimate the biases in the corrected S2 scale in this early period are ±4 per meg or less.

Desorption effects

As the pressure in a tank drops through usage, gases that are physisorbed onto the tank walls will tend to be released into the gas phase. This process has the potential to alter the O_2/N_2 ratio of the air in the tank because O_2 and N_2 generally will have different surface affinities.

The same working tank data which we used to constrain thermal fractionation effects (Figure 2) also constrains desorption effects. The percent depletion of our primary tanks ranges from 5 to 25% from 1990 through 2002, excluding those tanks which leaked. Since the mean drift rate of our working tanks was no larger than a few per meg over a 75% pressure drop, the working tank drift translates to a maximum desorption effect in our primaries of 1 per meg or less over their lifetime, or less than 0.1 per meg yr^{-1}.

6.1.5 Conclusions

Table 3 summarizes the estimated contributions of the various processes to uncertainty in our O_2/N_2 (S2) calibration scale. The table also illustrates how the results can be combined to estimate the probable bounds on scale drift over various periods. For example, from 1990 to 2000, the estimated bounds are ±6 per meg, while from 1992-2002 the bounds are ±4 per meg.

There are two principle caveats with these results. First, the estimated bounds depend, to some degree, on subjective assessments of probabilities, the clearest example being the assumption about matching of corrosion rates of different tank types. Second, the bounds are limited to variations caused processes that we understand, and we cannot rule out the possibility of there being additional processes causing tank drift that we have overlooked. These caveats are unavoidable, given that our methods for assessing absolute stability depend on relative measurements. To provide stronger constraints, we would need to develop absolute O_2/N_2 standards, or absolute analysis methods.

Probably most importantly, the results show that the O_2/N_2 ratio of air delivered from our primary reference tanks exhibits a high degree of stability with respect to corrosion effects, leakage and permeation effects, thermal fractionation effects, and desorption effects. The results emphasize the importance of using strict protocols for delivering gases from tanks, for maintaining a suite of reference tanks of diverse sizes and material types, of insulating tanks and orienting them horizontally to minimize thermal effects, and of tracking drift in rapidly-depleted surveillance (i.e. working) tanks as a means of assessing fractionation.

Table 3: Estimated uncertainties in S2 scale.

Process	uncertainty
Corrosion	±0.3 per meg yr^{-1}
Leakage & permeation	±0.2 per meg yr^{-1}
Thermal fractionation after 7/92	±2 per meg
Thermal fractionation before 7/92	±4 per meg
Desorption effects	±0.1 per meg yr^{-1}
Overall 1990-2000 uncertainty	±6 per meg
Overall 1993-2003 uncertainty	±4 per meg

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6.2 An Intercomparison of Standard Air for Measurements of the Atmospheric O_2/N_2 Ratio Among Tohoku University, Princeton University and National Institute for Environmental Studies

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6.2.1 Introduction

The number of research groups devoting to measuring the atmospheric O_2/N_2 ratio has been increasing since Ralph Keeling [Keeling and Shertz, 1992] made first systematic measurements in 1989; the O_2/N_2 ratio is an effective proxy in understanding the global carbon cycle. Various groups have developed their analytical systems based on different principles such as interferometry, mass spectrometry, gas chromatography and paramagnetism. Since all these techniques constitute a relative measurement method that relies on comparison with a reference, air standards with known O_2/N_2 ratios are required for determining the ratio of the air sample. For this purpose, the groups involved in the O_2/N_2 ratio measurement have prepared their own air standards and have used them for their measurement programmes. Therefore, it is likely that some systematic differences exist in the results obtained by these groups. To address this issue, Tohoku University, Princeton University and National Institute for Environmental Studies (NIES) recently made an intercomparison of standard air for measurements of the atmospheric O_2/N_2 ratio using glass flasks. The results obtained are briefly reported here.

6.2.2 O_2/N_2 measurements at Tohoku University, Princeton University and NIES

For measuring the O_2/N_2 ratio, Tohoku and Princeton use a mass spectrometer in which the ion current ratio of mass 32 (O_2) to mass 29 (N_2) is measured [Bender et al., 1994; Ishidoya et al., 2003]. On the other hand, NIES uses a gas chromatograph equipped with a thermal conductivity detector by which the chromatogram ratio of O_2+Ar to N_2 is measured [Tohjima, 2000]. Since the Ar concentrations of standard air samples prepared by NIES for the intercomparison were different, the contribution of Ar to the O_2/N_2 ratio was corrected by separately measuring its concentration for each standard. The analytical precision of flask samples was estimated to be 5.4 per meg for Tohoku, 4.0 per meg for Princeton and 7.0 per meg for NIES

The flasks prepared by the respective institutes for this intercomparison were all Pyrex glass flasks with two Viton O-ring seal stopcocks, and the volume of the flask was 0.55 L for Tohoku, 1.5 L for Princeton and 1.0 L for NIES.

6.2.3 Intercomparison between Tohoku University and Princeton University

For the intercomparison between Tohoku and Princeton, Tohoku prepared 5 standard air with different $\delta(O_2/N_2)$ values of 666 to -192 per meg. These values were determined against a Tohoku's primary standard air using a 0.55 L glass flask. The CO_2 concentrations of the 5 standard air ranged between 300 and 545 ppmv. All Tohoku's standard air were stored in 48 L aluminium high-pressure cylinders. Forty flasks were prepared by Princeton, and 8 flasks were allocated to each standard air. After connecting 2 or 3 flasks in series, each standard air was passed through the flasks at a flow rate of 1 L/min for about 20 minutes; the flasks were then closed at atmospheric pressures. All the flasks filled with the standard air were sent to Princeton by airfreight for their O_2/N_2 ratio analyses.

The difference between the $\delta(O_2/N_2)$ values determined by Princeton and Tohoku is plotted in Figure 1 against the Tohoku values. The result shows that the Princeton values are clearly higher than the Tohoku values. It is also evident in Figure 1 that the difference between the Princeton and Tohoku values increases with increasing $\delta(O_2/N_2)$. One possible cause is that the mass spectrometer response is slightly nonlinear to the O_2/N_2 ratio of the sample air, which is too small to be undetectable due to our experimental imprecision. In this regard, we confirmed that our mass spectrometers responded linearly to the O_2/N_2 ratio of the air sample, at least within our experimental errors.

Figure 1 also shows that the result obtained for the standard air PLM37171 deviates clearly from the value expected from the remaining 4 standards. It may be noted that the CO_2 concentration of this standard air is 545.4 ppmv, which is significantly higher than 300.9-360.4 ppmv of the other standards. It is known that when the sample air is introduced into an ion source of the mass spectrometer, CO_2 molecules in the air sample are partly dissociated and the resultant CO molecules with mass 29 interfere with the ion current for N_2 with mass 29. Of course, the $\delta(O_2/N_2)$ values of the standard air determined by Tohoku and Princeton were corrected for this effect, using the relationship determined experimentally for each mass spectrometer. However, to elucidate the cause of this difference, further detailed examination of the CO_2 correction is required for the mass spectrometers used.

6.2.4 Intercomparison between Tohoku University and NIES

For the intercomparison between Tohoku and NIES, NIES prepared 3 standard air samples with $\delta(O_2/N_2)$ of –129, -216 and -296 per meg. These O_2/N_2 ratios were determined against a NIES' primary standard by introducing the standard air directly into the gas chromatograph from 48 L high-pressure cylinders. The CO_2 concentrations of the respective standards were 0, 388.3 and 388.9 ppmv. NIES and Tohoku prepared a total of 20 flasks, and 6 or 8 flasks were allocated to each standard air. After 3 or 2 flasks were connected in series and the outlet of the last flask was equipped with a backpressure regulator, each standard air was passed through the flasks at an over-pressure of 0.1 Mpa at a flow rate of 100 mL/min for about 100 minutes, and each flask was then filled with the standard air at the same pressure. Just after filling the standard air in the flasks, NIES analyzed their $\delta(O_2/N_2)$ values. By this analysis, the sample pressures decreased to almost atmospheric pressures. Then, all flasks were sent to Tohoku for their mass spectrometer analysis.

The difference in the $\delta(O_2/N_2)$ values determined by NIES and Tohoku is plotted in Figure 2 against the Tohoku values. The results indicate that the NIES values appear to be higher than the Tohoku values. One possible cause of this difference is that the 0.55 L Tohoku flasks were too small for the gas chromatograph analysis at NIES, since their analysis requires a relatively large quantity of air sample.

The difference between the NIES and Tohoku values increases with increasing $\delta(O_2/N_2)$, similar to the intercomparison result between Princeton and Tohoku, but the trend of the difference relative to the Tohoku value in this case is steeper than before. The difference for the standard air with no CO_2 seems to deviate from that expected from the remaining two data points, which is more prominent for the Tohoku flask than for the NIES flask. To interpret these results, we need to re-examine the Ar correction applied by NIES and the size of flask to be used, in addition to the nonlinear response effect and the CO_2 correction for the Tohoku's mass spectrometer.

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*Ishidoya, S. S. Aoki and T. Nakazawa, High precision measurements of the atmospheric O_2/N_2 ratio on a mass spectrometer, J. Meteorol. Soc. Japan, **81**, 127-140, 2003.*

*Keeling, R. F and S. R. Shertz, Seasonal and Interannual variations in atmospheric oxygen and implications for the global carbon cycle, Nature, **358**, 723-727, 1992.*

*Tohjima, Y., Method for measuring changes in the atmospheric O_2/N_2 ratio by a gas chromatograph equipped with a thermal conductivity detector, J. Geophys. Res., **105**, 14575-14584, 2000.*

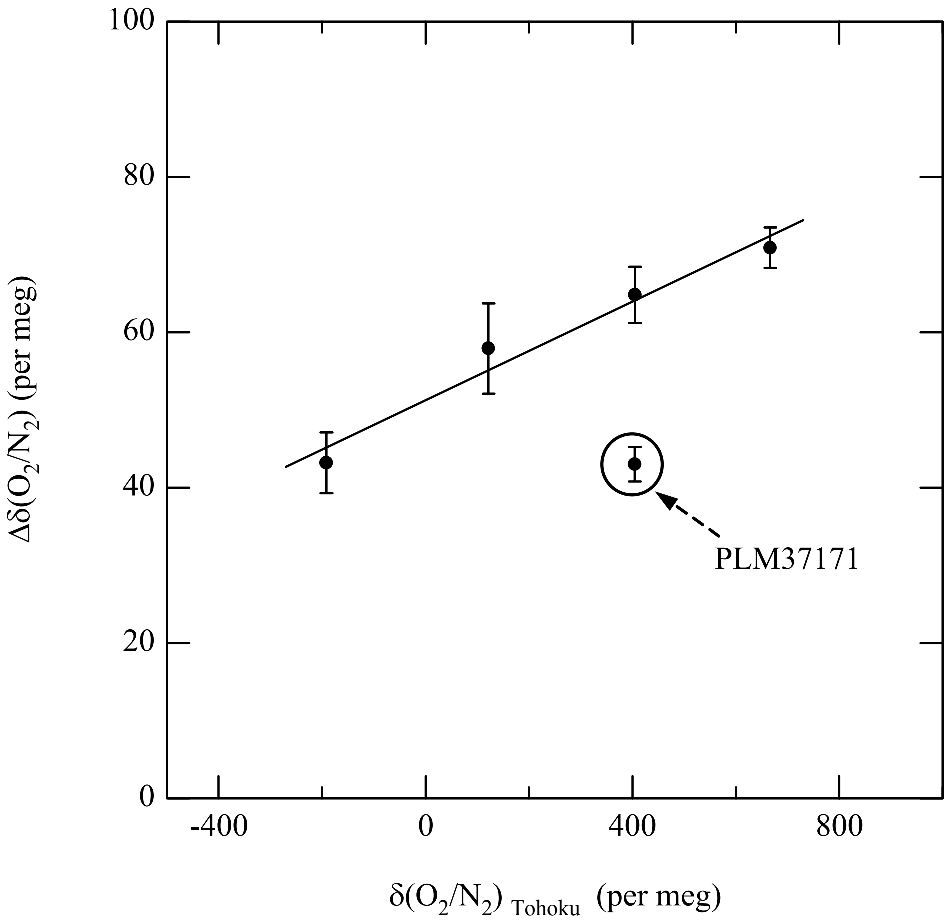

Figure 1: Differences between the $\delta(O_2/N_2)$ values determined by Princeton University and Tohoku University for five standard air.

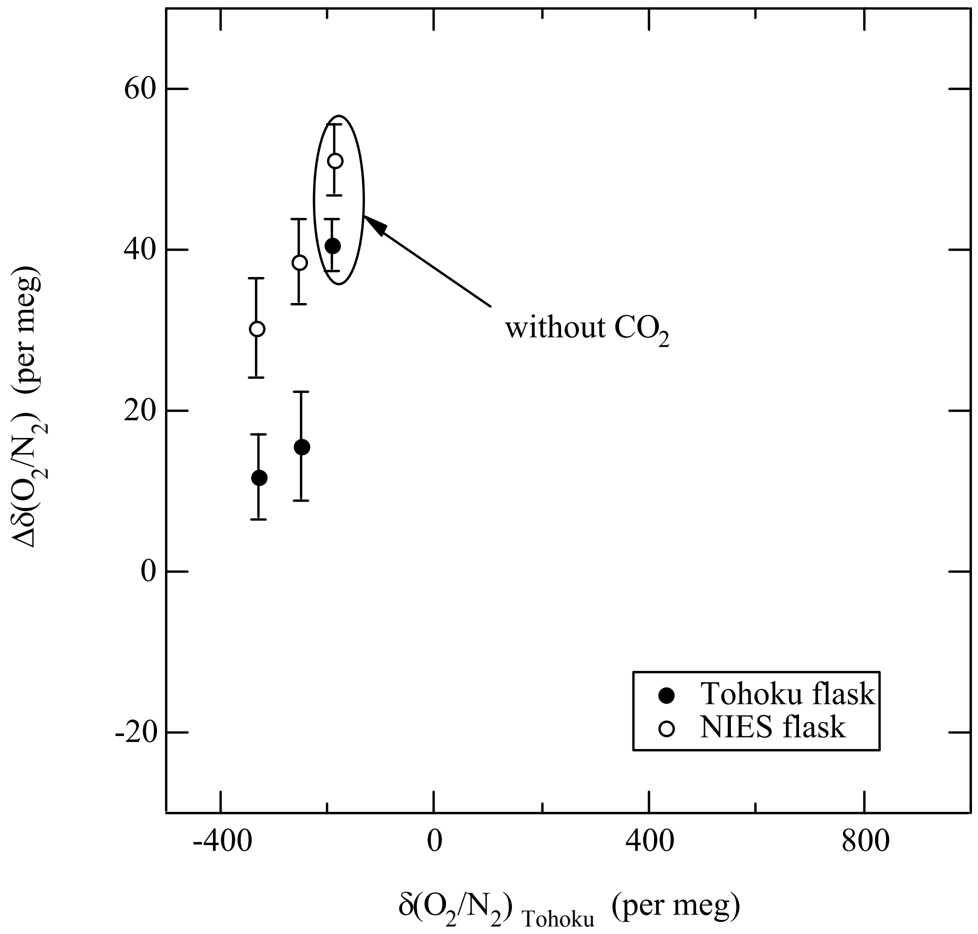

Figure 2: Differences between the δ(O_2/N_2) values determined by National Institute for Environmental Studies and Tohoku University for three standard air.

6.3 O_2/N_2 Storage Aspects and Open Split Mass Spectrometric Determination

Willi A. Brand[‡]

Abstract

A measurement system for high precision determination of O_2/N_2 ratios in air samples using an open split inlet system and mass spectrometric detection is described. A major advantage of the system is the low consumption of sample gas (about 2 ml STP per minute). The open split system is made from fused silica capillaries moving alternately within a glass tube thereby providing the function of a Changeover Valve commonly used in stable isotope ratio mass spectrometry for high precision comparison of the isotopic composition of two clean gases. Long term precision of the measurements, comparing ½ hour averages are close to 2 per meg.

Storage of air samples in glass flasks has been improved considerably by replacing the soft polymer O-ring with a lathe machined PCTFE seal. In one litre flasks air samples kept at 2 Bar (abs.) do not alter their O_2/N_2 ratio by more than 7 per meg in 100 days.

An effort to calibrate O_2/N_2 ratio measurements across laboratories has been made using high pressure tanks. The original values of the tanks (measured by R. Keeling, SIO) were reproduced within an error of 1% of the assigned difference.

6.3.1 Introduction

The routine measurement of O_2/N_2 ratios in air sampled in containers has been plagued by the stability of the gas mixture over time. This has proven to be the case for high quality stainless steel containers[1] as well as for glass flasks[2]. Some of the instability over time can be attributed to oxidizable, mostly organic material on the surfaces or within the O-ring material.[3] One of the major reasons for changes observed over time is permeation through O-ring seals which depend on the strongly temperature dependent permeability of the polymer as well as the pressure gradient between the air inside the flask and ambient.[2] Using published permeation coefficients we estimate that a typical 1 litre glass flask with two valves sealed with Viton O-rings can loose roughly 0.2 ml (STP) of air through diffusion over the period of one year when the pressure difference is one atmosphere. Owing to the differences in permeability these 0.2 ml of 'air', however, comprise about 55 % O_2 and only 45 % N_2. Hence, the remaining air in the flask has been altered by about 200 per meg[4] in the O_2/N_2 mixing ratio. Due to these storage effects, most air samples have been collected by filling the flasks to ambient pressure. On the other hand, sampling for trace gas concentration measurements often requires pressures above ambient for subsequent gas chromatographic quantification. Samples at higher pressure require proportionally less space. This is a logistical advantage especially when sampling in remote areas where routine shipment of flasks is a permanent challenge.

6.3.2 Experimental setup

In Jena, we have established routine precision quantification of trace gases (CO_2, CH_4, N_2O, H_2, CO and SF_6) in air as well as high precision isotopic analysis of CO_2. Trace gas quantification in general requires above ambient pressure, while the isotopic measurements can be made at sub-ambient pressures without special treatment. All measurements are made from the same flasks with a volume of 1 litre and a collection pressure of 2 bar. In order to analyse the collected air samples for O_2/N_2 as well we have devised a low flow open split inlet system ('BG-

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[1] Langenfelds RL, Francey RJ, Steele LP, Battle M, Keeling RF, Budd WF, GEOPHYS. RES. LETT. 26 (13): 1897-1900 1999

[2] P. Sturm, M. Leuenberger, C. Sirignano, R. Neubert, H.A.J. Meijer, R. Langenfelds, W.A. Brand and Y. Tohjiama, Permeation of atmospheric gases through polymer O-rings used in flasks for air sampling, JGR (2003) accepted for publication

[3] Keeling RF, Manning AC, McEvoy EM, Shertz SR, J. GEOPHYS. RES. (ATM.), 103 (D3): 3381-3397 1998

[4] 1000 per meg equals 1 per mill in the delta notation. Due to the nominal O_2 content in air of 20.95%, 4.8 per meg are equivalent to 1 ppm.

AirFlo') already briefly mentioned in Werner et al.[5] at a preliminary stage. The system in the current version is depicted schematically in Figure 1.

Air samples are attached to a 16 port multiport valve (VICI-Valco, www.vici.com) using ½" Ultratorr (Swagelock, www.swagelock.com) connectors. The selected port is connected to a 6-port 2-position valve (VICI-Valco) which has a pressure gauge mounted between two ports and a membrane pump for initial evacuation and vacuum control of the connecting joint. In addition, the flask pressure can be determined this way. In the connecting line between the two valves a small stainless steel tube filled with $Mg(ClO_4)_2$ serves as a guard trap against residual water (we exclusively sample dry air). From the 6-port valve a fused silica capillary restricts the flow to an open split which is made from a small glass tube closed at one end. For a pressure difference of 1 bar the flow amounts to about 2 ml per minute. The fused silica capillary enters the open split down to the tip where a transfer capillary to the mass spectrometer is taking gas into the ion source of the mass spectrometer (Delta+XL, Finnigan MAT, with small modifications in the ion source region). The capillary from the 6-port Valco valve is mounted on a piston so that it can be switched in and out of the open split assembly. A second fused silica capillary providing a continuous flow of reference air from a high pressure tank is alternately switched into the open split.

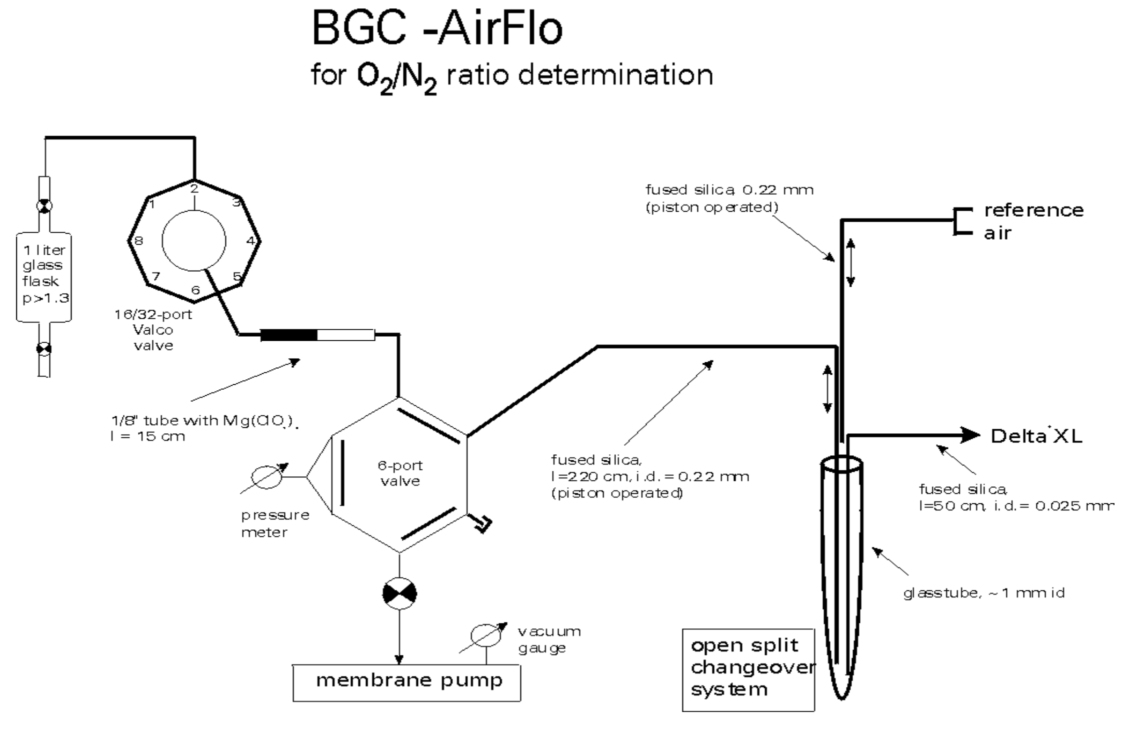

Figure 1: Schematic layout of the air inlet system including a multiport valve (VICI-Valco) and the glass tube with fused silica capillaries acting together as a Changeover Valve.

The arrangement serves the function of a changeover valve as is common in isotope ratio mass spectrometry. The major advantage of the open split setup is that the mass spectrometer does not record any change in pressure during switching. Pressure surges have a negative influence on the attainable precision due to the fact that sensitive equilibria between material and oxygen in the ion source are temporarily altered and require time for reestablishment: freshly bombarded surfaces are a pressure dependent sink for oxygen, the hot tungsten filament has a pressure dependent oxydation state, etc.. A second advantage relates to the common observation

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[5] *Roland A. Werner and Willi A. Brand, Referencing Strategies and Techniques in Stable Isotope Ratio Analysis, Rapid Comm. Mass Spectrom. 15 (2001) 501-519*

that the measured O_2/N_2 ratio usually is very sensitive to pressure differences and great emphasis must be laid upon high precision flow balancing of sample and reference gas. By using the open split principle the pressure between sample and reference gas remains precisely balanced with no further action required. Longer term pressure changes due to changing weather conditions do not interfere because they happen on a different time scale. An open split setup similar to ours with the additional capability to work against a constant sub-ambient pressure has been described by Leuenberger et al.[6].

6.3.3 Results and Discussion

6.3.3.1 Alteration of sample air in glass flasks during storage

In order to study the effects of sample gas alteration or aging inside our routine operation glass flasks we have observed the O_2/N_2 ratio in a series of flasks over a period of 160 days. A total of 7 flasks sealed with **PFA O-rings** were involved in this study. All flasks were filled with dry air in a 'sausage' (connected in series with Cajon Ultratorr adapters) at a constant filling pressure of 2 bar (abs.). The flow through the system was 3 l per minute for 30 minutes. The analysis results are presented in Figure 2.

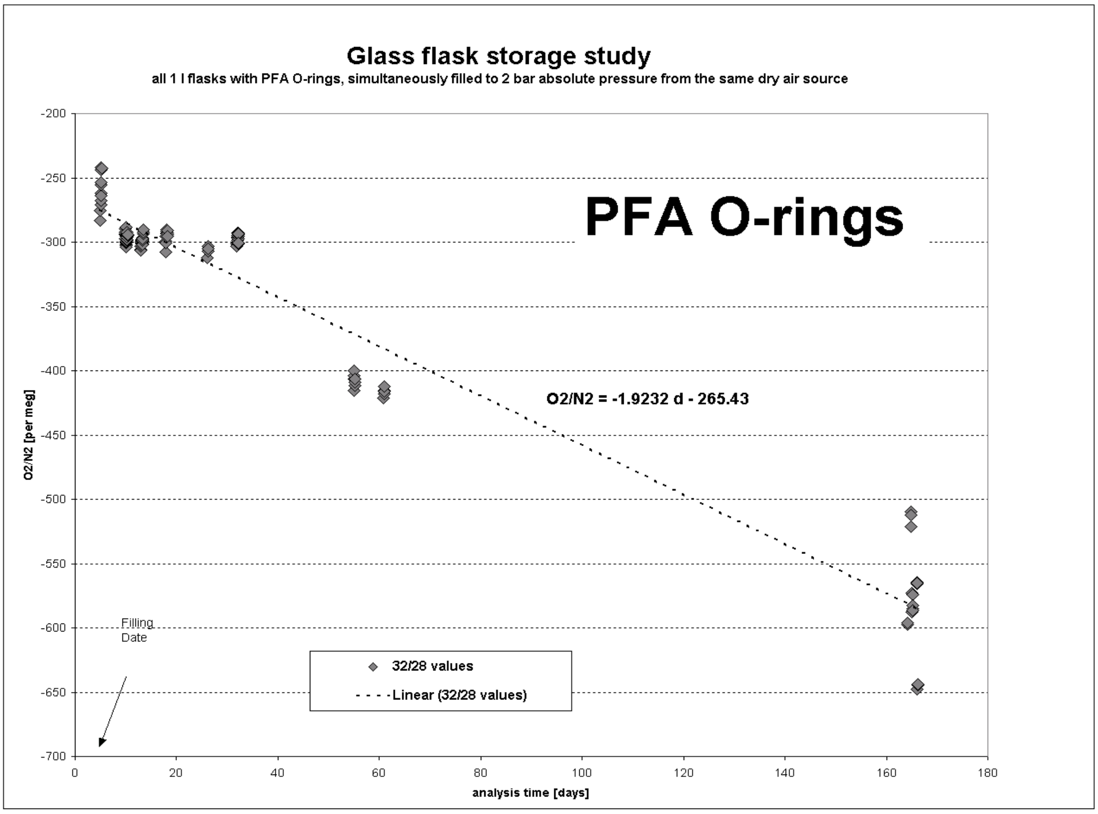

Figure 2: Air sample storage tests for O_2/N_2 using PFA O-ring seals.

The flasks were measured repeatedly, with the first analysis varying over time. Within the limits of precision we did not detect any change of gas composition as a function of pressure drop. Two features are evident from Figure 2: there is a clear highly correlated (R^2 = 0.95) drop of the measured O_2/N_2 ratio with time and the scatter of the data increases over time as well. The drop in ratio amounts to an average of -310 per meg in 166 days. The scatter at the beginning was ± 12 per meg and increased to ± 50 per meg over the same observation period. The latter may be

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[6] *Leuenberger M, Nyfeler P, Moret HP, Sturm P, Huber C, RAP. COMM. MASS SPECTROM. 14 (16): 1543-1551 2000*

understood in terms of the details of the diffusion characteristics: The diffusion length and diffusion area control the diffusion rate in a linear fashion[2]. Both are a function of the O-ring geometry in its compressed form. We did not select the O-rings for maximum comparability in size nor did we use a torque wrench for controlling the force onto the O-rings.

In order to reduce the aging effects we devised two possible pathways: The preferred solution was to get rid of the permeation effect entirely (within measurement precision) by searching for a better polymer sealing material. In case this would prove unsuccessful, the effect should at least be minimized. Commonly used solutions to the problem (filling to ambient pressure and using large volumes of gas) are of this second type. We tried a third solution by adding a buffer volume in between two O-rings. The buffer volume is initially filled with sample air at the sample pressure. This gas acts as a shield towards alteration of the sample gas itself over time. The results of this study have been published elsewhere[2] and will not be considered further here.
The search for an alternative material quickly revealed that **PCTFE (Kel-f®)** would be a good alternative (see table in reference 2) primarily owing to its low permeability constants compared to all other materials. However, the material is much harder than usual O-rings suitable for sealing on glass. It is in common use in high quality vacuum valves or in high quality pressure regulators where force is not critical due to the use of metal as the counter-seal material. In an early attempt, our routine flasks were equipped with O-rings made from PCTFE. In spite of the difficulties in achieving a good seal, storage tests were conducted over an extended period of time[7] revealing that the storage problems could be overcome using this material provided the seal could be made in a reliable fashion with a torque size compatible with glass valves. By reducing the contact area and using a machined seal with tight size specifications instead of a simple O-ring we succeeded in generating a valve seat that can be used on the valve stems already in use in our glass flasks[8]. Storage tests for O_2/N_2 are shown in Figure 3.

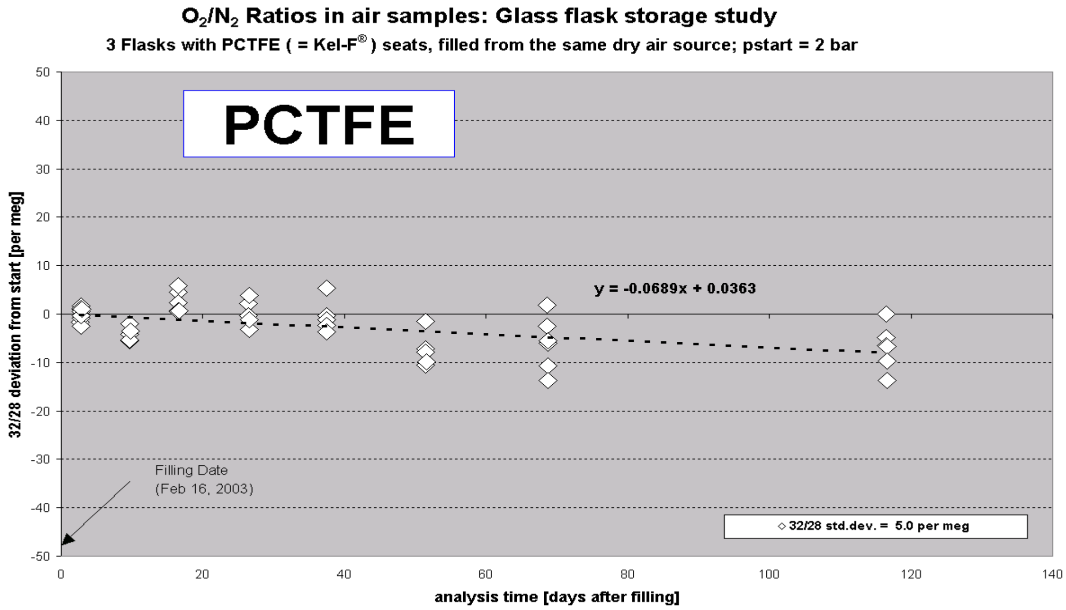

Figure 3: 32/28 stability in glass flasks sealed with PCTFE.

The conditions and flask filling was identical to the earlier experiment. The data suggest that the effect of preferential oxygen loss from sample flasks has been reduced considerably. A residual loss corresponding to a concentration change of about 7 per meg in 100 days is observed

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[7] *Ray Langenfelds, private communication*

[8] *The valves are from Glass Expansion, GE, Australia. In a close collaboration with QVF (Ilmenau, Germany) we have been successful in developing a new glass valve for this purpose using Kel-F seats. These are available commercially now (www.glasapparate.de).*

which must be taken into account when analysing and reporting the flask results. Even without correcting for this drift, the total precision in the data, expressed as standard deviation is ± 5 per meg, exhibiting a considerable improvement over the previous data set obtained with PFA seats.

6.3.4 O_2/N_2 scale calibration

The improvements in storage stability described above offer new opportunities for calibrating O_2/N_2 measurements over longer periods of time and in between laboratories. Provided the elevated pressure in the flasks does not impose new artifacts on analytical setups that are used to measure O_2/N_2 in air samples interlab-precision could be brought to the ± 5 per meg level by filling a number of flasks and sending them to participating laboratories for intercomparison. In our lab (as in most others doing these kinds of analysis) high pressure tanks are used for maintaining the local scale. Differences between tanks are routinely monitored and kept in a record file. Tanks are kept horizontally in order to minimize effects of diurnal temperature cycling and the regulators are carefully selected for inertness towards changes in the measured oxygen concentration. We have obtained a pair of air tanks filled and calibrated for our institute by R. Keeling at Scripps Institution of Oceanography (SIO). We have used these tanks to establish a firm O_2/N_2 value for a third tank serving as a continuous flow working reference on the BGC AirFlo system depicted in Figure 1. The SIO tanks were connected to one of the flask ports and the differences between the respective tank and the working reference were monitored over considerable periods of time. Figure 4 exhibits the results obtained for the working reference assuming that the respective SIO tank assignment is correct. Each data point corresponds to a ½ hour average in the observed 32/28 ratio. On average over the whole measurement period we find a residual offset of +2.0 permeg between the measurements, i.e. our measurements indicate a slightly larger difference between the SIO tanks (224 per meg) than assigned (222 per meg). For arriving at the correct O_2/N_2 ratio for the tanks the raw data in Figure 4 have been corrected for the difference in CO_2 concentration (421 ppm and 379.6 ppm): CO^+ (m/z 28, isobaric with $N_2^{+\bullet}$) is formed from excited $CO_2^{+\bullet}$ ions in the ion source and comprises about 10% of the total ion current formed by electron impact ionization of CO_2 gas. This contribution to the m/z 28 ion current (a per meg correction of 0.13 times the CO_2 concentration difference) has been removed resulting in a reduction of the observed scale difference from 7.4 per meg to 2.0 per meg.

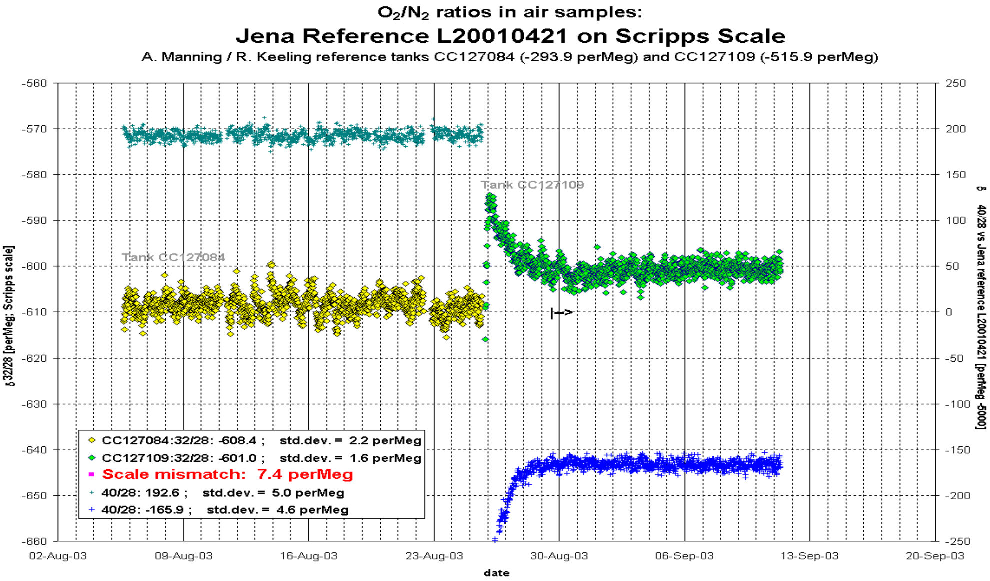

Figure 4: Determination of a Jena working reference tank using two tanks with different O2/N2 ratios calibrated by R. Keeling, SIO.

Taking the complexity of the analysis into account as well as the fact that the analysis principles in both laboratories are entirely different we consider this error of about 1% an excellent result which provides further confidence that O_2/N_2 measurements can also be reliably calibrated using selected high pressure aluminium tanks.

6.3.5 Conclusions

Precise determination of O_2/N_2 ratios in air samples is possible using an open split changeover system and a low sample flow of less than 2 ml/min. For two ½ hour determinations a sample consumption of less than 120 ml is possible. Together with improvements in gas stability over time when PCTFE is used as a sealing material in glass containers, this offers the possibility to measure the major trace gas concentrations (CO_2, CH4, N_2O, CO, H_2 SF_6), O_2/N_2 ratios as well as CO_2 isotope ratios from a single 1 litre glass flask filled to a pressure of 2 bar (abs.)

6.3.6 Acknowledgments

Flask conditioning and filling has been made by Michael Rothe. The communication of preliminary results on storage tests using PCTFE by Ray Langenfelds is highly appreciated. These results triggered and encouraged the work presented in this contribution. Ralph Keeling and Andrew Manning generously provided the tanks for the calibration exercise.

6.4 Global N_2O Measurements: Challenges and Perspectives

H.E. Scheel

6.4.1 *Introduction*

Since nitrous oxide (N_2O) is one of the atmospheric constituents related to issues of stratospheric ozone and climate, it is included in the GAW measurement programme recommended for global stations (WMO-GAW Report No. 80, p. 33, [Ref. 1]).

N_2O has both natural and anthropogenic sources. These include oceans, fossil fuel, biomass burning and agricultural fertilisers. It contributes about 6% to the enhanced greenhouse effect. N_2O is increasing at a rate of about 0.7 ppb per year. It is inert in the troposphere, and photochemical transformation in the stratosphere constitutes its dominant sink. Because of its long atmospheric lifetime (150 years), background levels of nitrous oxide can be representatively determined at GAW global stations. Regional stations, in addition, provide useful new insights into the global N_2O budget.

6.4.2 *Analytical techniques*

For N_2O measurements at GAW stations, the method of choice is gas chromatographic (GC) analysis with packed columns (porous polymers or zeolites) and electron capture detector (ECD). Since this is not an absolute method, calibration gases are required, which are usually stored in high-pressure cylinders.

The analytical set-up can vary within a wide range, depending on details such as type (manufacturer) of the GC, columns used for the separation, type of carrier gas (e.g. Ar/CH_4 (95/5) or N_2 with dopant), valve switching configuration (e.g. use of pre-column and backflush), type of make-up gas for the ECD, if any (e.g. Ar/CH_4 (95/5) or doped N_2), peak integration system. Depending on the GC system, the analytical precision at ambient levels ($\approx$ 315 ppb) varies between 0.5% (old GCs) and 0.05% (state of the art). Possible difficulties and/or problems of the method are mainly related to the non-linearity of the ECD and chromatographic interference of the N_2O peak with CO_2 and /or SF_6

6.4.3 *Global N_2O measurements (Networks / Locations)*

Contributions to global N_2O data are coming from different sources, which can roughly be divided into three major categories. (i) Global networks, such as NOAA CMDL (www.cmdl.noaa.gov) and AGAGE [2]; (ii) other stations, of which some are part of GAW, with either global or regional status; and (iii) a number of laboratories and sampling sites.

Concerning the spatial data coverage, considerations will have to be given to the question of whether the current spatial coverage (stations / sampling sites) is sufficient or not. If geographical gaps need to be closed, some of the newly established Global GAW stations might contribute by adding N_2O to their measurement programme, as was foreseen in the GAW Report No. 142. For data contributions from regional stations and other sites, which are welcome, the same strict Data Quality Objectives (DQOs) as for global stations will have to be applied.

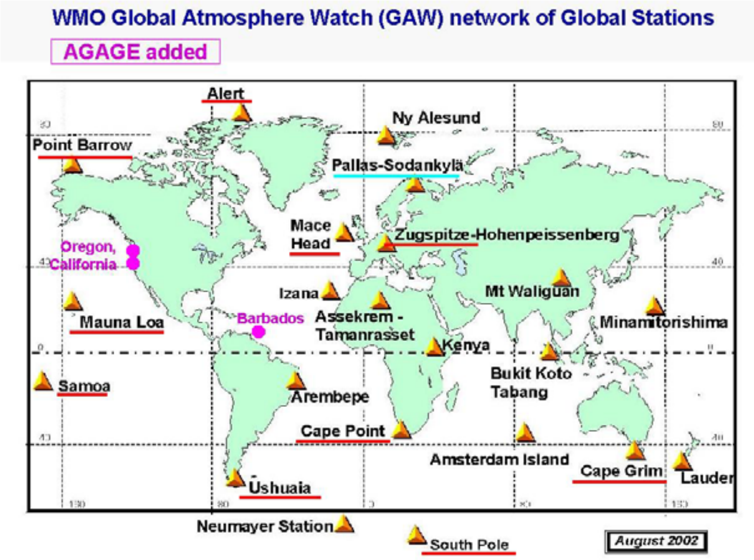

Figure 1: Map showing the global WMO GAW stations (source: www.wmo.ch/web/arep/gaw/stations.html). As a modification, here the names of sites where N_2O is monitored are underlined. In addition the stations of the AGAGE network are shown by solid circles.

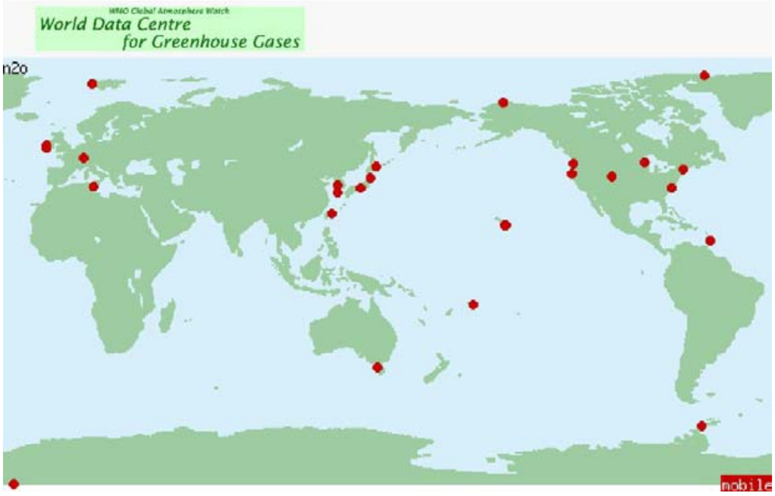

Figure 2: Data reporting stations: N_2O data collected by the WDCGG (http://gaw.kishou.go.jp/wdcgg.html) as of September 2003.

6.4.4 Calibration scales

Within the framework of global N_2O measurements, there are two prominent calibration scales. One is the scale developed at Scripps Institution of Oceanography [3]. The current SIO X98 scale is used by the AGAGE network of station [2]. The other major scale is the NOAA CMDL scale (www.cmdl.noaa.gov/hats/index.html). The CMDL scale has been designated as calibration scale for the GAW network [4]. Therefore CMDL will act as the Central Calibration Laboratory (CCL) for GAW. At different sites around the globe, there are other scales in use, which are related to laboratories or manufacturers of gas mixtures. The goal of future activities - predominantly within GAW - is to enable the traceability of N_2O data to a single calibration scale.

When considering N_2O time series archived by the WDCGG, it becomes evident that the existing data cannot be simply combined to yield a global picture, which is due to different calibration scales. For example, as a minimum requirement it is necessary that the interhemispheric difference of N_2O mole fractions ($\approx$ 1 -1.5 ppb) remains detectable when using data of different organisations. This establishes certain minimum requirements for the DQOs.

In consequence, the implementation of coordinated Quality Assurance and Quality Control (QA/QC) measures within GAW is of importance. Specifically, the implementation of a World Calibration Centre for Nitrous Oxide (WCC-N_2O) has been regarded as an urgently needed GAW activity, as stated in the WMO/GAW Strategic Plan 2001-2007 [4].

6.4.5 Introducing the WMO GAW World Calibration Centre for Nitrous Oxide

The WCC-N_2O is hosted by the Forschungszentrum Karlsruhe and is located at IMK-IFU (Garmisch-Partenkirchen, Germany). The build-up of the WCC-N_2O began in 2001, and in November 2002 this new GAW facility became operational. Its activities are funded by the German Environmental Agency (UBA) and conducted under supervision of the QA/SAC Germany, a division of UBA at Langen, Germany.

Similar to other WCCs, the tasks of the WCC-N_2O are (cf. [4]):

- Development of quality control procedures,
- maintaining global calibration standards (based on standards provided by the CCL),
- conducting performance and system audits at stations,
- conducting round-robin experiments (intercomparisons),
- supporting network-wide quality review,
- providing training and long-term technical help for station scientists and technicians.

In this context reference is made to the definition of audits [4]. A 'Performance Audit' is defined as a "voluntary check for conformity of a measurement where the audit criteria are the Data Quality Objectives (DQOs) for the specific parameter. In the absence of formal DQOs, an audit will at least involve ensuring the traceability of measurements to the Reference Standard." A 'System Audit' is more generally defined as a "check of the overall conformity of a station with the principles of the GAW system."

In summary, the overall aims of the WCC-N_2O are: Improving the data quality in the network, harmonising the results from different stations and different monitoring programmes, and thus increasing the global N_2O data coverage. It is emphasised that close communication and interaction with the Scientific Advisory Group for Greenhouse Gases (SAG GG) is of major importance for the WCC-N_2O.

The concept for calibrations, as adopted by the WCC-N_2O, is summarised schematically in Figure 3. The main principles are: CMDL acts as Central Calibration Laboratory (CCL), with the NOAA CMDL calibration scale serving as N_2O reference for the GAW network. CMDL-calibrated gas mixtures are used as Laboratory Standards of the WCC-N_2O. On the next level, WCC-calibrated gas mixtures in high-pressure cylinders are employed for audits and round-robin experiments (Transfer Standards / Travelling Standards).

The following activities have so far been conducted by the WCC-N_2O: (i) Build-up of the laboratory and acquisition of five CMDL-calibrated standards (250 - 350 ppb), calibration of two series of five transfer standards each (260 - 360 ppb), (ii) two audits, (iii) preparation of a first draft of the future Standard Operating Procedure (SOP) for N_2O.

The SOP-N_2O is covering: Measurements at stations (method, technical requirements, calibration procedures), data quality objectives as well as audits (SOP for performance audits).

So far system and performance audits (based on preliminary DQOs) were performed by the WCC-N_2O at two stations, one of regional and the other of global status. Thereby several crucial points related to N_2O measurements came to the fore, notably the concentration range needed for characterising the detector response, problems with CO_2 interference, the total number of components in gas mixtures used for intercomparisons and audits as well as systematic differences between calibration scales. The latter have underlined the necessity of future intercomparisons.

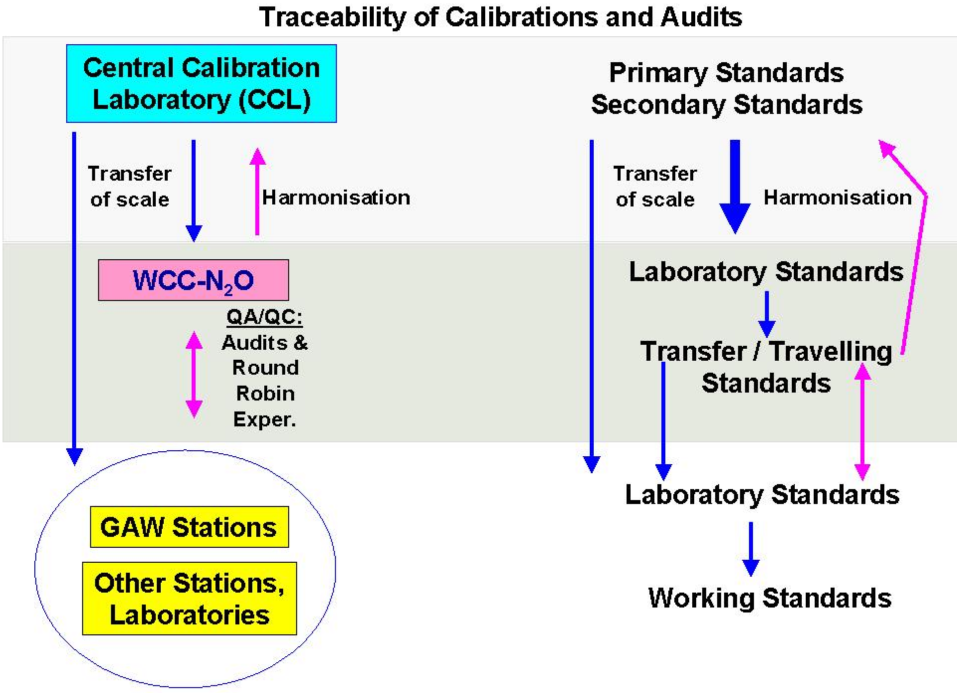

Figure 3: Schematic illustrating the traceability of calibrations and audits. The left part shows the relationsships in terms of institutions involved, the right part explains the hierarchy of standards.

6.4.6 Quality Control and Data Quality Objectives

The major elements of N_2O quality control within GAW involve:

- Acquisition of a sufficient number of calibrated laboratory standards by a station: This is primarily relevant for stations outside the CMDL or AGAGE network.
- Internal quality control at a station.
- Regular comparisons of working standards with laboratory standards traceable to the reference scale.
- Ongoing intercomparisons of a station with another station or laboratory (ambient air samples).
- Round-robin experiments, organised by the WCC-N_2O. Small-scale experiments will involve only GAW stations, while large-scale round-robins will also include other networks and laboratories.
- Audits to be performed by the WCC-N_2O, with focus on stations outside the well-established networks (e.g. new GAW stations).

Up to now, no formal Data Quality Objectives for N_2O within GAW have been issued. Preliminary numbers were given for precision and accuracy in WMO Report No. 80 [1]. With limits for precision and accuracy of only 1 and 2 %, respectively, these DQOs do not meet the requirements of the scientific community. Moreover, the request of only three calibration levels between 280 and 320 ppb in that report is insufficient given the present-day ambient mole fractions. Therefore the upper limit needs to be increased, and at least five levels of N_2O mole fractions should be involved. In consequence, an important point of the work of both WCC-N_2O and SAG GG is the definition of refined DQOs. Details of the current requirements and future goals, as agreed upon, are given elsewhere in this report.

Moreover, a modification of the terminology involved is suggested. The future use of terms related to data quality should be in agreement with ISO definitions [5, 6]. In particular the widely used term "accuracy" (which is only a qualitative concept), should be replaced by the concept of "uncertainty" (for details see [6]). The assessment of uncertainty with respect to calibration standards, individual analytical results as well as network comparability will be requested.

6.4.6 Summary and conclusions

In contrast to CO_2, coordinated efforts for N_2O data quality within GAW were lacking in the past. However, based on recent decisions and initiatives, WMO GAW with its facilities, such as QA/SAC and WCC, now offers a platform for global QA/QC activities. At present, an uncertainty value < 0.5 ppb N_2O is achievable for network comparability. Efforts need to be made to reduce these limits according to the requirements of the scientific community. In order to avoid misunderstandings and misinterpretations, specific terms, such as precision, accuracy, etc., should be clearly defined based on ISO guidelines. The final establishment of the SOP for N_2O including DQOs is an urgent task. On all issues related to DQOs, definite recommendations of the GAW SAG GG are needed as a basis for the future work.

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[6] ISO Publications, Guide to the expression of uncertainty in measurement, International Organization for Standardization (Geneva, Switzerland), ISBN 92-67-10188-9, 110 p. (1995). The abbreviation of this title is GUM.

6.5 Measurements of methane and carbon dioxide isotopes for London air and local sources using Micromass Trace Gas

R. Fisher, D. Lowry, S. Sriskantharajah and E. Nisbet

Abstract

The Micromass Trace Gas has been used to measure $\delta^{13}C$ of methane in a NOAA standard tank with a precision of better than 0.22‰ (1σ) for ten consecutive analyses. $\delta^{13}C$ and $\delta^{18}O$ of CO_2 were also measured for the same tank with precisions of up to 0.08‰ and 0.09‰ respectively for 10 analyses. The precision is not yet good enough for background studies, but its rapid analysis time of 16 minutes and the small sample volume required (100ml) make it particularly useful for diurnal studies to identify local sources and measure the regional build-up of emissions. Two diurnals have been carried out, one measuring $\delta^{13}C$ of CH_4 and the other measuring $\delta^{13}C$ and $\delta^{18}O$ of CO_2. There was a very close correlation between mixing ratios and isotope measurements. Source calculations suggest that the major local sources of methane were landfill sites and gas distribution losses, with vehicle exhaust emissions significantly enriching the methane in ^{13}C during the early evening rush hour. The main source of CO_2 was fossil fuels. Source studies have also been carried out at a landfill site with samples of up to 270 ppm of methane analysed by the Trace Gas and $\delta^{13}C$ values ranging from –58.9‰ to –13.3‰ depending on the amount of oxidation of the methane. The aims are to improve the precision by making minor modifications to the system until it is better than ±0.1‰ to allow background station measurements at high Northern latitudes and also to automate the system so that it can be used for more diurnal measurements.

6.5.1 Introduction

Measurement of the stable isotopes of methane and carbon dioxide is an important way of determining the sources of the gases and verifying the accuracy of emissions inventories. The method to extract methane from air samples and then convert the methane to CO_2 that has been used in the atmospheric laboratory at Royal Holloway since 1995 is a National Institute of Water and Atmospheric Research (NIWA)-designed cryogenic extraction line *[Lowe et al. (1991) and Lowry et al. (2001)]*. The technique has a mean precision of ±0.03‰ on replicate $\delta^{13}C$ analyses and ±0.04‰ on long-term measurements of standards. However conventional techniques such as this are time consuming (approximately 2 hours to analyse one sample) and require large volumes of air (40-80 litres), which is often costly and inconvenient to transport. The Micromass (now GV Instruments) Trace Gas which was installed in the laboratory at Royal Holloway in March 2003 uses much smaller air samples (100ml for background air) and a quicker analysis time (16 minutes for CO_2 or CH_4 analyses), but with a precision of approximately 0.3‰. It is coupled to an IsoPrime continuous flow mass spectrometer. Other labs have also strived to measure methane isotopes in background air on small samples and employ similar chromatographic techniques to the Trace Gas, but have required purpose-built prototype extraction systems *[Rice et al. (2001) and Miller et al. (2002)]* and are not based around a commercially available preparation system.

The laboratory at Royal Holloway is situated 32km WSW of the centre of London, on the first significant incline west of the city (52˚25.6'N, 0˚33.7'W) and is ideally situated to measure fairly clean, near background air when it comes from the South-West and London air from the East. During high pressure anticyclonic events methane mixing ratios often exceed 3000 ppb and carbon dioxide sometimes exceeds 500 ppm as an inversion builds up over the London basin. Measurement of the mixing ratios and isotopes of methane and carbon dioxide throughout the night during these night-time events and comparison with wind direction measurements can give an indication of the sources of the gases in the local area *[Zondervan et al., 1996]*. These diurnal experiments have been carried out in the past by collecting air in 22 litre tanks at approximately 2 hour time intervals and later analysing these tanks on the cryogenic extraction line. From these experiments the main local methane sources has been identified as landfill emissions at –52‰ *[Lowry et al., 2001]* and the main CO_2 source as fossil fuel emissions at –30‰ *[Holmes, 2000]*. The fast analysis time of the Trace Gas means that it can be used to measure air samples more frequently, enabling individual peaks from local plumes to be identified more clearly as the wind changes direction throughout the night.

6.5.2 Set-up of the system

Figure 1 shows the set-up of the Trace Gas system when it is used for the analysis of $\delta^{13}C$ of methane. A flow of helium transports the air sample through magnesium perchlorate and Carbosorb traps to remove water and carbon dioxide and a Sofnocat catalyst which oxidises carbon monoxide to carbon dioxide. The remaining impurities are then trapped in a liquid nitrogen filled cryotrap. The methane is oxidised to carbon dioxide in the combustion furnace at 900˚C which contains a braided platinum, nichrome and copper wire catalyst. The resultant CO_2, created by the oxidation of methane, is trapped and cryofocused in the liquid nitrogen and passes through a Nafion membrane to remove any more water. The sample then goes into the GC column and to the IsoPrime mass spectrometer for isotopic analysis. The system was initially calibrated by analysing samples of a CO_2 standard from ECN (Petten, Holland) with a known isotopic composition.

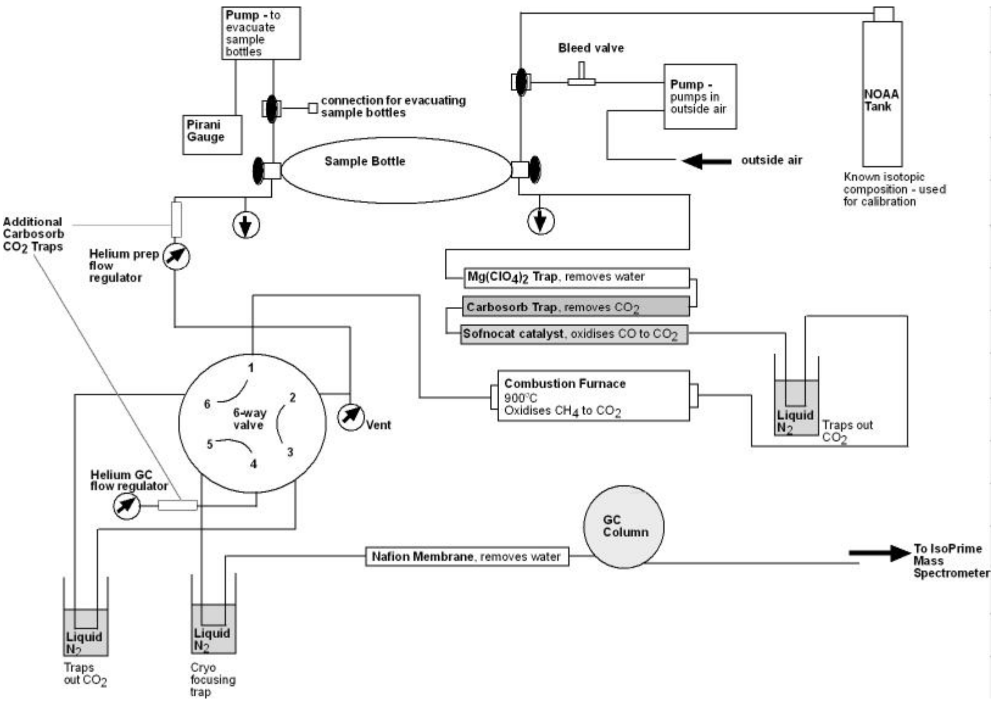

Figure 1: Set-up of the Trace Gas for CH_4 analysis.

A system has been set up so that a 150cm^3 sample bottle is connected to, and evacuated by, a rotary pump and also connected to a tank of known isotopic composition (a National Oceanic and Atmospheric Administration (NOAA) standard tank or an internal secondary standard). The tank is measured at regular intervals (e.g. every 4th analysis) and allows corrections to be made to the samples being analysed in between. This is because for methane the values measured for a particular tank usually become more depleted in ^{13}C throughout the day. The sample bottle is also connected to a pump which pumps in air from an inlet on the roof of the building allowing measurements of outside air to be made.

6.5.3 Reproducibility

Two NOAA tanks have been analysed for the $\delta^{13}C$ and $\delta^{18}O$ values of CO_2. Some of the results are shown in table 1. The precision is better for a group of samples run consecutively. The precision for $\delta^{13}C$ of CO_2 has improved since using a steel 150cm^3 sample bottle connected directly to the NOAA tank, rather than the glass 100cm^3 bottles initially used.

Table 1: CO_2 Analysis of the NOAA tanks.

Tank	**Date**	**Number of Analyses**	**Sample Volume**	**[CO_2] (ppm)**	**Average $\delta^{13}C$ (‰)**	**Precision (1σ) (‰)**	**Average $\delta^{18}O$ (‰)** **V-PDB-CO2**	**Precision (1σ) (‰)**
NOAA 2	31/7/03	3	100 cm^3	420.1	-12.04	±0.03	-5.24	±0.03
NOAA 3	30/7/03 - 7/8/03	10	100 cm^3	372.1	-8.71	±0.15	-1.17	±0.09
NOAA 3	8/8/03 - 14/8/03	10	100 cm^3	372.1	-8.64	±0.16	-1.07	±0.21
NOAA 3	22/8/03 - 28/8/03	10	150 cm^3	372.1	-8.47	±0.08	-1.22	±0.12
NOAA 3	10/10/03 - 23/10/03	10	150 cm^3	372.1	-8.41	±0.08	-1.44	±0.27

The NOAA 3 tank is also regularly analysed for the $\delta^{13}C$ value of CH_4. There has been a trend in the results over the last 7 months, with the readings gradually becoming less negative. The reason for this needs to be investigated further, but may be due to the oxidation ability of the catalyst being reduced over time. In total between April and October 2003, 223 measurements have been taken of the NOAA 3 tank over 40 days, with an average $\delta^{13}C$ of –46.3‰ ± 1.5‰. However the precision for CH_4 is better for a group of samples taken on the same day as shown in table 2. This could be due to different degrees of furnace oxidation, slightly different flow rates or a memory effect, most likely caused by the catalyst in the furnace. Figure 2 shows variations in $\delta^{13}C$ of CH_4 for consecutive analyses of the NOAA 3 tank on the same day. The value obtained for this tank using the conventional cryogenic extraction line and PRISM mass spectrometer was –47.2‰.

Table 2: CH_4 analysis of the NOAA 3 tank.

Date	Average $\delta^{13}C$ (‰) from 10 measurements	Precision (1σ)
15/7/03	**-47.21**	**±0.22**
4/8/03	**-48.02**	**±0.21**
6/8/03	**-47.68**	**±0.15**

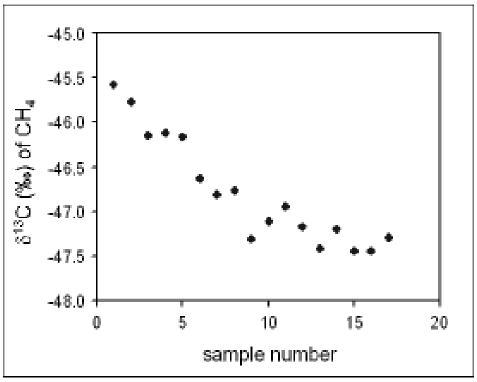

Figure 2: Variations in $\delta^{13}C$ of CH_4 for consecutive analyses of the NOAA 3 tank (15/7/03).

6.5.4 Diurnal Results

The Trace Gas has been used to measure isotopes of methane and carbon dioxide during two diurnal experiments. During the first, from the 4th to 5th August 2003, $\delta^{13}C$ of CH_4 was measured in samples of outside air at approximately 30 minute intervals. The NOAA 3 tank was also measured at regular intervals and the offsets of these results from the true $\delta^{13}C$ value of the tank were used to correct the outside air measurements. The $\delta^{13}C$ values were compared with methane mixing ratio measurements made at the same time by the gas chromatograph (HP 5890 GC-FID) in the lab. The results are shown in figure 3. There appears to have been a strong correlation between mixing ratio and $\delta^{13}C$ of methane with the $\delta^{13}C$ decreasing to a minimum value of –48.7‰ as the mixing ratio of methane increased to 2340 ppb, peaking just before 04.00 GMT. There could have been up to five minutes difference in the timings of the measurements of the mixing ratios and isotopes. A Keeling plot (figure 4) and source calculations for this diurnal (figure 5) indicate that the sources had $\delta^{13}C$ values of between –37.9‰ (typical of gas leaks) and –54.0‰ (landfill emissions). The methane was most enriched in ^{13}C in the early evening, during the rush hour, suggesting that at this time vehicle exhaust emissions are a measurable local source of methane. The average through most of the night (00.00 GMT to 06.00 GMT) was –52.7‰. This implies that landfill sites were the dominant source of methane.

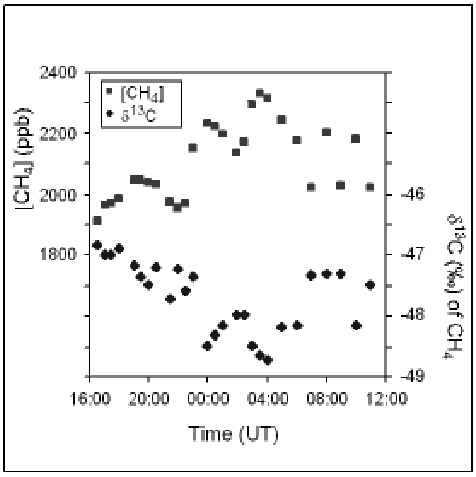

Figure 3: Methane mixing ratios and isotopes measured during diurnal 1, 4th – 5th August 2003.

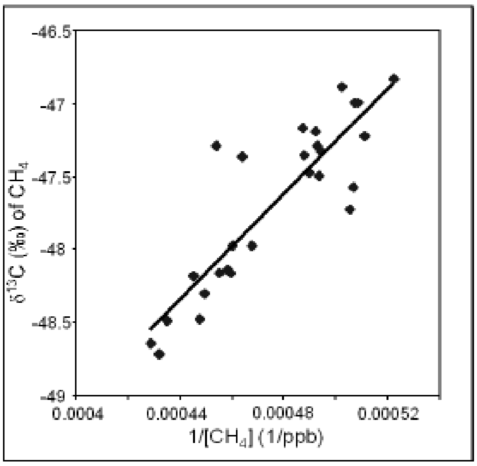

Figure 4: Keeling plot for methane measurements during diurnal 1, 4th – 5th August 2003.

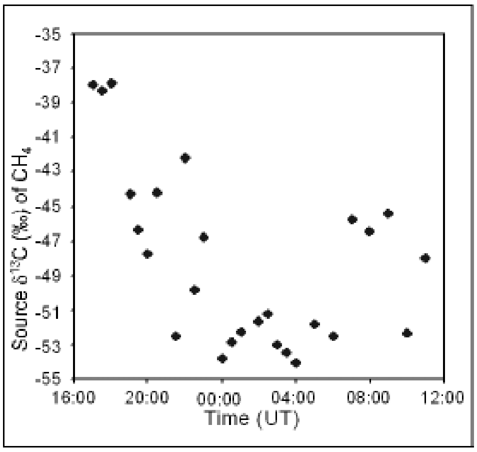

Figure 5: Methane source calculations for diurnal 1, 4th – 5th August 2003.

Another diurnal was carried out on the 4th to 5th September 2003 in which CO_2 isotopes were measured at approximately 30 minute intervals. Graphs of CO_2 mixing ratio, which was measured on the LICOR 6252 NDIR analyser in the lab compared with $\delta^{13}C$ of CO_2 and $\delta^{18}O$ of CO_2 are shown in figures 6 and 7. Again there is a strong correlation between the mixing ratio and isotope measurements, with a sharp increase in mixing ratio corresponding to a decrease in the $\delta^{13}C$ and $\delta^{18}O$ values starting shortly after 04.00 GMT.

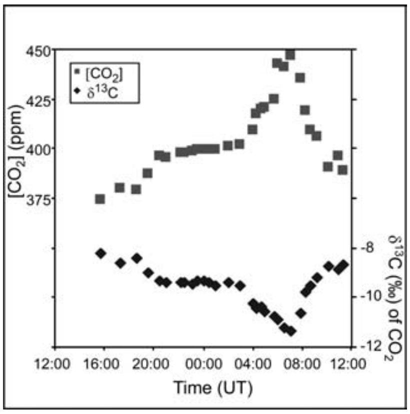

Figure 6: Carbon dioxide mixing ratio and δ^{13}C measurements for diurnal 2, 4th – 5th September 2003.

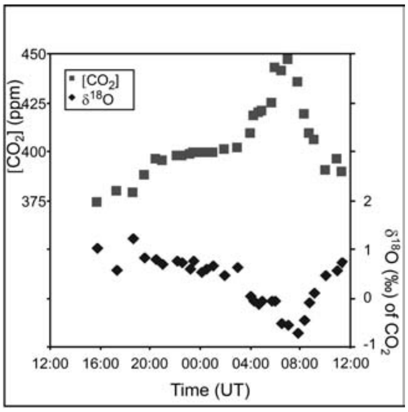

Figure 7: Carbon dioxide mixing ratio and $\delta^{18}O$ measurements for diurnal 2, 4th – 5th September 2003.

The Keeling plot of the measurements made in this diurnal is shown in Figure 8. The R^2 value of the line of best fit is 0.92. The baseline intercept of –31.0‰ implies that the source emissions are dominated by fossil fuels, and the top line intercept of –22.5‰ suggests that there is also a significant biological input to the CO_2 emissions. The average source $\delta^{13}C$ is –27.1‰ and throughout most of the night the measurements were close to this value. Variations in the calculated source $\delta^{13}C$ throughout the diurnal are shown in figure 9. The minimum source value of –34‰ (a fossil fuel signature) occurred at around 17.30 GMT, close to the evening rush hour. The minimum values, indicating biological sources, were measured during the late morning.

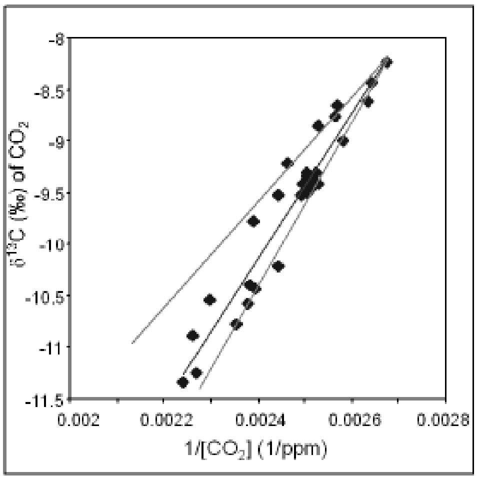

Figure 8: Keeling plot of CO_2 measurements during diurnal 2, 4th – 5th September 2003.

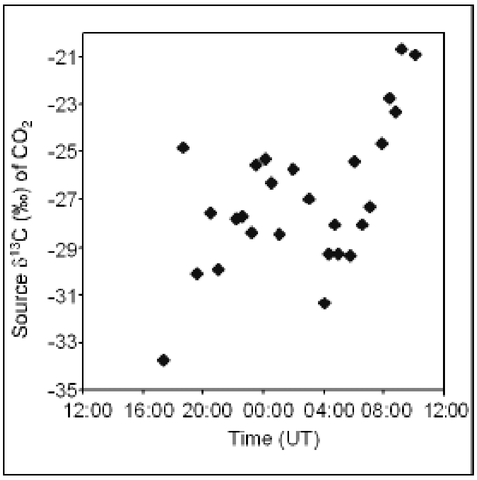

Figure 9: Carbon dioxide source calculations for diurnal 2, 4th – 5th September 2003.

During the same diurnal, air was collected in 3 litre tanks for later analysis of methane isotopes on the Trace Gas. The results are shown in figure 10, along with the half hourly methane mixing ratio measurements recorded on the gas chromatograph. The methane measurements follow a similar pattern to the carbon dioxide measurements with a sharp increase in mixing ratio after 04:00 GMT corresponding to a decrease in the δ^{13}C values. The calculated source δ^{13}C for the tanks during the night ranged from –50.9 to –52.9, which supports the results from the first diurnal study, implying that landfill sites are the major local methane source.

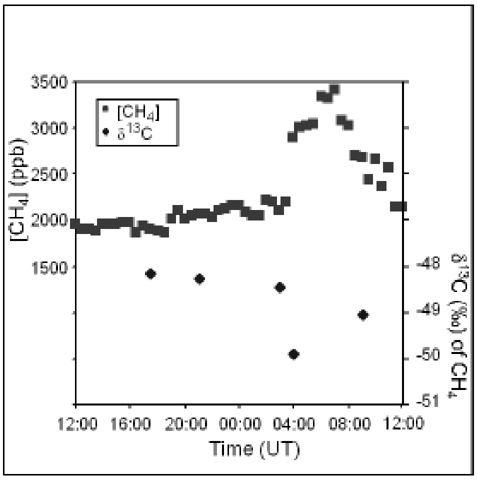

Figure 10: Methane mixing ratios and δ^{13}C measured in the tanks collected during diurnal 2, 4th – 5th September 2003.

6.5.5 Source Studies – Landfill Site Emissions

As the precision of the Trace Gas has not yet reached the level required for background measurements, it is first being used for source studies. Measurements of the isotopes of methane in air samples taken both above and below ground have been made at Norlands Lane Landfill site, which is located 3.2km ESE of Royal Holloway. Samples have been taken at bi-monthly intervals over the last year in order to investigate the seasonal variations in methane emissions and the amount of oxidation that subsequently occurs before the methane leaves the soil. The results are shown in table 3. The results highlight the range of mixing ratios and delta values that the Trace Gas can be used for with a reasonable precision.

Table 3: CH_4 Analysis of Air Samples from Norlands Lane Landfill Site.

Collection Date	Depth (cm)	$[CH_4]$ (ppb)	Sample Volume (cm^3)	Number of Analyses	Average $\delta^{13}C$ of CH_4 (‰)	Standard Deviation (1σ)
26/11/02	10	9167	100	3	-55.07	0.16
	25	2026	100	2	-51.95	0.40
27/1/03	0	2491	100	3	-50.77	0.31
	10	2343	100	2	-51.18	0.13
	20	2125	100	2	-50.67	0.24
	35	1995	100	2	-48.77	0.01
12/3/03	0	1875	100	3	-49.94	0.24
	10	2117	100	2	-49.86	0.04
23/5/03	5	270461	1	4	-43.89	0.32
	10	205739	1	2	-43.86	0.52
8/8/03	0	2167	100	3	-47.90	0.10
	10	6009	100	4	-13.34	0.42
	20	51900	3.2	3	-16.08	0.03
21/10/03	0	27675	3.2	3	-58.86	0.14
	5	44473	3.2	4	-58.53	0.27
	15	42116	3.2	4	-22.19	0.46
	20	37282	3.2	3	-32.88	0.44
	30	31323	3.2	3	-51.46	0.19

The methane emissions and amount of oxidation show strong seasonal variations and are very dependent on the weather conditions when the samples are taken. The most oxidation occurred at a depth of 10 to 20 cm, in the summer when the ground was drier. For example the August samples were taken during high pressure conditions when the weather was particularly hot (32ºC). Under these conditions the methane was trapped below the baked cap of the landfill and much more oxidation would have taken place than usual. When the October samples were taken there was a leaking borehole 10 metres away which meant that the air above ground had a particularly high methane concentration and more negative $\delta^{13}C$ value, and some of this methane penetrated downwards into the top of the soil, affecting the 5cm results.

6.5.6 Development Plans

The major aim is to improve the precision of the Trace Gas so that precision for methane approaches that for carbon dioxide, but without major changes to the commercial unit, to allow it to be used for background studies as well as the source studies it is currently being used for. The aim for the next 6 to 12 months is to get a precision of better than ±0.1‰ for $\delta^{13}C$ of CH_4 and $\delta^{13}C$ and $\delta^{18}O$ of CO_2. Parameters that could initially be varied are the timings of valve changes and flushing in the process, flow rates, furnace temperature and catalyst (material and degree of oxidation). The system is also being adapted so that it can automatically measure outside air samples, for example at time intervals of 30 minutes. This works at present with manually operated valves, but automated valves would mean that a more continuous record could be obtained leading to a better understanding of local and regional methane sources. Another aim is to develop a pyrolising interface to measure the D/H ratio of CH_4.

6.5.7 Acknowledgements

This research is funded by the UK Natural Environment Research Council (NERC) and GV Instruments (formerly Micromass). The atmospheric laboratory at Royal Holloway has been supported since 1994 by grants from the EEC, NERC and INTAS. Andy Phillips and colleagues at GV Instruments are to be thanked for setting up and helping to develop the instrument.

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Since this manuscript was written in 2003 the system has been greatly improved by continued development work. As of April 2005, precisions of 0.05‰ for $\delta^{13}C$ ***of*** CH_4***, 0.03‰ for*** $\delta^{13}C$ ***of*** CO_2 ***and 0.05‰ for*** $\delta^{18}O$ ***of*** CO_2 ***have been achieved on 10 consecutive analyses of a standard tank. The improvements were made with the use of a fixed automated inlet system developed by RHUL and GV Instruments.*** CH_4 ***reproducibility has been further improved by using a palladium powder on quartz wool catalyst in the furnace instead of the Pt/Cu/NiCr catalyst. The new catalyst does not require oxidation as it uses oxygen from within the air sample and hence the depletion in measurements throughout the day discussed in section 6.5.2 has been eliminated.***

6.6 Meth-Moniteur - Methane Monitoring in the European Union and Russia

Meth-MonitEUr Group

6.6.1 Background

Meth-MonitEUr aims to create a European monitoring programme for atmospheric methane. This includes measurement of methane concentration in chosen locations spread across Eurasia, with attention to major source areas (both industrial regions and also gasfields, especially Russia). Measurement of methane isotopes allows the study and location of methane sources by character and seasonality. This is only done in a small number of groups.

The key technical issues are in intercomparison between laboratories, and in sharing methodology. Most EU methane groups operate on a very small scale, and are poorly funded. Thus though best-practice is well known, financial limits mean that many groups have problems maintaining anything more than the most basic measurements. In these circumstances, quality not quantity of results is the first priority.

6.6.2 Achievements

Methane monitoring is under way at a number of sites across Europe: Ireland, UK, Svalbard, Ascension, France, Germany, Poland, Finland, and Russia. This work is building up long-term time series for mixing ratio. At a small number of sites the isotopic ratio of carbon in ambient methane is also regularly measured. Field campaigns have been carried out in the Ob River gas fields and wetlands, one of the world's most important methane-emitting regions and source of a very significant and increasing part of Europe's gas supply.

Meth-MonitEUr has supported intercomparison of results from different groups, by round robin exercises of measurement of specific samples, to create a data set that can be used seamlessly in modelling. This is crucial – without the tedious intercomparison effort, the data are only of local use. With intercomparison, a genuine European data set can be created, and used globally if intercompared with US, Canadian, and Australian/NZ work.

The first Round Robin experiment is complete, involving analysis of the same sample at Heidelberg, Paris, London, Svalbard, Krakow, Helsinki and St Petersburg. Results, given in a separate report are very encouraging. This is the critical step in creating a seamless European data set. The second round which includes also isotopes is under way, with plans to link with US and Australian/NZ work.

Modelling methane in the air, by regional and global models, is crucial if the greenhouse is to be understood and agreements like Kyoto are to succeed. Our work is designed both to use the data collected, and also to pinpoint data requirements by close interaction between monitoring and modellers. Modelling is not a prime focus of the project, but nevertheless integral to its success. Models are used to interpret the acquired data and also to simulate the temporal and spatial variabilities that are be expected in the real world. Such studies are then statistically analysed to determine necessary sampling densities and data qualities required to create a data set that would capture real-world features similar to those modelled. The use of model in this way is essential when designing a cost effective monitoring network capable of resolving the questions society needs to be answered.

Modelling needs have been identified: the requirement is for high precision intercompared data – here lies the significance of our intercomparison exercises. If there is a difference in calibration between two stations, then the data set is useless as the step-fault between national datasets corrupts the results of modelling.

The ultimate users are policy makers. Results from models using the methane data set will be very relevant to policy decisions. Assessing sources on local, regional and global scales allows understanding of methane's contribution to global warming. Thus the more distant end-users are those involved in greenhouse gas decision making – Kyoto and UNFCCC.

The project has created an effective methane community across Europe, and much progress has been made in the work of intercomparing our results and making our data useful on a pan-European scale.

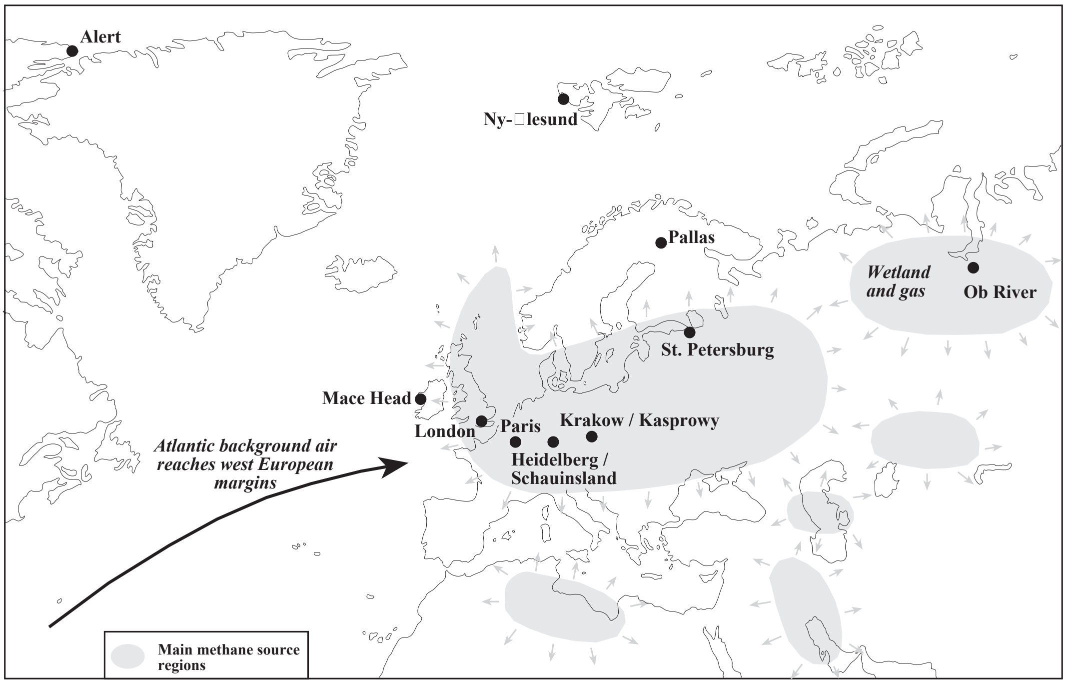

Figure 1: The Meth-MonitEUr sites.

6.7 Analyser for CO_2 and O_2 on Jungfraujoch, Switzerland

Markus Leuenberger

Abstract

We have built an oxygen analyser which is capable of measuring the atmospheric oxygen concentration with high precision (i.e. better 5 permeg for a time integration of 120 seconds). Further, this system allows us to compare two different measuring principles: (1) the paramagnetic method with the (2) the fuel cell method consisting of two different fuel cell brands. The methods show good agreement on short-term variations. However, on the long-term scale (hours to days), the two fuel cell brands behave strongly different, one showing a distinct time trend. This trend behaviour can be taken care off by applying standard gases frequently. In order to maintain the high precision on the permeg level, it is important to control pressure, temperature and gas flow to their limits.

6.7.1 Introduction

Carbon budgeting studies are of high importance in the light of the Earths climate variability. The increasing amount of fossil fuel led to a significant increase of carbon dioxide during the last 150 years as documented in several publications. In order to differentiate between the natural and anthropogenic sources of carbon dioxide and their variability additional information is needed. Such information can be gained from carbon isotope records as well as high precision oxygen measurements since both parameters can quantitatively been used for disentangle different carbon dioxide sources. Carbon isotopes are commonly used to quantify the influence of the biosphere whereas oxygen values are a measure for the oceanic source component. Within the framework of the EC-project AEROCARB, we have started oxygen concentration determination on ambient air samples. Our method, which we applied was based on the mass spectrometric principle developed by [*Bender et al.*, 1994]. However, we built our own inlet system mainly using fused silica tubing. The advantages are that the memory effects driven by adsorption/desorption processes at metal surfaces are strongly damped. Therefore, the equilibration of gas with the exposed surfaces after switching from standard to sample, that generally differ in their amounts of oxygen, is quickly reached [*Leuenberger et al.*, 2000]. The precision of our oxygen analyses is about 5 permeg. Since this method is limited only to flasks analyses of remote stations, we started a project to monitor oxygen amounts continuously.

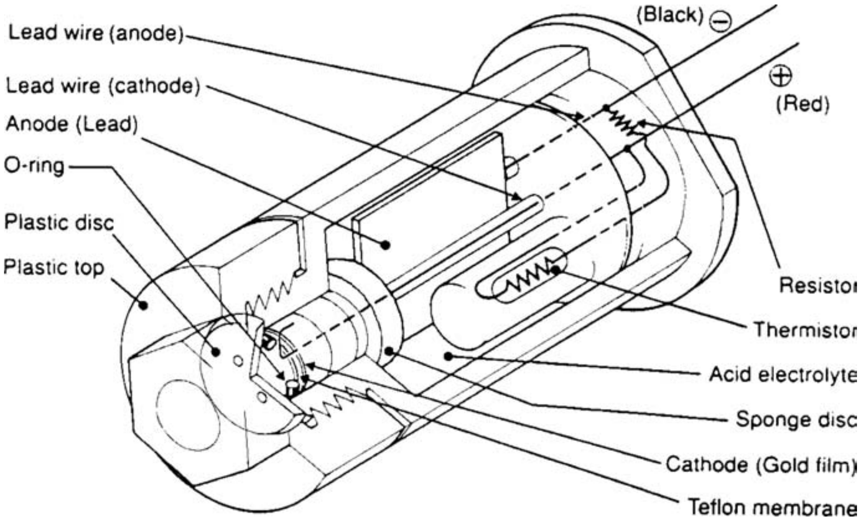

Figure 1: Principal of the fuel cell technology.

6.7.2 Methods

After discussions with colleagues that already made experiences with online oxygen systems, we decided to use and compare the two generally used methods: (i) the paramagnetic cells and (ii) the fuel cells. (i): The paramagnetic cell is based on the strong paramagnetism of oxygen. The oxygen molecules are distorted from their main path through a magnetic field. This distortion of the oxygen molecules lead to a partial pressure gradient within the cell and a displacement of a dumbbell. This movement is counterbalanced by applying an electric current through a wiring wrapped around the dumbbell. The current applied is linearly dependent on the oxygen concentration present in the cell. (ii): The principle of the electro-chemical cell or fuel cell is based on an oxidation of a light acidic fluid within the cell producing a small electron current, which is transformed into a small voltage in the milli-volt range over a resistance. The output of the fuel cell is varies linearly with the oxygen content of the sample. Figure 1 shows and documents the fuel cell.

These methods are available as commercial analysers but with a far to large uncertainty range. It was proved by [*Manning et al.*, 1999] that such systems can be trimmed to yield precisions down to the permeg level when controlling the temperature, pressure and flow rate to an extremely high degree. We followed this approach with one modification that the flow rate was controlled not by a conventional flow controller but a precisely controlled pressure gradient along the measuring cell. Figure 2 shows the layout of our system.

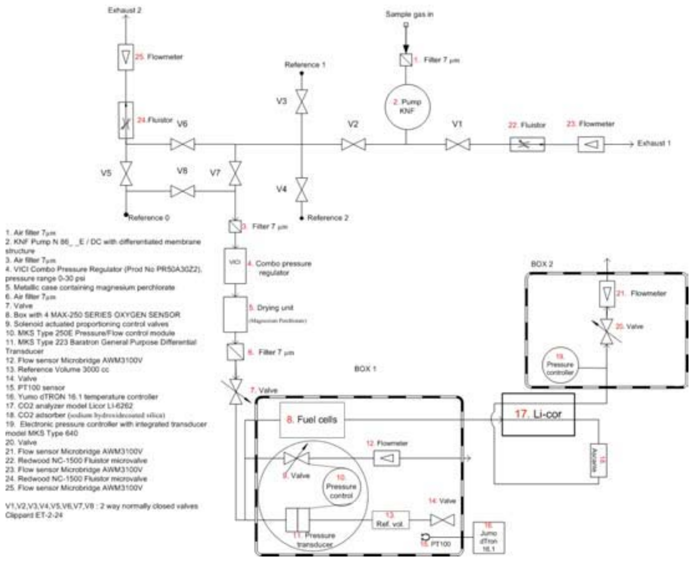

Figure 2: Layout of our combined O_2 – CO_2 analyser.

6.7.3 Results

So far, we have only test measurement, including sensitivity tests of the two methods on temperature, pressure and flux. Based on these dependencies we control the temperature to one hundreds of a degree, the pressure to 1 microbar and the pressure gradient along the measuring cell defining the gas flux to a few microbar. These stabilisation leads to a measurement precision of a couple of permeg for the oxygen concentration. Prior to that, we looked at the stability of our electronic unit. Figure 3 shows the variations seen when applying a constant voltage to the electronics rather than the output of the oxygen cells documenting the electronic noise. The magnitude is of the order of 5 permeg, however, this test was performed without temperature control.

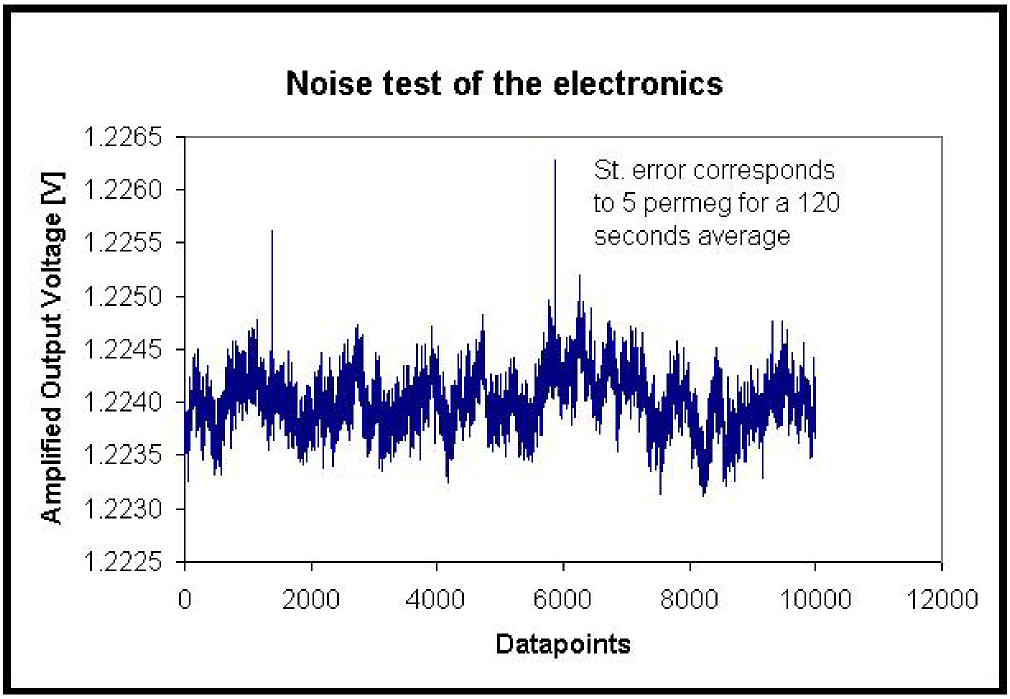

Figure 3: Noise of the electronic unit.

A first comparison between the two principles, fuel cell and paramagnetism, showed good agreement over a half day period (Figure 4, note that the different absolute values for oxygen for the two methods are due to uncalibrated measurements). The fluctuations are mainly temperature and pressure driven, documenting a very similar dependence of the both methods on these two variables. The variations are far above the seasonal atmospheric oxygen changes, strengthening the need for a highly pressure and temperature controlled unit for such analyses.

We measured the oxygen concentration of standard air to look at short- and long-term stability of the analyser cells. Figure 5 shows the array of four fuel cells of such a unit.

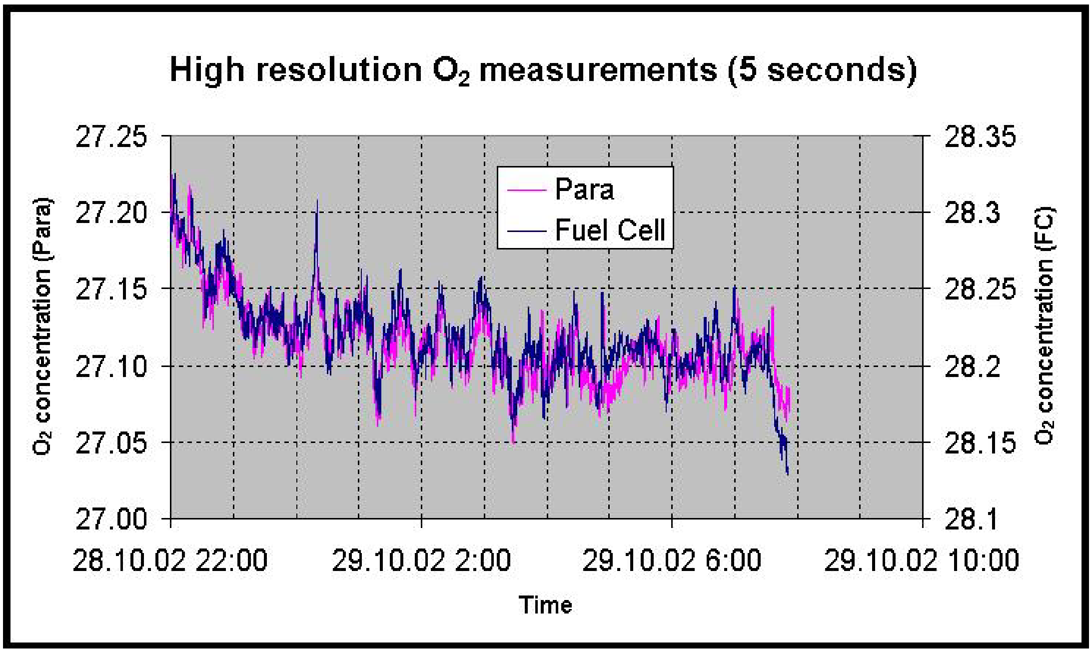

Figure 4: Comparison between the paramagnetic (light) and fuel cell (dark) method.

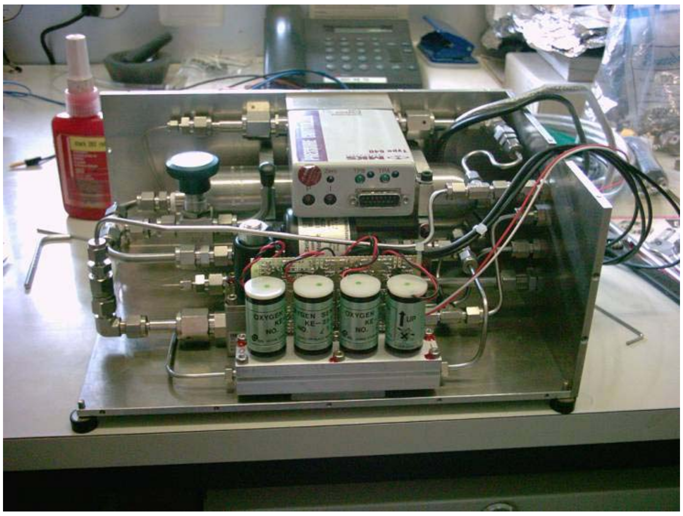

Figure 5: View of the fuel cell setup.

In Figure 6 and 7, a comparison of the standard gas response of two different brands of fuel cells are shown. Distinct differences can be seen in the long-term behaviour of the two fuel cell brands (Figaro and Maxtec). Maxtec cells exhibit a clear long-term trend of more than thousand permeg, whereas the Figaro cells are much more constant. However, the short-term variability (i.e. measurements after removing the long-term trends) is better for the Maxtec cells (15-30 permeg) compared to 40 permeg for the Figaro cells for 10 second intervals. This corresponds to about 5-12 permeg for a two minute interval commonly used for continuous oxygen measurements.

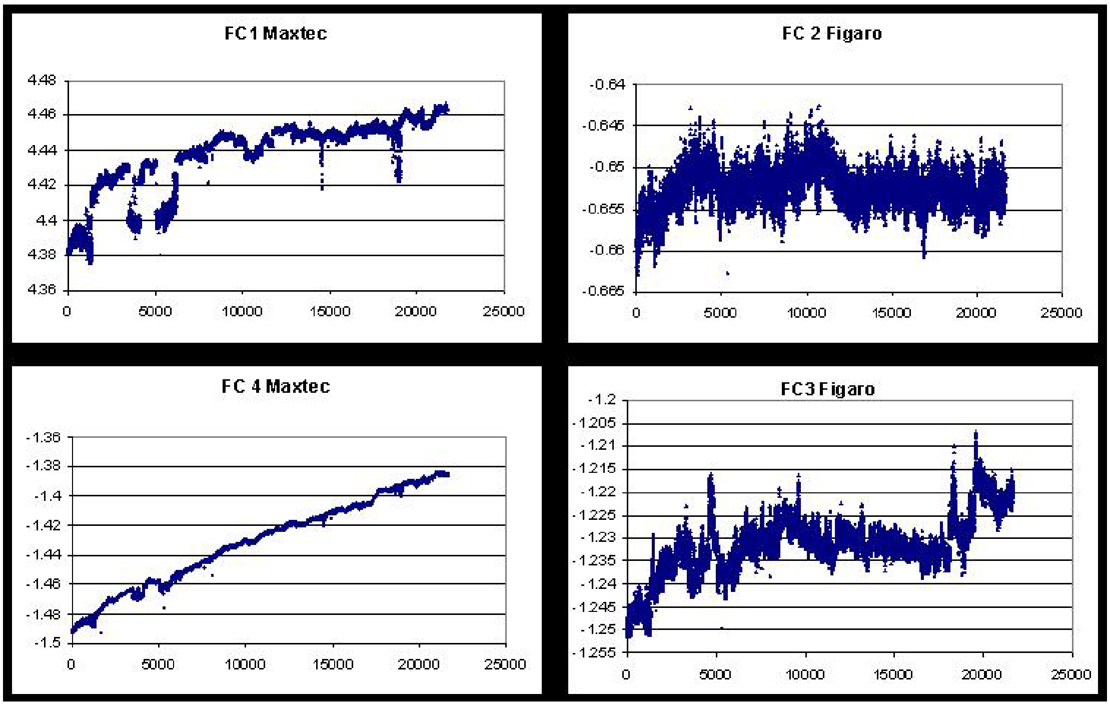

Figure 6: Long-term variations of two different brands of fuel cells. Units of readings are milli-volts on the y-axis and seconds on the x-axis.

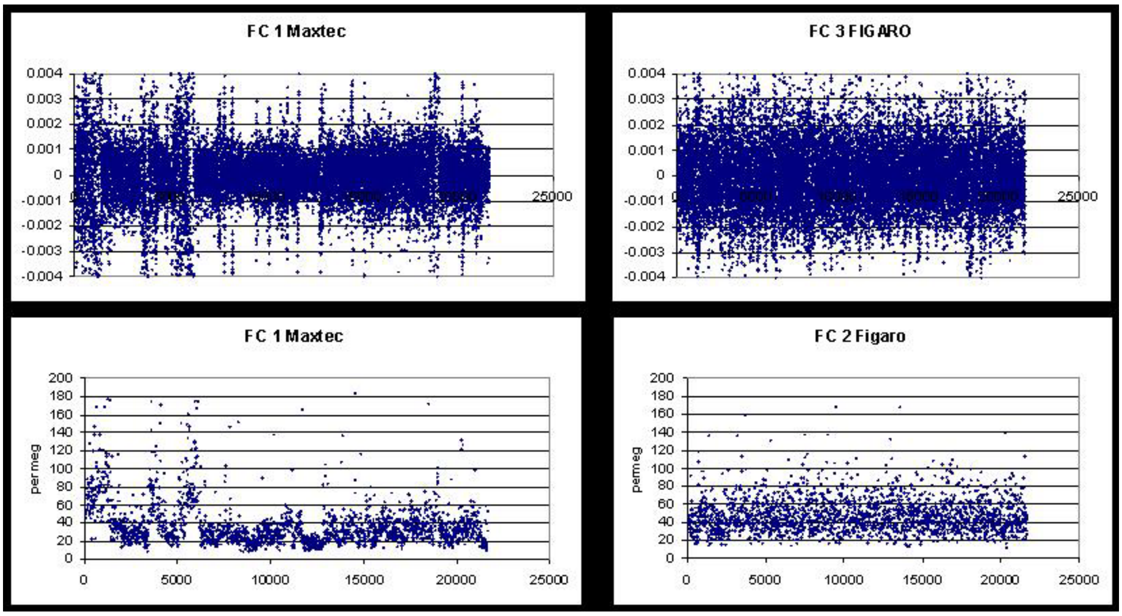

Figure 7: Short-term variations of two different brands of fuel cells. Units of readings are milli-volts on the y-axis and seconds on the x-axis upper panels and permeg against seconds on lower panels.

6.7.4 Perpectives

Shortly, we will install a continuous system at Jungfraujoch. Based on the ongoing flask sampling for oxygen and carbon dioxide concentration determination, we hope to learn much about the behaviour of our online system. Additionally, we shall carefully compare the results from both applied methods.

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7. NATIONAL REPORTS

7.1 THE NETWORK FOR BACKGROUND CO_2 MEASUREMENT IN ITALY

F. Apadula, F. Artuso, P. Chamard, F. De Nile, A. di Sarra, L. Lauria, A. Longhetto, F. Monteleone, S. Piacentino, R. Santaguida and C. Vannini

7.1.1 Introduction

Measurements of background CO_2 concentration are carried out in Italy at three remote stations, by three different Institutes: CESI operates at Testa Grigia Observatory, an alpine station at an altitude of 3480 m; the Air Force Meteorological service runs a station at 2165 m, Monte Cimone, in the Appennines; ENEA performs measurements at the remote island of Lampedusa, in the central Mediterranean. The three Institutes use the same technique for the determination of the CO_2 concentration, and WMO standards. The data sets with a brief description of the measurement methods used at the three stations are reported in this paper.

Figure 1: Italian stations for background CO_2 concentration.

7.1.2 The CESI Station for greenhouse gas measurements at Plateau Rosa

On the initiative of CESI, a continuous monitoring programme of atmospheric concentration of greenhouse gases was started at the CNR-IFSI-Torino (Institute of Inter-planetary Space Physics - Turin Section, National Research Council) “Testa Grigia” observatory (Plateau Rosa) in April 1989. The Plateau Rosa station is located in the North-Western Italian Alps (45.9°N, 7.7°E, 3480 m a.s.l.), and is one of the highest atmospheric monitoring station all over the world. Due to its elevation and geographical position, Plateau Rosa is frequently representative of the atmospheric background conditions. In 1989 a flask sampling programme was started in collaboration with the Italian Meteorological Service to measure the concentration of atmospheric CO_2. Air samples were collected weekly, and the concentration of carbon dioxide was determined at the laboratory of Mt. Cimone. Starting from April 1993, in situ continuous measurements of CO_2 have been executed by CESI at Plateau Rosa station by means of a NDIR analyser [Apadula et al., 2003]. Concentration of CH_4, N_2O, CFC-11 and CFC-12 (beside other atmospheric parameters) are also measured at the station.

Measurement technique: Air samples were collected in two pairs of 2-L stainless steel electropolished flasks. Flasks were filled to about 300 kPa. From April 1993 up to now the continuous measurements have been carried out by means of a non-dispersive IR analyser (Siemens ULTRAMAT 5E). A water trap at –70°C has been utilised to dry the air samples before the measurements. The CO_2 flask measurement was performed in parallel with continuous measurements up to 1997; the comparison between the two data series resulted in a good agreement.

Calibration: The CO_2 concentration is referred to the international X85 WMO scale. Nowadays the analyser is calibrated once a year with 5 international primary standards (CMDL/NOAA in X2002 WMO scale). Four secondary standards and two working standards are automatically checked every three days and every six hours respectively, by means of a specific information gathering system. In 1999 and 2002 the Plateau Rosa laboratory participated to the CO_2 round robin test.

Data: The monthly mean CO_2 concentration obtained at Plateau Rosa in the period April 1989-December 2002 is shown in figure 2 (the data from April1989 to October 2001 represent the background monthly values, the remaining values are simply the monthly mean).

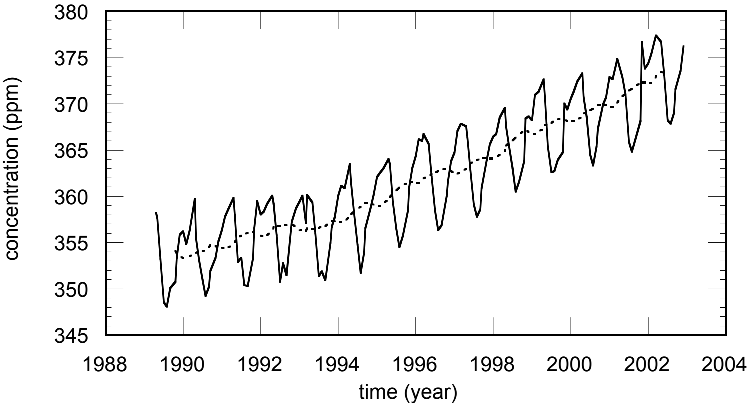

Figure 2:. Monthly mean CO_2 concentration at Plateau Rosa (solid line), and trend (dashed line).

7.1.3 The Italian Air Force Meteorological Station at Monte Cimone

The Meteorological Service of the Italian Air Force maintains a baseline observatory on the top of Mt. Cimone (44.1°N, 10.7°E, 2165 m a.s.l.), the highest peak of the Northern Appennine chain. Among other activities carried out to detect changes of atmospheric physical and chemical composition, carbon dioxide is being continuously monitored since March 1979 [Colombo et al., 2000]. Measurements of atmospheric CH_4 were recently started, in a collaborative effort with ENEA. Other greenhouse gases are measured at Mt. Cimone by the University of Urbino.

Measurement technique: Continuous measurements of atmospheric CO_2 concentration at Mt. Cimone began in March 1979 using a Hartman & Brown URAS-2T NDIR analyser. After 1988 a SIEMENS ULTRAMAT-5E has been used. The air inlet is installed 12 m above the rocky ground of Mt. Cimone. A water trap at about –70°C is used to dry the air samples.

Calibration: The CO_2 concentrations are referred to the international WMO mole fraction scale and expressed in ppm. The analyser is calibrated once a year with five international primary standards. Three secondary standards are used every twenty days and two working standards are automatically checked every three hours by means of a dedicated system. In 1999 and 2002 the Monte Cimone laboratory participated to the WMO CO_2 round robin test.

Data: The monthly mean of the CO_2 concentration measured at Mt. Cimone from March 1979 to December 2002 is shown in figure 3. The dashed curve shows the evolution of the yearly concentration.

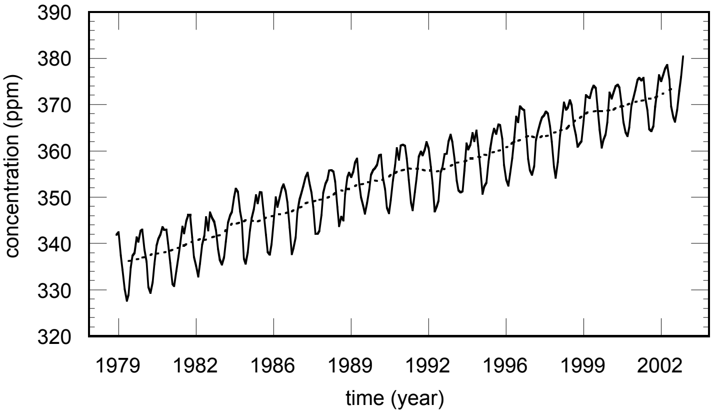

Figure 3: Mt. Cimone CO_2 monthly mean (solid line), and trend (dashed line).

7.1.4 The ENEA Station for Climate Observations "R. Sarao" at Lampedusa

Lampedusa (35.5°N, 12.6°E), a small rocky island in the central Mediterranean, with poor vegetation, relatively few inhabitants, and very limited sources of pollution, was selected in 1992 for a greenhouse gas measurement programme. Since then air samples are collected in flasks on a weekly basis; the concentration of CO_2 and CH_4 were initially determined in the laboratory of Rome. Measurements of N_2O and chlorofluorocarbons were started in 1996. A station for climate observations was established at Lampedusa by ENEA, the National Agency for New Technologies, Energy, and Environment of Italy, in 1997. Instrumentation for the determination of the concentration of several greenhouse gases (CO_2, CH_4, N_2O, CFC-11 and CFC-12) was installed at Lampedusa in 1999, when continuous measurements were started. Flask sampling has also continued up to date.

Measurement technique: Air samples are collected at Lampedusa each Friday in two pairs of 2 L glass flasks. Flasks are evacuated prior to the sampling, and pressurized to 280-300 kPa with ambient air at the sampling site. During sampling air is passed through a Magnesium Perchlorate water vapour trap. CO_2 concentration is determined using a NDIR analyser (Siemens Ultramat 5E). During the measurement, filtered air is dried by a Permapure Nafion dryer (PD-1000-24SS) to a dew-point of about -40°C. Residual water vapour is removed by means of a cold trap at -70°C. The CO_2 weekly flask programme is performed in parallel with continuous measurements since 1999; the combined analysis of the two data series is in progress.

Calibration: calibration of the Ultramat 5E is accomplished every three hours using two cylinders containing CO_2-in-air, used as working standards. The CO_2 concentration of the working standards is determined every 15 days against eight standard air mixtures that work as primary standards. The primary standards have been provided by the Climate Monitoring and Diagnostic Laboratory (CMDL) at the National Oceanic and Atmospheric Administration (NOAA) and referred to the World Meteorological Organization scale. Standards provided by the Central Calibration Laboratory of the Scripps Institute of Oceanography (SIO), La Jolla, California, were used before 2000. In 1992, 1996, 1999 and 2002 the standards used at Lampedusa station were compared to standards from the NOAA Climate Monitoring and Diagnostic Laboratory as part of a round robin-format intercomparison exercise. The standard scale was X85 from 1992 to 1994, and X93 from 1994 to 2000.

Data analysis: The time series of the monthly mean CO_2 concentration measured at Lampedusa in the period May 1992 - May 2003 is shown in figure 4. The graph shows a general increase of CO_2 concentration throughout the period of analysis, with large yearly variations. The CO_2 records have been evaluated through a Fourier analysis and a least-squares fit, and some relevant parameters, such as the growth rate (GR) and the annual and semiannual amplitudes, have been obtained [Chamard et al., 2003]. The amplitude of the mean annual cycle is about 9 ppm. The GR shows a significant peak during 1998, passing from a value of 2 ppm yr^{-1} to 4.5 ppm yr^{-1}. A peak of 4 ppm yr^{-1} was also observed in 1998 at Monte Cimone and Plateau Rosa laboratories. This GR increase is related to the strong 1997-98 El Niño event.

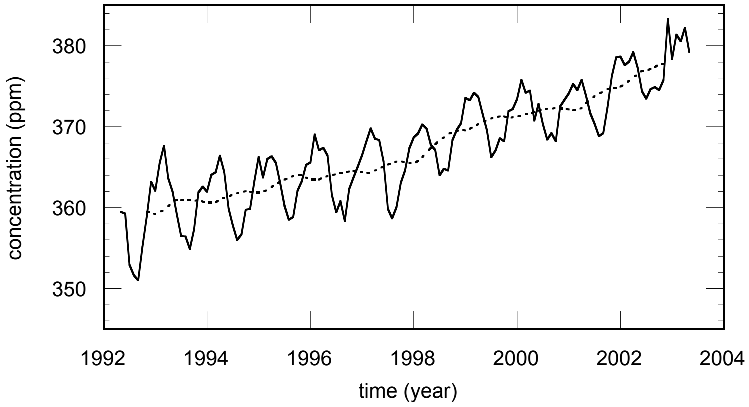

Figure 4: Monthly mean CO_2 concentration at Lampedusa (solid line), And trend (dashed line).

7.1.5 Conclusions

Background CO_2 concentration measurements are performed in Italy at three remote stations: the ENEA station for climate observations sited in Lampedusa island, the Italian Air Force Meteorological station at Monte Cimone and the Testa Grigia laboratory sited at Plateau Rosa and managed by CESI. The collaboration among the laboratories carrying out measurements of greenhouse gases at these stations, has recently been strengthened, and a national network for greenhouse gas measurements has been established. The objectives of the network, relatively to the CO_2 measurements, are:

- to obtain a unified series of CO_2 measurements, well compared and intercalibrated, at the national scale;
- to update and thoroughly compare measurement methodologies and techniques;
- to maintain also in the future an inter-calibration among the three national laboratories.

To reach these objectives, routine comparisons and intercalibrations of the measurements will be performed; criteria for data analysis and selection will be compared; analyses aimed at comparing old and contemporary data will be carried out to identify possible biases and latitudinal/regional differences, that may be of significance for the carbon budget in the Mediterranean and at the global scale.

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7.2 The New Zealand CO_2 and O_2 Measurement Programme at Baring Head

G W Brailsford, A J Gomez, D Ferretti, K Riedel and A.C. Manning

7.2.1 Introduction

The Baring Head Clean Air Station has been the site of New Zealand's CO_2 measurement programme since 1972. It is located south east of Wellington (41° 29' S, 174 ° 52' E) 40m from the sea on an 85m cliff. The on shore air arrives at the site for 30% of the time and has travelled long distances without local contamination. Typical back trajectories for stable southerly conditions indicate air descending from 750 hpa that has not been over land for at least 5 days.

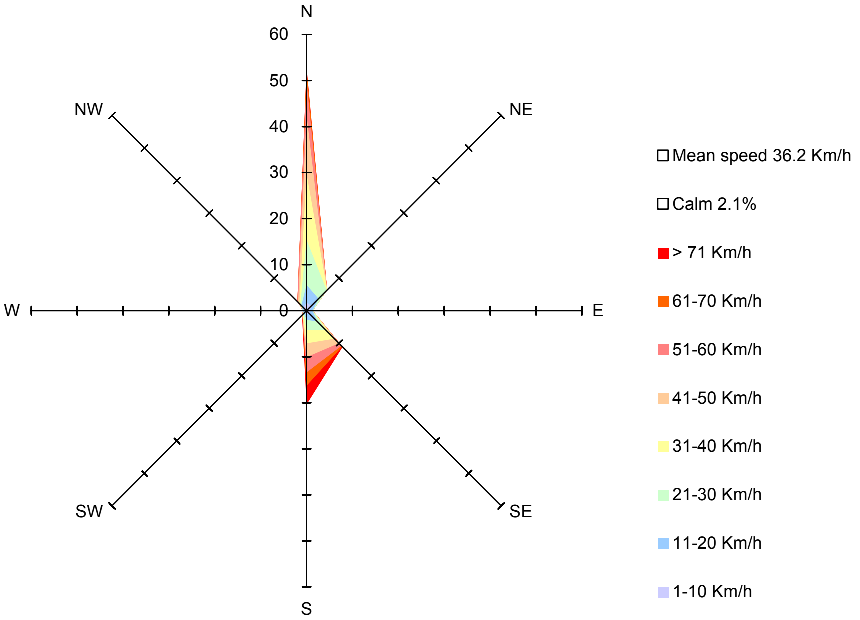

Figure 1: The wind rose demonstrates the fact that about 30% of the time the air arriving at the site is from the south to southeast sector.

The NIWA trace gas programme at the site includes the continuous in-situ measurements of CO_2 and O_2/N_2, as well as the collection of samples for later concentration and isotopic analyses. NIWA has undertaken the determination of the isotopic composition as well as the mixing ratios of a number of trace gas species to assist in constraining the global carbon budget and infer long term changes in the atmosphere.

Table 1: Listed are the trace gas species measured at Baring Head and the method of measurement and calibration scale used.

Species	**Continuous**	**Flasks**	**Scale**
CO_2	Ultramat III	GC	NOAA
O_2/N_2	Paramax 101		SIO
CO		GC-RGD	NOAA
CH_4		GC-FID	NIST
N_2O		GC-ECD	SIO
$\delta^{13}CO_2$, $\delta C^{18}O_2$		GC-IRMS	VPDB
$\delta^{13}CO$, $\delta C^{18}O$		IRMS	VPDB
$\delta^{13}CH_4$		IRMS	VPDB
$^{14}CO_2$, ^{14}CO, $^{14}CH_4$		AMS	Oxalic acid

In addition to collections at Baring Head we also maintain monthly flask and pressurised cylinder collections at Arrival Heights, Antarctica (77°48’ S,166°47’E)

7.2.2 *Methodology*

The in-situ measurements of CO_2 and O_2/N_2 are run with minimal intervention requiring users to attend the site only once per week. All systems operating at Baring Head including the flask collections are remotely accessed via a microwave link and backup modem links.

Continuous CO_2 measurement

- CO_2 is measured using an UltraMat III NDIR
- Air from 2 intakes is dried using a refrigerator trap and a peristaltic pump followed by -80°C cryogenic trapping.
- During stable air conditions, when the standard deviation of 5-minute averages of ambient CO_2 over a 4 hour period falls below 0.2 ppm, working tank measurements are determined hourly. In non-stable air, working tank measurements are determined roughly every 2 hours.
- Measurements of working tanks define a real time system sensitivity for preliminary data.
- Working tanks and reference air are prepared on site using RIX Sweet Air oil free compressors. Usage of these cylinders last approximately 9 months.
- Prior to incorporation into an operational suite, working tanks are preliminarily assigned mixing ratios based on the CCL tanks.
- CCL calibration gases are measured every 2 weeks. In the subsequent processing of the raw data these define the instrument sensitivity and precise working tank concentrations.
- During stable CO_2 conditions the CO_2 system sends a steady air signal to an automated flask sampler triggering the collection of glass flasks and pressurised canisters. These flasks and canisters are later analysed for the range of species listed in Table 1.

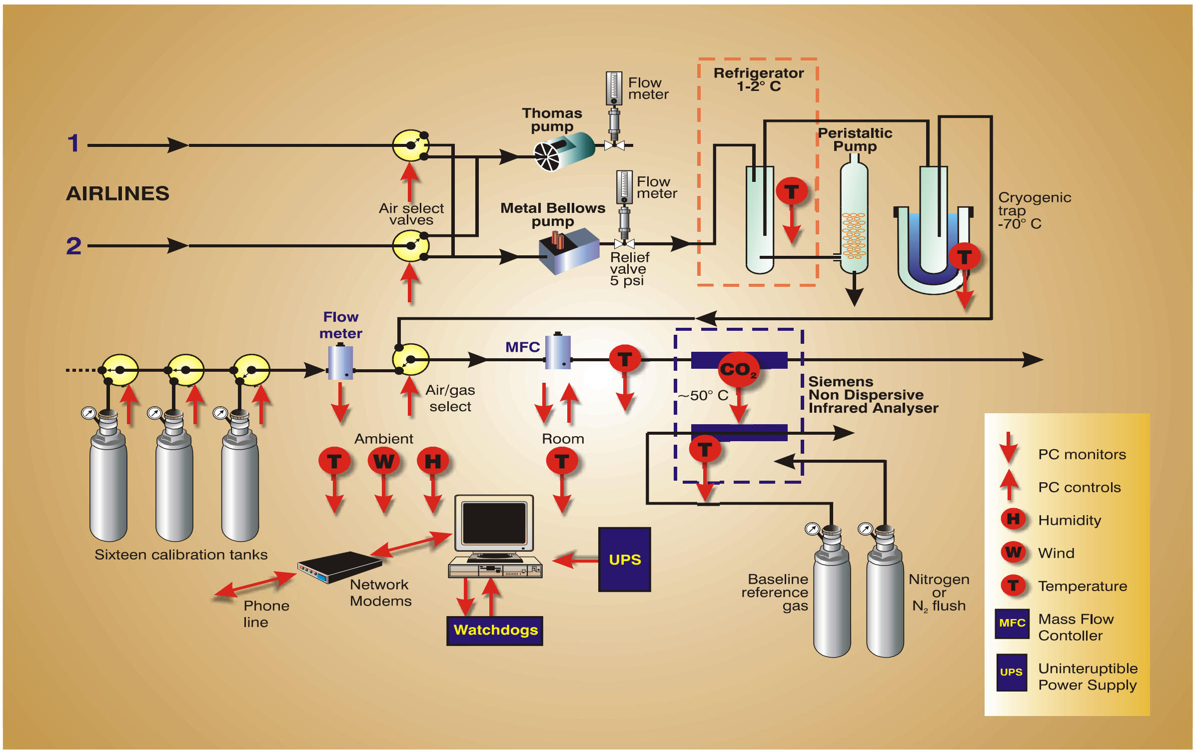

Figure 2: Schematic of the CO_2 analyser system.

Continuous O_2/N_2 measurement

- A Columbus Instruments Paramax 101 paramagnetic analyser is used for the determination of O_2/N_2.
- A constant flow and pressure regime is essential during measurements.
- A four stage drying process is used. Air flows through a fridge trap before and after the sample pump, then through a large cryogenic trap at -80°C and finally through another smaller cryogenic trap at the same temperature. Working tank and calibration gases pass through the same smaller trap prior to measurement.
- Span and sensitivity is calculated every 24 hours using High and Low span tanks.
- Calibrated archive tanks with a range of O_2/N_2 ratios are measured periodically to maintain a long-term scale.
- Air bracketed by working tank determinations allows for any short-term variability in the instrument to be monitored.
- Working tanks are prepared on the site in 48 litre Luxfer cylinders, using Rix Sweet Air oil free compressors. These cylinders last for approximately 6 weeks before being refilled.
- CO_2 corrections are derived from NDIR instrument.

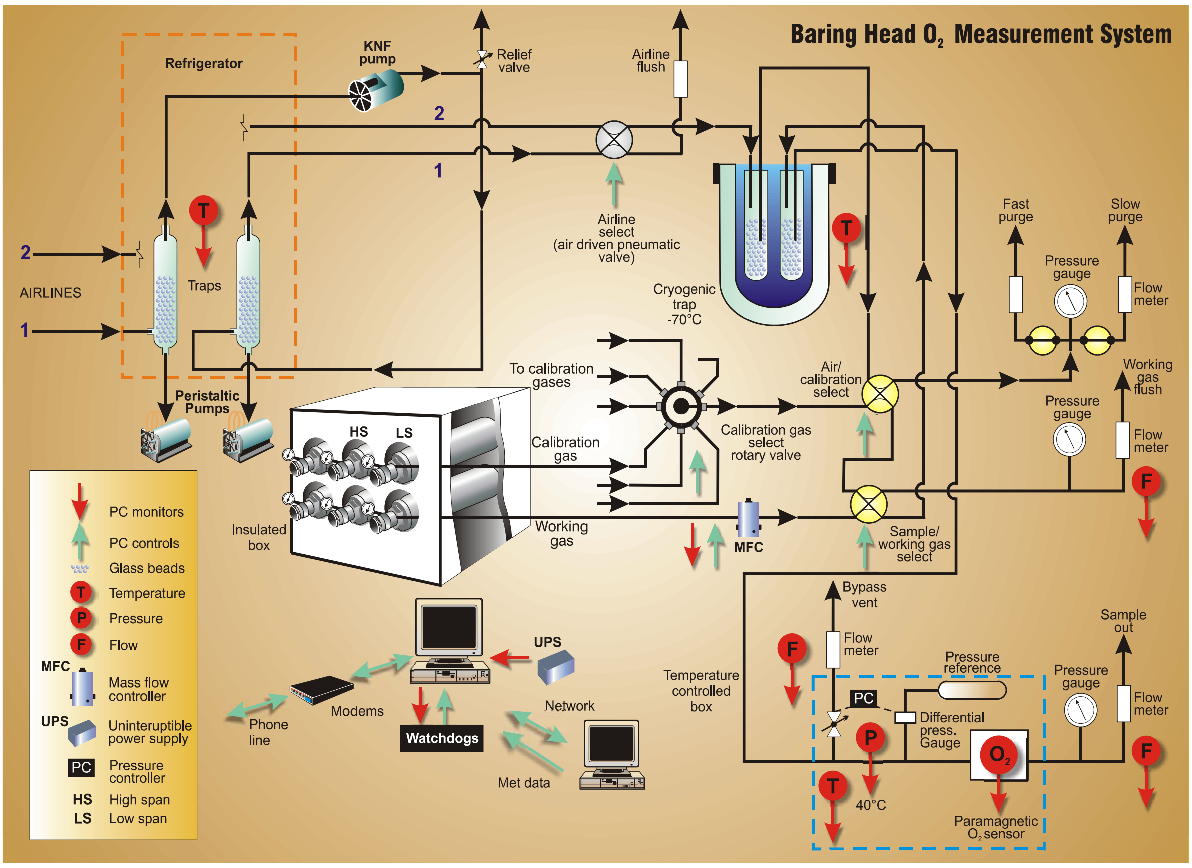

Figure 3: Schematic of the O_2/N_2 analyser system.

7.2.3 Calibration

The calibration scales used for CO_2 determinations at Baring Head have been based on CCL scales, SIO originally from 1972 and since 1994 the CMDL mole fraction scale has been adopted. There are a total of 8 cylinders of CCL calibrated air used on the CO_2 NDIR system. These provide a direct link to the mole fraction scale for our air values. The CCL assignments for individual tanks are used to determine air concentrations, and can also be used to determine the CO_2 concentration of a cylinder if it is treated as an unknown. Table 2 below contains three periods when the concentration of CO_2 has been determined in cylinders with CMDL calibrations, by the NIWA system. In period A and C there has been a combination of 4 cylinders originating from SIO and 4 from CMDL, while in period B all 8 cylinders originate from CMDL. The difference between the CMDL determined concentrations and the NIWA determined values is smallest when only tanks originating from CMDL are used, and larger when SIO tanks with high concentrations are included. .

The O_2/N_2 ratio measurements use a sensitivity that is determined from High and Low span gases. These are tied to the SIO Keeling scale by way of 4 archive tanks that have been extensively measured on the SIO Interferometer. Repeatability of the paramagnetic analyser system is 1.3 per meg for reference gas and 1.5 per meg for air.

Table 2: NIWA determinations of CCL tanks.

Tank#	**CMDL**	**A**	**Diff**	**B**	**diff**	**C**	**diff**
5872	349.88	349.85±0.07	0.03	349.89±0.03	-0.01		
5874	355.76	355.77±0.05	-0.01	355.72±0.05	0.04		
5875	360.71	360.73±0.05	-0.02	360.67±0.03	0.04		
5876	372.18	372.26±0.05	-0.08	372.16±0.03	0.02		
6866	353.61			353.62±0.06	-0.01	353.45±0.06	0.16
6867	362.00			362.02±0.02	-0.02	362.01±0.02	-0.01
6868	367.50			367.54±0.05	-0.04	367.62±0.04	-0.12
6869	381.75			381.74±0.05	0.01	381.57±0.04	0.18

The $\delta^{13}CO_2$ measurements are defined on the VPDB scale against NBS19. This has been achieved by using a suite of 3 reference gases that have been measured by CAR CSIRO against their NBS19 defined scale. When the references gases are treated as unknowns, isotopic ratios determined are very close to their declared values.

Table 3: Mean isotopic ratios of reference gases when treated as unknowns.

Tank #	**$\delta\ ^{13}C$**	**$\delta\ ^{18}O$**
AIR1	7.614 ± 0.026	0.020 ± 0.046
AIR2	8.192 ± 0.029	2.549 ± 0.053
AIR3	7.920 ± 0.041	0.870 ± 0.060

NIWA takes part in a number of CO_2 and $^{13}CO_2$ intercomparisons with other laboratories (CSIRO, CMDL, INSTAAR, SIO) which involve the exchange of real air samples. An intercomparison programme with CSIRO involves the collection of air samples from Baring Head which are analysed and returned to CSIRO where they are re-analysed. The flasks are refilled at Cape Grim and the process reversed. In addition to this, a larger 44 litre stainless steel vessel of air is continually exchanged between laboratories for long term stability tests. With NOAA, paired flasks are collected at Baring Head. A single flask is analysed at NIWA for a range of concentration and isotope species before both are sent to CMDL and INSTAAR for analysis.

7.2.4 Data

The seasonal cycles of all 3 species are closely linked, however at these southern hemisphere latitudes the amplitudes are small. A larger increase in the CO_2 mixing ratio since 2001 is reflected in a shift to isotopically lighter CO_2 during the same period. The decrease in O_2/N_2 is consistent with the overall increase in CO_2.

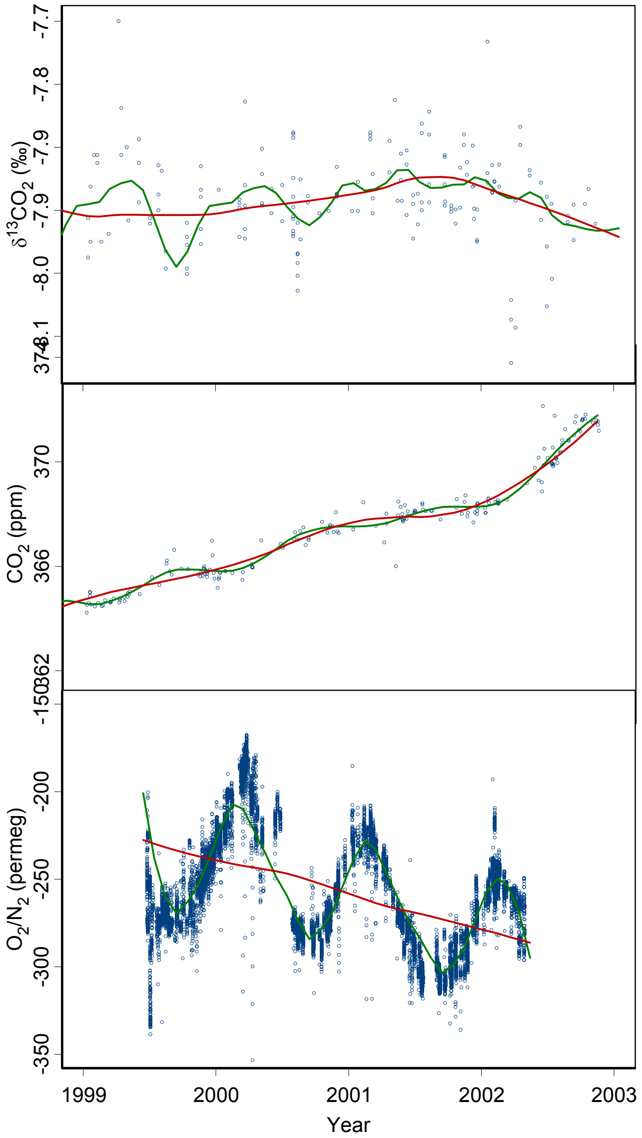

Figure 4: The Baring Head data are plotted as stable southerly values for CO_2, O_2/N_2 and flask measurements of $\delta^{13}CO_2$.

7.2.5 Conclusions

The precision reached for the CO_2 and $\delta^{13}CO_2$ analyses is not always within the WMO recommended southern hemisphere limits. However for CO_2 we are within the prescribed limits when only CMDL reference gases are used. More robust linkages to defined scales and continued ICPs for both $\delta^{13}CO_2$ and O_2/N_2 are required to maintain intercomparable data for these species.

7.3 Cape Point GAW Station Report

Ernst-Günther Brunke, Casper Labuschagne and Hans-Eckhart Scheel

Long-term measurements of important atmospheric parameters have been conducted in South Africa for more than two decades now. The country's main monitoring and research activities within the WMO Global Atmosphere Watch (GAW) network comprise (i) the Baseline Surface Radiation Network (BSRN) site at De Aar, (ii) two column ozone monitoring stations, which form part of the Global Ozone Observing System (GO3OS) as well as (iii) the Cape Point GAW station, for which a small summary report is given below.

Figure 1: Aerial view of Cape Point and photo showing the air intake mast together with the laboratory building, which is partly integrated into the surrounding rock face.

Measurements at Cape Point (34°S, 18°E) date back to the late 1970s, when the Council for Scientific and Industrial Research (CSIR) started measurements of CO together with the German Max Planck Institute in Mainz. Over the years the measuring programme has been enlarged and consolidated, with close co-operation involving the Fraunhofer Institute IFU (now IMK-IFU of the Research Centre Karlsruhe). Major milestones in the Cape Point activities were the integration into the WMO's GAW network (1995) and the transition of the station management from the CSIR to the South African Weather Service (SAWS) in 1997. The staff comprises two atmospheric chemists, a meteorologist and an electronic technician with IT and data processing experience.

The current measuring programme includes CO_2, CH_4, N_2O, CO, surface O_3, five halocarbons, ^{222}Rn, total gaseous mercury, solar radiation and standard meteorological parameters (see Table below). Over the past seven years four quality control audits on behalf of WMO/GAW have been performed at Cape Point, involving the measuring systems for O_3, CO, CH_4 and N_2O.

Table 1: Current measuring programme at Cape Point.

Trace species / Parameter	**Measurements since**	**Analytical method**	**Frequency of analysis**
CO	Dec 1978	HgO reduction detector combined with GC technique	5 hr^{-1}
CO_2	Aug 1992	Non-dispersive infrared absorption	continuous
O_3	Feb 1982	UV absorption at 254 nm	continuous
CH_4	Jan 1982	Gas chromatography (GC); flame ionization detector (FID)	4 hr^{-1}
N_2O	Feb 1983	GC / electron capture detector (ECD)	4 hr^{-1}
$CFCl_3$ CCl_4 CH_3CCl_3 $CCl_2F\text{-}CClF_2$ CCl_2F_2	Jul 1979 Apr 1980 Nov 1985 Nov 1985 Aug 1991	GC / ECD	1 hr^{-1}
SO_2	Aug 2001	Pulsed fluorescence	continuous
^{7}Be & ^{210}Pb	Feb 1992	High volume sampling followed by gamma ray counting & filter analysis for aerosols	1 $week^{-1}$
UVA	May 1989	Weston selenium barrier layer photoelectric cell	continuous
UVB	Feb 1994	UV sensitive phosphor	continuous
Global radiation (Total & diffuse)	Feb 2000	Thermo-electric thermopile	continuous
Wind (30m Dir/Vel)	Mar 1988	Propeller & vane	continuous
Wind (10m Dir/Vel)	Feb 2000	Cup & vane	continuous
Pressure & Temp.	Mar 1988	Standard met. equipment	continuous
^{222}Radon	Mar 1999	Alpha counting	0.5 hr^{-1}
Wet precipitation	Jun 2000	Ion chromatography	Sporadic
Total Gaseous Mercury (TGM)	Nov 1998	Atomic absorption / fluorescence spectrometry	1 day^{-1}
Passive Samplers (NO_2; NH_3; SO_2; O_3)	Oct 1995	Wet chemical analysis	1 $month^{-1}$

Measurements of ^{222}Rn have been made at Cape Point since 1999 in close co-operation with the Australian Nuclear Science & Technology Organisation (ANSTO). This programme in addition to isentropic back trajectories (NOAA CMDL) has contributed towards a better understanding of the origin and distribution of trace gases measured at the site.

Whilst the overall trend for CH_4 remained positive, its actual growth rate has declined from the early 1980s (12 ppb yr^{-1}) until it stabilized during 1993 - 1995 at about 4 ppb yr^{-1}. In 1996 the CH_4 growth rate started to climb again, reaching a level of about 7 ppb yr^{-1} three years later (1999). Recently the increase of CH_4 has levelled off significantly, yielding a near-zero growth rate. However, the most recent data shows a slight increase again. Nitrous oxide (N_2O), which has displayed an almost constant growth (0.7 ppb yr^{-1}) for the 1990-2000 period, has shown a lesser increase during the past two years.

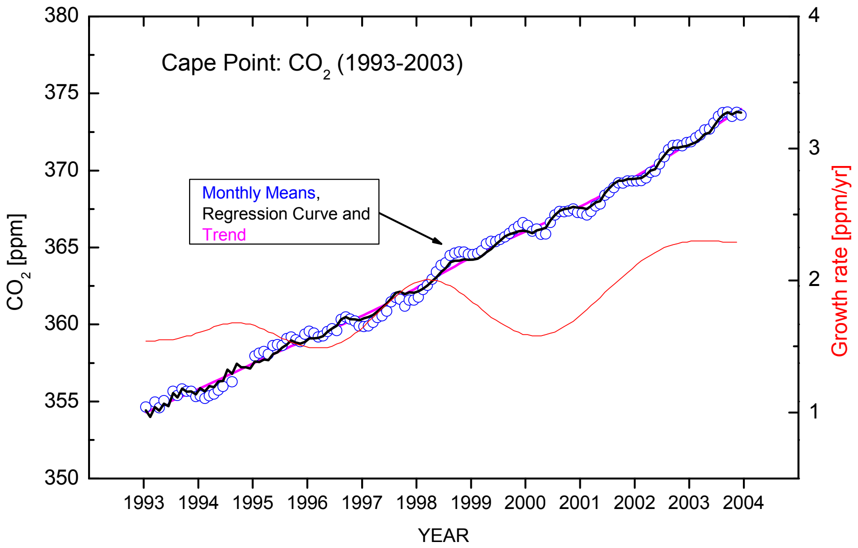

Figure 2: Carbon dioxide time series showing monthly means and trend estimate.

The concentration of CO_2 (for which measurements commenced in 1993) was found to have increased at an average growth rate of 1.8 ppm yr^{-1}, fluctuating between 1.5 and 2.3 ppm yr^{-1} respectively. This has resulted in a 16 ppm ambient CO_2 concentration increase for Cape Point, during the period 1993 to 2002. The smoothed growth rate curve in the figure above shows the largest increase for the period 2001 through to 2003 (around 2 ppm yr^{-1}) and a slight tapering off thereafter. Ambient mixing ratios recorded at the end of 2003 were around 373 ppm.

Surface ozone has shown a small, but constant rise of about 0.4 ppb yr^{-1} since the 1990s with minimum concentrations during austral summer (16 ppb) and maxima (31 ppb) during July - September.

With regard to halocarbons, our data show a decrease in the atmospheric concentration levels of these trace gas species in response to the worldwide implementation of the Montreal Protocol (1987). This holds for CFC-11 ($CFCl_3$), carbon tetrachloride (CCl_4), and for methyl chloroform (CH_3CCl_3). Methyl chloroform, which is relatively short-lived compared to other halocarbons, has shown the strongest concentration change. Its growth rate has decreased drastically and currently amounts to about -10 ppt yr^{-1}. By this, CH_3CCl_3 has contributed significantly to the overall decrease of the atmospheric chlorine burden. Due to reduced industrial production of CFC-12 (CF_2Cl_2), the atmospheric growth rate of this gas decreased from previously 16 ppt yr^{-1} (average over 1987-1991) to 5.5 ppt yr^{-1} (1991-1998), and is now approaching zero.

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7.4 National Report on the Hungarian CO_2 Monitoring and Research Programmes

László Haszpra, Zoltán Barcza and Klára Tarczay

7.4.1 Monitoring systems

There used to be two measuring sites in Hungary, K-puszta (46°58'N, 19°33'E, 125 m asl) and Hegyhátsál (46°57'N, 16°39'E, 248 m asl), where the atmospheric mixing ratio of carbon dioxide was continuously monitored (Fig.1). Both stations were located in rural environment, as far as it is possible in the highly industrialized, densely populated Central Europe. At K-puszta, which is the environmental monitoring site of the Hungarian Meteorological Service, CO_2 monitoring was begun in 1981 (*Haszpra*, 1999a). During the last decade the Meteorological Service has focused on the weather prediction giving lower priority to the environmental issues including CO_2 monitoring. There was no way to follow the technical development in the monitoring technique at K-puszta. The lack of resources for the operation and maintenance of the worn-out instrument resulted in decreasing reliability and increasing data gaps. Therefore, the data were not reported to the WMO data centre from 2000, and by now the analyzer is completely out of operation.

The monitoring site close to the village called Hegyhátsál is located at a TV transmission station owned by Antenna Hungária Corporation. This greenhouse gas research site is jointly operated by several Hungarian and foreign institutions dominated by the Department of Meteorology, Eötvös Loránd University, Budapest. The ongoing monitoring and research projects receive financial support from the European Union and other funding agencies. Here CO_2 monitoring was started in 1993, in the framework of a U.S.-Hungarian joint research project, in cooperation with NOAA.

The monitoring site called Hegyhátsál is located on a fairly plain plateau in a hilly region in Western Hungary (Figure 1). It is surrounded by agricultural fields (mostly crops and fodder of annually changing types) and forest patches. The small village close to the site has 170 inhabitants. There is no notable industry in this dominantly agricultural region. The station is fairly free from direct anthropogenic influence.

The base of the measurements is a TV-transmission tower. First a NOAA flask sampling site (station code: HUN) was established here for the global co-operative greenhouse gas monitoring network in 1993. Samples have been taken every week at 96 m above the ground. Late 1994 the continuous monitoring of atmospheric CO_2 mixing ratio was started at four elevation levels from 10 m to 115 m. Basic meteorological parameters like temperature, humidity and wind are also available from these levels. The system is based on a Li-Cor 6252 analyzer and NOAA

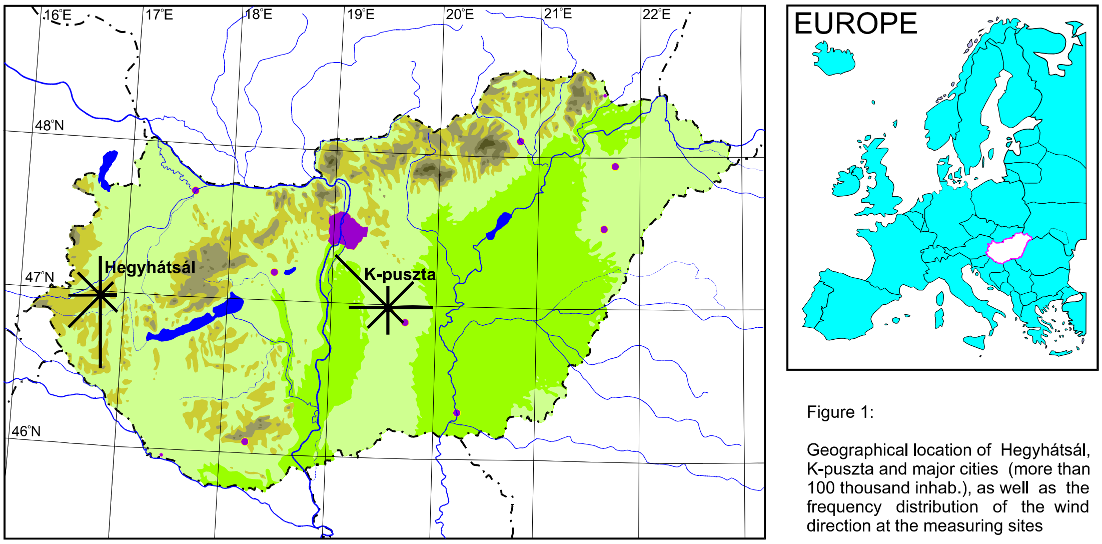

Figure 1:

Geographical location of Hegyhátsál, K-puszta and major cities (more than 100 thousand inhab.), as well as the frequency distribution of the wind direction at the measuring sites standards. Details of the measuring system are given in *Haszpra* et al. (2001). Unfortunately, the insufficient technical support, the lack of local staff and the long distance from our institute in Budapest can cause occasional data gaps due to technical problems.

In May, 1997, an ultrasonic anemometer and a fast response Li-Cor 6262 CO_2 analyzer were installed at 82 m above the ground, while in early 1999, in co-operation with NIRE (now NIAIST), Tsukuba, Japan, similar instrumentation was also installed at 3 m elevation. Both systems are used for the continuous determination of the vertical flux of carbon dioxide by means of eddy covariance technique. The footprint of the measuring system located at 82 m elevation covers several types of ecological systems (agricultural fields of different types, forest patches) while the low level system samples the underlying semi-natural grass (*Barcza*, 2001; *Barcza* and *Haszpra*, 2001; *Haszpra* et al., 2001; *Barcza* et al., 2003). The significant interannual variation in the biosphere/atmosphere exchange of carbon dioxide has inspired us to study the potential environmental factors influencing the process. For this purpose soil temperature, soil water content and radiation sensors have been added to the existing meteorological ones.

In the framework of a Dutch-Hungarian co-operation involving the Geochemical Research Laboratory, Hungary, and Centrum voor IsotopenOnderzoek, University of Groningen, the Netherlands, the stable isotope composition of carbon dioxide and N_2/O_2 ratio are also measured at Hegyhátsál from event samples. The sampling elevation is 96 m above the ground. The computer controlled continuous air drying and flask sampling system (see *Spijkervet* et al. (2001) for details) contains twenty flasks which can be filled at preset times, after preset intervals, or by online remote control. It also allows to study the temporal variation of CO_2 mixing ratio and its stable isotope composition, that of CH_4 and CO mixing ratios and O_2/N_2 ratio with 1-2 hours time resolution during selected environmental conditions (air pollution episodes, clean air conditions, etc.). The samples are analyzed by Centrum voor IsotopenOnderzoek, University of Groningen. One of the purposes of this project is to reveal the relation between the isotope composition characterizing the anthropogenic influence and carbon monoxide. Carbon monoxide could be a good qualitative indicator of the anthropogenic influence which can be monitored continuously at relatively low cost.

In the framework of the EU supported international AEROCARB project the vertical profile measurements of CO_2, CO, CH_4, N_2O, SF_6 mixing ratio, CO_2 stable isotope composition and N_2/O_2 ratio has been extended up to 3000 m above the ground (3250 m above the sea level) over Hegyhátsál by means of occasional airplane measurements (Figure 2). The airplane carries a flask sampler and takes samples at 7 elevation levels (200 m, 500 m, 1000 m, 1500 m, 2000 m, 2500 m, 3000 m). The samples are analyzed by Laboratoire des Sciences du Climat et de l'Environnnement, CEA-CNRS, France, and by the Centrum voor IsotopenOnderzoek, University of Groningen, the Netherlands. The average sampling frequency is one flight per month.

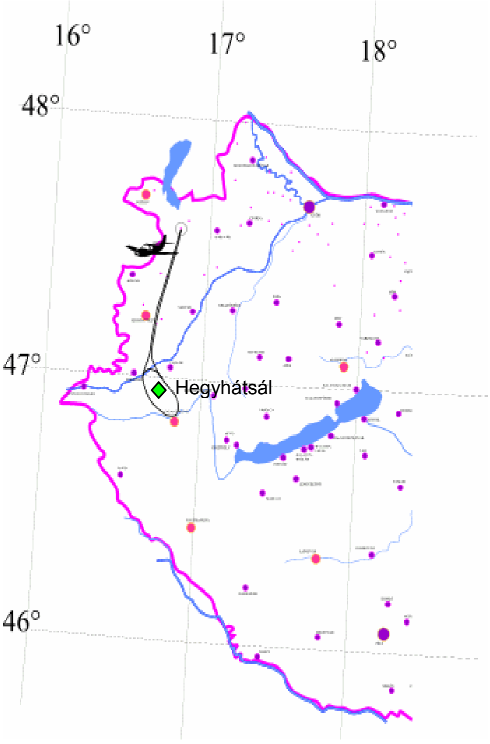

Figure 2: Route for aircraft sampling.

7.4.2 Long term trend

More than 5 years of reliable parallel data series are available from K-puszta and Hegyhátsál for comparison. At both sites NOAA standards were used for calibration which, in principle, guarantees the comparability. On an annual base the comparison shows little differences (+/-0.5 ppm) during the daytime hours, but remarkable ones during nighttime, especially in summer (*Haszpra*, 1999b). It reflects the differences in the surrounding vegetation, soil composition, and perhaps in climate. That is why it is suggested to take into account only the daytime values in the comparisons, in trend studies in the case of low elevation mid-continental stations. Figure 3 presents the long term trend at K-puszta and Hegyhátsál while Figure 4 shows the temporal variation of the growth rates.

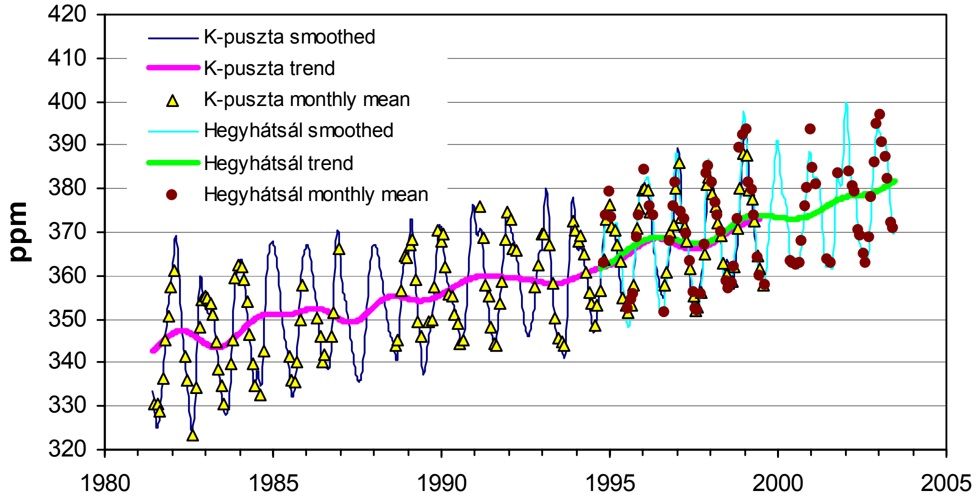

Figure 3: Temporal variation and long term trend of CO_2 mixing ratio at Hegyhátsál and K-puszta measured early afternoon at 10 m above the ground.

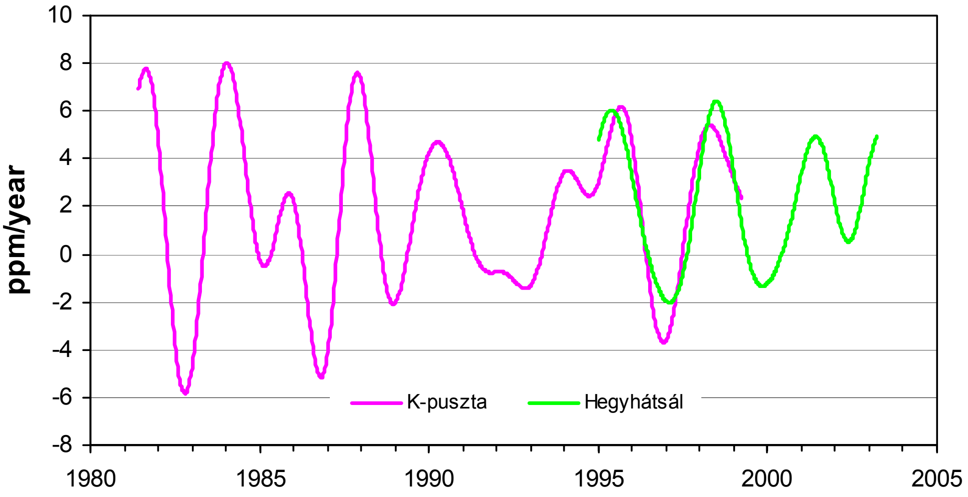

Figure 4: Growth rate of CO_2 mixing ratio at Hegyhátsál and K-puszta measured early afternoon at 10 m above the ground.

7.4.3 Biosphere/atmosphere exchange of CO_2

The tall tower measurements were initiated at Hegyhátsál to obtain regionally representative data on the long-term temporal variation of atmospheric CO_2 mixing ratio in the lower part of the planetary boundary layer, as well to obtain regionally representative data on the biosphere/atmosphere exchange of carbon dioxide. The footprint of the eddy covariance system mounted at 82 m above the ground covers an area of about 200 km^2. The TV-tower used for the measurements is surrounded by agricultural fields (mostly crops and fodder of annually changing types) and forest patches. The distribution of vegetation types (60% arable land, 30% forest and woodland, 10% other [vineyard, settlements, etc.]) within 10 km of the tower is not greatly different from the average for Western Hungary or for the whole country.

Because of the high elevation of the eddy covariance measurement above the ground special methods had to be developed to obtain unbiased flux values. The averaging time (1 h) and trend removal technique (linear trend removal) were chosen by spectral and sensitivity analyses of the measured data. Lag times caused by the long air inlet tube were determined to calculate the fluxes properly. Spectral corrections were applied to account for flux loss caused by the signal damping inside the tube, sensor separation, sensor line averaging, etc. (see *Barcza* (2001) for details).

Net Ecosystem Exchange (NEE) of CO_2 is determined as the sum of the eddy flux at 82 m and the rate of change of CO_2 storage below the measurement level. Carbon dioxide storage is estimated using the high precision CO_2 mixing ratio profile measured along the tower and an appropriate, similarity theory-based theoretical profile (*Barcza*, 2001). As the vertical profile measurements can also be used for filling the gaps in the eddy covariance measurements it is suggested to perform vertical profile measurements parallel to eddy covariance measurements on tall towers.

Table 1: Annual totals of carbon NEE, GPP and R_t for the region of the tower (Negative NEE means carbon uptake by the vegetation).

year	NEE [g C m^{-2} $year^{-1}$]	GPP [g C m^{-2} $year^{-1}$]	R_t [g C m^{-2} $year^{-1}$]
1997	-96	-1095	999
1998	-102	-1156	1054
1999	-101	-1136	1035
2000	n.a.	n.a.	n.a.
2001	-54	-1092	1038
2002	n.a.	n.a.	n.a.

The annual NEE values can be seen in Table 1. In 2000 and 2002 no reliable annual total could be calculated because of the long data gaps. According to the available measurements the region acts as a net sink of CO_2 on an annual time scale sequestering 50-100 g C/m^2.

The footprint of the eddy covariance system mounted at 3 m above the ground on a mast covers only the semi-natural grass surrounding the tower. It is important to note that twice a year the grass is cut and the mowed grass is taken away, the decomposition of a part of the organic matter happens elsewhere. Consequently the local ecosystem CO_2 release becomes smaller, and the annual NEE becomes larger (i.e. more negative). The temporal variation of NEE and its dependence on the environmental conditions are given in *Barcza* et al. (2003).

The regional scale CO_2 flux can be estimated using the mass conservation equation inside the convective boundary layer (CBL) (*Denmead* et al., 1996). During specific conditions, the CBL can be treated as a box which has a vertically moving top (e.g. the capping inversion). The surface flux can be inferred from measured changes in the CO_2 mixing ratio and the CBL height over time.

The method can be used during fair weather conditions, and the results represent the ensemble NEE of a region of a few tens to a few hundreds of square kilometres over flat terrain. The method has been tested at Hegyhátsál where all the required input data are either available or can be approximated. In addition, the results of the direct flux measurements can be used for model validation.

Figure 5 presents the result of the comparison between the results obtained by the CBL model and measured by the eddy covariance system. Within the limit of agreement, the method can be applied to any other CO_2 monitoring sites where calibrated CO_2 mixing ratio data series are available.

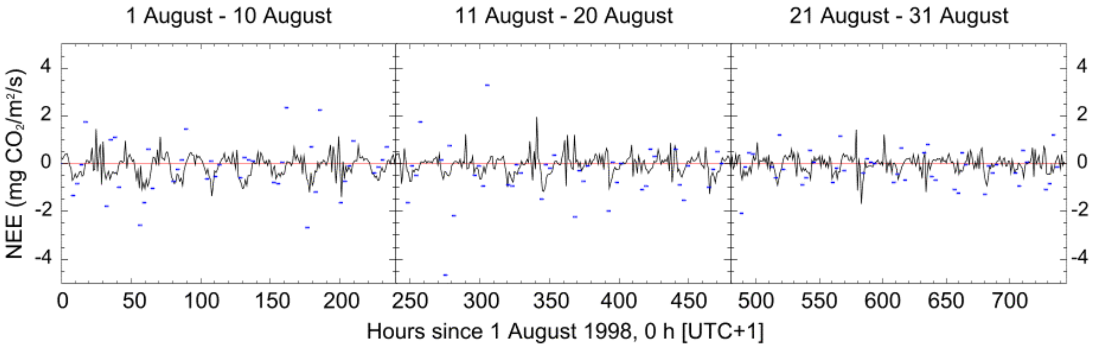

***Figure 5: NEE in August, 1998, obtained from the CBL budget method (blue lines) and by the eddy covariance system (black solid line). The budget method is only applied for daytime with 3 hours integration period*.**

7.4.4 Future plans

The high precision carbon dioxide vertical profile measurements, as well as the direct vertical CO_2 flux measurements at 3 m and 82 m above the ground will be continued. The measuring system will be completed by GC based quasi-continuous methane, nitrous oxide, sulphur hexadluoride and carbon monoxide measurements in the framework of CHIOTTO project. The occasional aircraft sampling will be continued at the present frequency till 2005. There are plans to equip the aircraft with a continuous CO_2 monitor and to increase the sounding frequency. The boundary layer model is under development. The aim is to develop a model which can estimate the net ecosystem exchange of CO_2 at sites where high precision CO_2 measurements are available but there are no direct flux measurements.

7.4.5 Acknowledgments

Use of the TV-tower and transmitter building is kindly provided by Antenna Hungária Corporation. The research projects were/are supported by the Hungarian National Scientific Research Fund (N31783 [2000-2003], T32440 [2001-2004] and T42941 [2003-2006]), by the Environmental Fund of the Hungarian Ministry for Environmental Protection (K0441482001/HP-02-0555 [2002], K-36-02-00010H [2003]), by the European Union 5th R&D Framework Programme (AEROCARB - EVK2-CT-1999-00013 [2000-2003], CHIOTTO EVK2-CT-2002-00163 [2003-2005]), and by the Netherlands Organization for Scientific Research (OTKA-NWO 451003 [2000-2003]). The trend lines and the fitted smoothed functions in Figure 3 and 4 were calculated by means of the software developed and described by Thoning et al. [1989].

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7.5 Continuous GC Measurements of Trace Gases at the Ochsenkopf Monitoring Station

A. Jordan, A. Manning, M. Gloor, U. Schultz and T. Seifert

7.5.1 Introduction

The current global network of atmospheric monitoring stations has a bias towards coastal background locations. Such locations had been chosen to avoid local influences on the concentration results. However, the data collected using this strategy provide insufficient constraints to quantify the spatial distribution of the global land sink for atmospheric CO_2. Measurements from tall towers at continental sites can contribute to closing this information gap on regional and continental scales[1]. When the air intake on the tower is above the diurnal mixed layer, local influences from the ground are significantly reduced. Information that allows us to differentiate the origin of different air masses is obtained via the multiple species approach and by measuring at high temporal resolution.

The Ochsenkopf TV tower is located at the top of a small mountain in the Fichtelgebirge, Northern Bavaria (50.07 N; 11.80 E; 1193 m asl). Next to the tower, analytical equipment has been installed in a container laboratory to measure a variety of trace gases. The species measured are: CO_2 (detected by both GC-FID and NDIR), O_2/N_2 (Oxzilla fuel cell analyser), CH_4, N_2O, SF_6 (GC-FID/ECD). CO is monitored by a partner institute (MPI-Chemistry Mainz). In addition two flask sampling systems (NOAA-CMDL and MPI-BGC) have been installed. Weekly sampling of flasks with the CMDL flask sampler started in March 2003. These samples are also used for an intercomparison exercise between the two laboratories.

7.5.2 System Setup

Air flow: At the Ochsenkopf tower, air intakes at three different heights (163 m, 90 m, 23 m) allow us to measure vertical gradients. Sample air is transported from the intakes to the container through 12 mm Dekabon lines using KNF Neuberger N828 pumps at flow rates of approximately 15 L/min. The bulk of sample air from each intake is vented through a pressure relief valve which is positioned in front of a multiport Valco valve (MPV in Figure 1) that selects one of the sampling lines for analysis on the GC. The air is directed through a two-stage drying system consisting of a glass trap filled with glass beads inside a refrigerator (3 °C, to remove the bulk part of the water) and cryochillers containing stainless steel traps in a methanol bath operating at -90 °C. Before the chiller trap becomes blocked with ice a second one takes over and the first one is allowed to thaw and is purged dry (not shown in Figure 1). A second Valco multiposition valve selects either ambient air, a reference gas (working standard) or one of four additional calibration gases, and the selected air proceeds to the GC sample loops.

GC components and procedure: The set-up of the GC system is similar to the instrumentation in our laboratory[2]. The chromatographic parameters are shown in Figure 1 and in Table 1. The system comprises of:

- an Agilent 6890 GC-FID/ECD equipped with a methanizer
- an isothermal oven for keeping the two sample loops at constant temperature (±0.1 °C)
- a packed chromatographic pre- and main column for each of the FID and ECD
- two Valco 10-port-2-position injection valves
- two Valco 4-port-2-position valves to bypass the oxygen from the methanizer and the ECD
- gas supply via gas generators (N_2, H_2, zero air) and high pressure cylinders

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[1] *Gloor M, Fan SM, Pacala S, Sarmiento J; Glob. Biogeochem. Cycl 14 (2000): 407*

[2] *Jordan A, Brand WA; Report of the 11th WMO/IAEA Meeting of Experts on CO_2 concentration and related tracer measurement techniques, WMO GAW Report No. 148(2001):140*

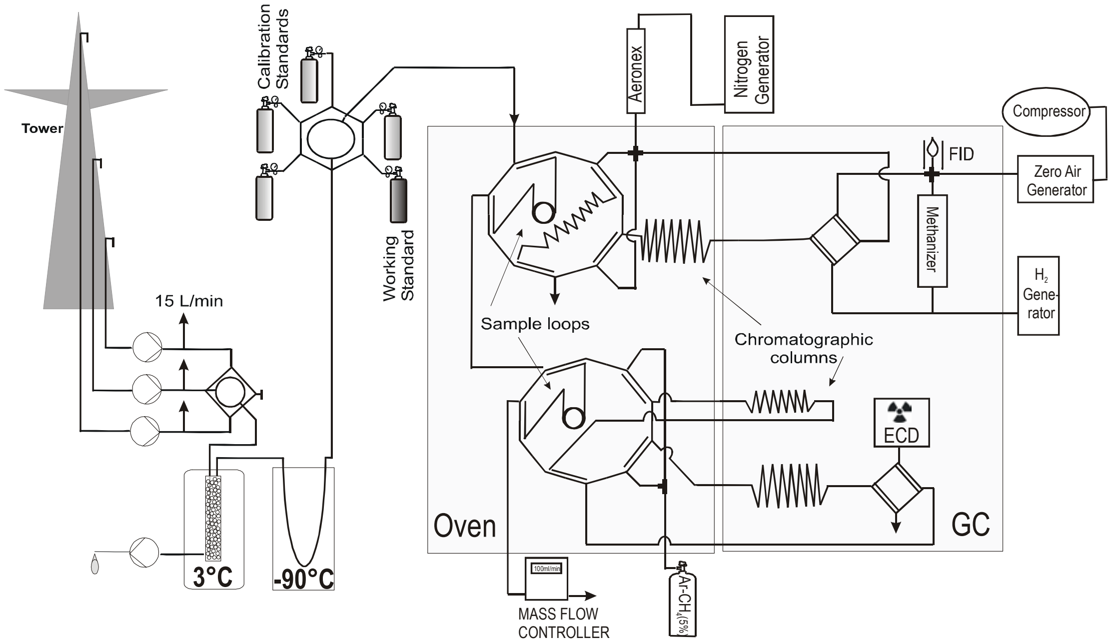

Figure 1: Schematic overview of the Ochsenkopf GC-system.

TABLE 1

a) Chromatographic settings

	FID		**ECD**
pre-column	6 ft	Hayesep Q, 3/16”	6 ft
main column	10 ft	Hayesep Q, 3/16”	12 ft
oven temperature	80 °C		80°C
sample loop volume	15 mL		25 mL
carrier gas	nitrogen		argon-methane (5%)
carrier gas flows	120 mL/min		100 mL/min
detector temperature	200 °C		385 °C
FID fuel gas flows:	air:	290 mL/min	
	H_2:	85 mL/min	

b) series of timed events [min]

	FID			**ECD**	
0.1	methanizer bypass	on	0.1	injection valve	inject
0.1	injection valve	inject	0.1	ECD bypass	on
1.55	methanizer bypass	off	1.96	ECD Injection valve:	backflush
2.31	injection valve	backflush	2.8	ECD bypass	off
4.5	start flushing of sample loop		4.5	start flushing of sample loop	
5.5	stop flushing		5.5	stop flushing	
5.6	carrier gas pressure 4.5 bar→1 bar				
5.95	methanizer bypass on				
6.0	carrier gas pressure 1 bar → 4.5 bar		6.5	end of run	

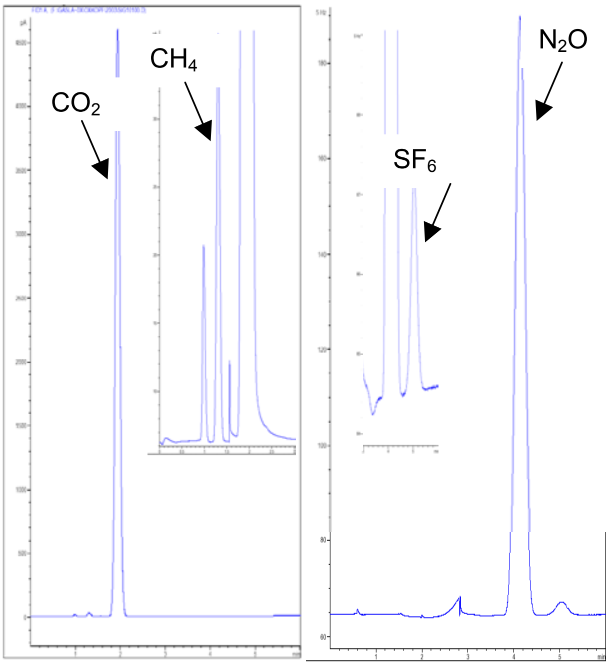

Figure 2: Chromatographic separation of CH_4, CO_2 and N_2O, SF_6.

The gas chromatographic procedure is summarized in Table 1. Sample loops are flushed for one minute at 100 mL/min. Switching the injection valves transfers the sample air to the pre-columns. After the analytes of interest have left the pre-column the injection valves are switched back to backflush the pre-columns. In addition, the sample loops can already be flushed with the next sample. After complete elution of CO_2 the FID carrier gas inlet pressure is reduced before switching back the methanizer bypass valve to prevent the FID flame from being blown out. The large amounts of oxygen included in 25 mL of sample air have proven to cause a drift in the sensitivity of the ECD. Therefore, the column effluent initially bypasses the detector until all oxygen has vented. Parameters are set such that CO_2 is separated from N_2O since CO_2 causes a very small negative response in the ECD signal. The chromatographic separation achieved is shown in Figure 2.

Computing and data handling: The entire analysis system including the GC is operated by a custom-written LabView software program in connection with Agilent's Chemstation software. This software synchronizes the GC and the Oxzilla measurements and controls the multi-position valves that select the different sampling heights and the different calibration gases. The GC raw data files are transferred automatically to a second computer and deleted from the GC computer. Data accessibility and remote interaction is made possible by PC Anywhere software (Symantec Inc.).

7.5.3 Standardization

The sequence of measurements is programmed such that each ambient air analysis is bracketed by analysis of an ambient level working standard gas. Calibration is done by daily analysis of four additional standard gases with different concentrations of the four measured trace gases. These standards have been calibrated at MPI-BGC-GasLab using high-pressure cylinder standard gases calibrated by NOAA-CMDL (CO_2 and CH_4), CSIRO-DAR (CH_4 and N_2O) and Institute of Environmental Physics, University of Heidelberg (SF_6). As a result of the small sample size required for GC analysis the lifetimes of the standard gases will be between > 2 yr (working standard) and 10-20 yr (calibration standards). Two of the standard gases are analysed every six hours. These data are used for the purpose of quality control only. To monitor the stability of the

Ochsenkopf calibration scale additional standard gases calibrated in the Jena laboratory will be brought to the station periodically.

7.5.4 Future Developments

The Ochsenkopf tower laboratory is also a prototype for additional monitoring stations that are planned in more remote continental areas. Being relatively close to the institute (200 km) it has allowed us to identify and address many problems associated with continuous remote operation before extending the programme into more remote locations. Two additional tall towers will be set up for continuous measurements by MPI-BGC. One tower in Bialystok, Poland, (53°12’N, 22°45’E) within the EU-CHIOTTO project, will be equipped in 2004 and a new tower in Zotino, Siberia (60°45'N, 89°23'E) will start operations in 2005. The set-up for these systems will incorporate the experience obtained in the operation of the Ochsenkopf system.

Acknowledgements

The tower facilities have been made available by the Bayerischer Rundfunk. Special thanks to the head of the tower, Mr. Heerdt. Recommendations by Doug Worthy regarding the chromatography have influenced the set-up of the system and are highly appreciated.

7.6 UK/Irish National Report: Methane Isotopes at Mace Head and Ascension Island, and Carbon Gases in London

D. Lowry, R. Fisher, S. Sriskantharajah, P. O'Brien, A. Roddy and E.G. Nisbet

7.6.1 Introduction

Carbon gases and their isotopes are measured at Mace Head, Ireland, near London, and on Ascension Island, through a partnership between the Dept. of Geology at Royal Holloway, University of London and the Martin Ryan Marine Science Institute at the National University of Ireland, Galway. Both groups are members of the larger Meth-MonitEUr Network.

Gas mixing ratios and their isotopic characteristics in the atmosphere can be viewed as the superposition of processes operating on different time scales: diurnal (24 hour daily cycles); mesoscale (the lifetime of large scale weather systems of typically 2-4 days); seasonal (winter/summer) and longer term inter-annual trends (years to decades).

The diurnal cycle in observations is a strong indicator of local emission sources, particularly when meteorological conditions permit low altitude thermal inversions to develop overnight, which effectively restrict the mixing and dispersion of emissions. Mesoscale events, associated with the movement of air masses over large distances can be investigated to assess the long-range transport of emissions, and to examine emissions on a regional scale. Seasonal variation in mixing ratios are indicative of hemispherical and global scale emission and sink activity. Often these are natural processes with inter-annual variation linked directly to an environmental response to different weather conditions prevailing each year. The longer term trends in gas mixing ratios are often closely associated with increased or changing anthropogenic activities, either as a direct response due to changes in emissions, or indirect response due to a feedback in the sink processes.

7.6.2 Mace Head Record

Mixing ratios of CH_4 and CO and $\delta^{13}C$ of CH_4 have been measured in tank samples collected twice a month at Mace Head since 1995. There are also complimentary AGAGE and NOAA data for the mixing ratios of these gas species at Mace Head. Figure 1 shows the time series of Mace Head tank sample data. It can be seen that the underlying trend in CH_4 mixing ratio increased steadily until 1999 with annual growth rates of up to 10 ppb/year, but has since levelled off with growth rates between 0 and 1 ppb/year, consistent with the reported global background

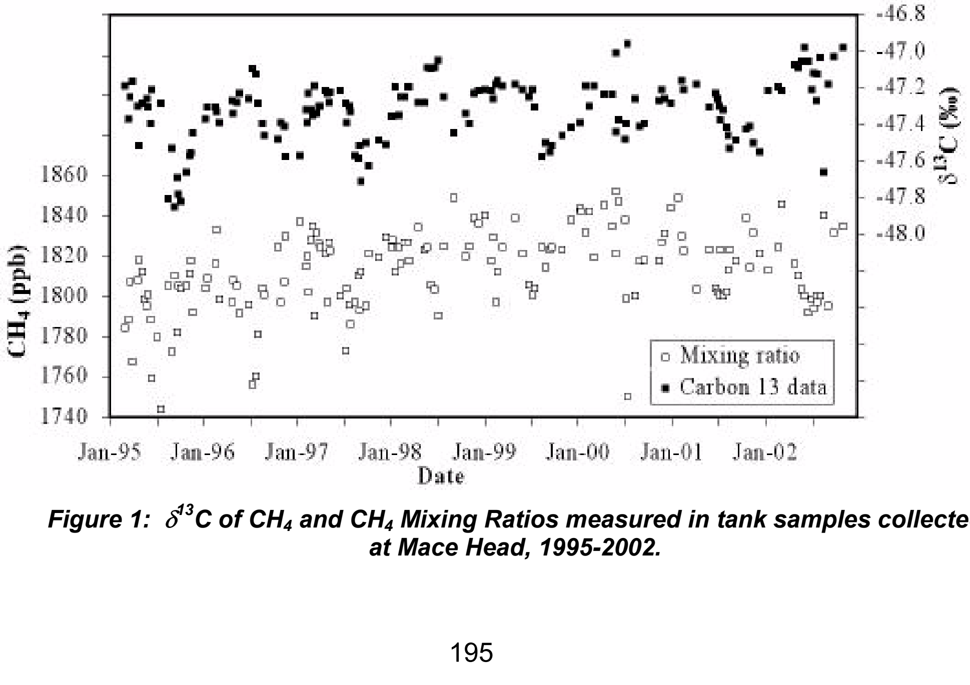

Figure 1: ***$\delta^{13}C$ of CH_4 and CH_4 Mixing Ratios measured in tank samples collected at Mace Head, 1995-2002.***

trends. A trend in $\delta^{13}CH_4$ of approximately 0.02‰ per year was observed at Mace Head between 1995 and 2000, but has also subsequently levelled off, with no significant trend. CH_4 displays a seasonal range in mixing ratio of 50 ppb, but this has been significantly greater during certain years (80-100 ppb in the mid '90s). The $\delta^{13}C$ of CH_4 shows a seasonal range of about 0.6‰.

7.6.3 Ascension Record

A programme of air tank sample collection at Ascension Island (8°S) was initiated in August 2000 in order to expand the Atlantic background site network. Mixing ratios are significantly lower than at Mace Head and other Northern hemisphere background sites and the data show a reduced seasonality of $\delta^{13}C$ in CH_4, around 0.2‰ to 0.3‰.

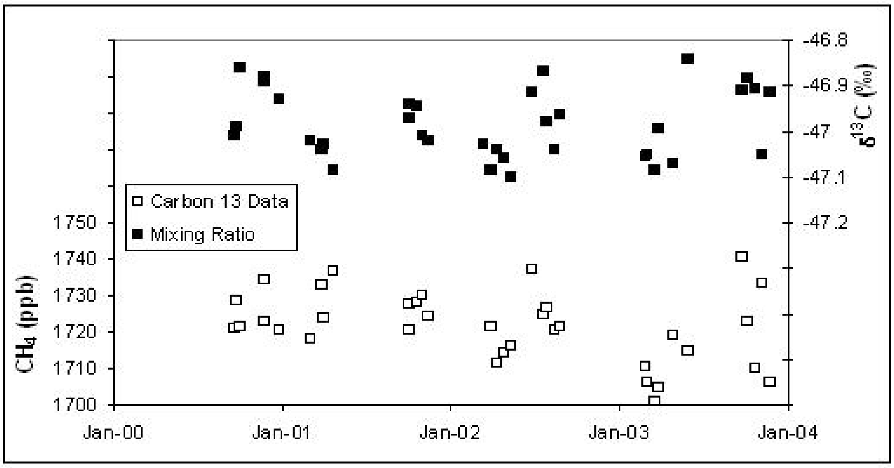

Figure 2: $\delta^{13}C$ of CH_4 and CH_4 Mixing Ratios measured in tank samples collected at Ascension Island, 2000 - 2003.

7.6.4 The London Record

The long-term carbon gas monitoring record from London extends from 1995-2003. As a consequence of the intercomparison work in Meth-MonitEUr, it is possible to compare results from London directly with results from other highly urbanised areas in Europe and with continental background sites. The sampling site at Royal Holloway is situated to the west of London, allowing opportunistic sampling of relatively clean air from the west and air influenced by London from the east.

With the Royal Holloway dataset the largest variations are seen on a diurnal timescale. The development of an overnight thermal inversion, with subsequent mixing layer growth during the day, can cause CO_2 to vary by 30 ppm on many summer days, whilst during uneventful winter days (i.e. mild days with moderate winds) CO_2 varies by about 5 ppm. These couple with noticeable rush hour concentration peaks at 08.30 and 18.30 GMT in winter (one hour earlier in summer). During major anticyclonic events the daytime/night time variation can be greater. An example of one such event is shown in figure 3 which occurred on 11th to 12th October 2003. The CO diurnal cycle broadly correlates with the CO_2 cycle, as does the CH_4 cycle, with the exception of very significant short lived peaks when CH_4 > 800ppb above baseline, which are not correlated to CO_2 or CO, and indicate emissions from other local source activities.

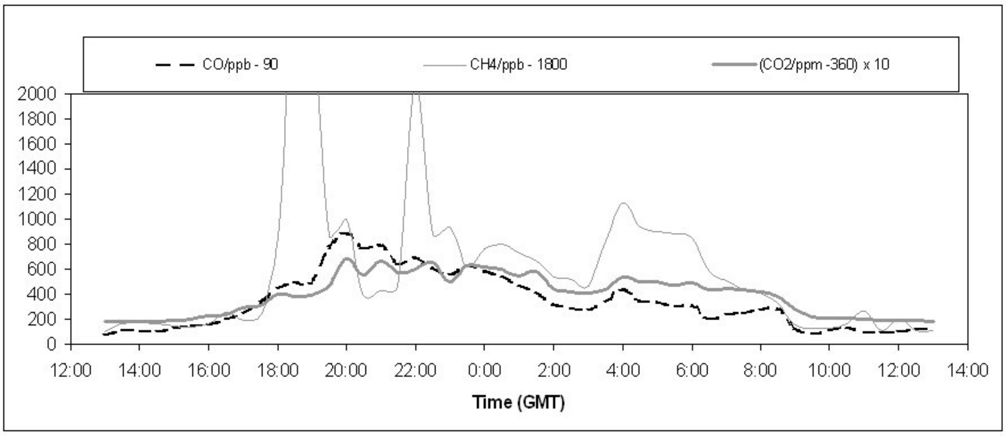

Figure 3: Correlation between carbon gas mixing ratios for an event from 11th - 12th October 2003: Mean monthly mixing ratios (plotted with CH_4 deviations from 1800 ppb; CO deviations from 90 ppb, and CO_2 deviations from 360 ppm multiplied by 10).

Seasonal variation (Figure 4) is also strong, though less marked than diurnal change. Mean monthly CO_2 mixing ratio is at a minimum during June and July and maximum in November, with a typical seasonal range of 20-25 ppm. The CO minimum occurs during September, with a maximum in February, with a range between of 300-500 ppb. The minimum CH_4 mixing ratio occurs about July, with a maximum in springtime (February-April). The range of the CH_4 seasonal variation appears to have lessen from 150ppb in the 1990s to <100 ppb in recent years. This is consistent with the Mace Head data, though more pronounced.

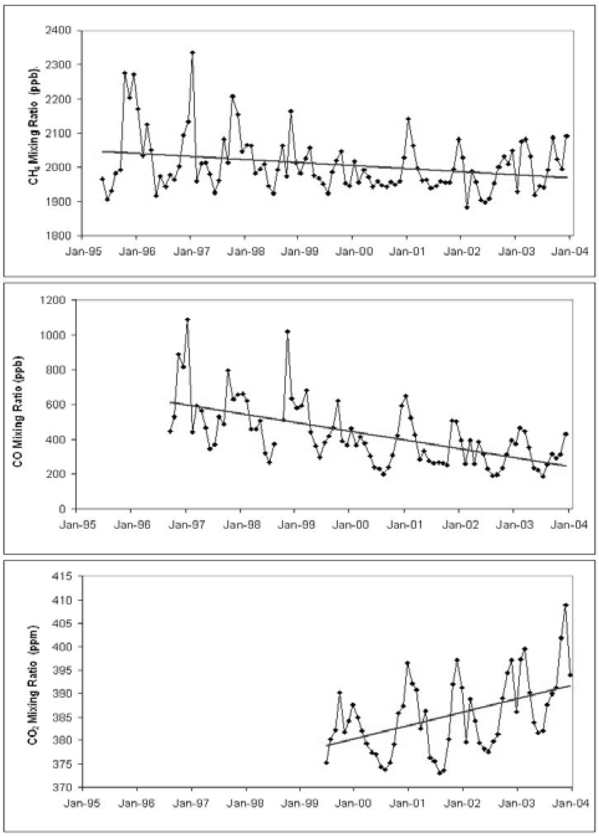

Figure 4: Mean Monthly Mixing Ratios of CH_4, CO and CO_2 recorded at Royal Holloway.

Year to year changes in mixing ratios are much smaller. As a rough guide to the relative scale compared to seasonal and diurnal change, CO_2 is increasing at a rate of approximately 3 ppm per year, CO is declining by 45 ppb per year, and CH_4 is declining by 8 ppb per year. These trend values represent changes which are only 5 to 10% of the daily variation. Thus extracting valid annual change in London air from the noisy continuous record is subject to the caveat that the long term trend signal is much weaker than the short term variability, and the above trends may not be significant. Nevertheless, the situation is at least static or improving within the London catchment for CO and CH_4, but not for CO_2.

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7.7 Measurements of atmospheric mixing ratios of carbon dioxide and methane in Poland

J.M. Necki, L. Chmura and K. Rozanski

Territory of Poland covers only slightly more than 3% of Europe. It is situated in central region of this continent and consists mostly of agricultural landscape, however big forest ecosystems are located in eastern part of country. Highlands coming into Carpathian mountain ridge are more industrialized mostly due to the mineral resources occurring in Southern Poland. Silesia - the largest Polish mining district may be regarded as an important methane source still active even the most of the mines are standing on the edge of bankruptcy. Last few decades shows that nevertheless Polish industry recession and energy sector reorganization CO_2 emission may be reasonably increased along the country production growth rate. Both CH_4 and N_2O are widely emitted from large natural wetlands and agriculture.

Scientific investigation concerning greenhouse gases emissions are preformed by academic institution, however statistic data are independently collected in agree with governmental injunctions. Monitoring of CO_2 concentration are continuously carried by the AGH – University of Science and Technology (http://www.ftj.agh.edu.pl/zfs) at two locations: (i) inside a large urban agglomeration (city of Krakow), and (ii) on a top of the mountain ridge (Tatra Mountains, Southern Poland). Measurement campaigns of CH_4, CO_2 mixing ratios were carried out since 1999 in the Silesian region revealing their almost continuously elevated values in compare to rest of the country. Some investigation within a large forest complex near Krakow were repeated occasionally in recent years. Independent carbon budget in local scale of Puszcza Niepołomicka forest was described by scientists from Jagiellonian University (http://www.eko.uj.edu.pl). Additionally Institute of Environment Protection (http://www.ios.edu.pl/pol/zaklady/puszcza/indexp.htm) is registering continuous record of carbon dioxide concentration at the border of large forest area in North-Eastern Poland.

7.7.1 Station Kasprowy Wierch

Station for regular observations of greenhouse gases in lower atmosphere was set up in 1994 in the High Tatra mountains, in the meteorological observatory at Kasprowy Wierch (49°N, 20°E, 1987 m a.s.l.). This station was presented in detail in WMO report No.146. The measurement programme consist of continuous analysis of CH_4 and CO_2 performed using in situ GC equipped with FID detector. Air sample is analysed every 30 minute in exchange with standard analysis. Working standard mixtures in 20L aluminium cylinders are prepared in Kraków laboratory and delivered every year to the station. The tanks after use at Kasprowy Wierch are recalibrated, evacuated and refilled with new gas mixture. Frequent standard analysis allows to estimate the reproducibility of single measurement, which usually oscillates near 0.1ppm and 3ppb for carbon dioxide and methane respectively (single analysis standard deviation). Since the beginning of 2004 second channel of the GC equipped with ECD detector is used to analyse N_2O concentration. All samples are dried before injection (-70°C).

Flasks samples are collected biweekly at midnight, transported to Kraków and analysed for mixing ratio of CO_2 and CH_4 (since 1996), SF_6 (since 2002), N_2O and SF_5CF_3 (since 2004) and rest of the air is used for CO_2 extraction and IRMS analysis of $\delta^{13}C$ and $\delta\ ^{18}O$. Prior to the collection air is dried with magnesium perchlorate.

In addition for isotope measurements, the atmospheric CO_2 is continuously sampled by sorption on the molecular sieve in biweekly intervals. Radiocarbon activity is measured after benzene synthesis on the liquid scintillation spectrometer, while $\delta^{13}C$ is determined by isotope ratio mass spectrometry. Typical uncertainty of isotope analyses (± 1 sigma) is in the order of ±0.1‰ for $\delta^{13}C$ and ±8‰ for $\delta^{14}C$. In this method silica-gel is used as a drying agent.

The CO_2 mixing ratio record available for Kasprowy Wierch station is shown in Figure 1. The presented record is based on selected and smoothed data. Selection procedure was described in (Necki et al., 2003). Smoothing method relays on routine recommended by NOAA/CMDL (CCGvu, version 4.40 – http://www.smdl.noaa.gov/ccgg/resources/sw/ccgvu). CO_2 concentration data are available via internet from a database at address http://fatcat.ftj.agh.edu.pl/~zfs/kaslab/. Also methane concentration may be obtained from this database. Kasprowy Wierch station has operated for seven years and the analysis of trend may be still questionable especially due to the large variation of seasonal amplitude. Detailed discussion of the record (till year 2000) is presented in (Necki et al., 2003). It is worth to emphasize much larger seasonal amplitude in compare to marine stations at the same latitude or stations situated closer to the ocean coast. During the wintertime CO_2 mixing ratio rises up 2ppm higher than latitudinal winter average and decreases through spring and summer 8ppm below values recorded at marine stations. Decline tendency begins approximately one month earlier before decrease observed for example at the Schauinsland station (Schmidt et al.2003) indicating affect of continental vegetation on atmosphere in Eastern Europe.

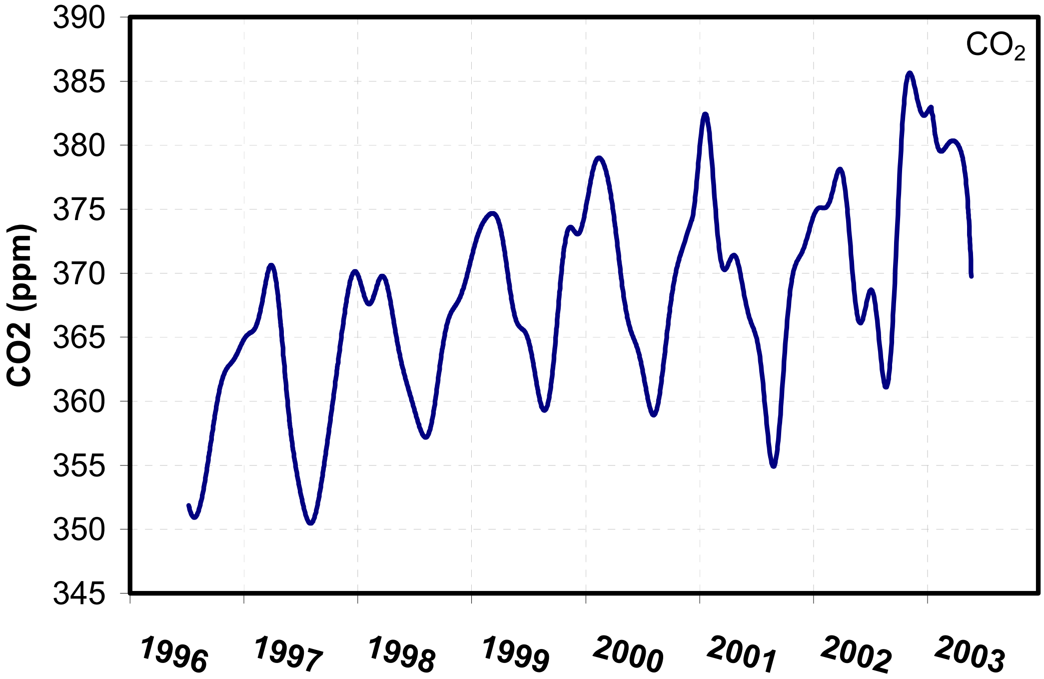

Figure 1: Record of CO_2 mixing ratios available for Kasprowy Wierch station. Diurnal averaged data obtained through on-site gas chromatographic measurements were selected and smoothed.

Methane concentration changes recorded at the station don't reveal seasonal variability but relatively high oscillation on weekly time scale (Figure.2). Large sources of this gas in Europe are not dependent on seasonal pattern and that explains constantly elevated level of CH_4 mixing ratio observed at Kasprowy Wierch in compare to marine stations. Using simple linear regression method increase trend can be detected at approx 7ppb/yr in years 1996-2003.

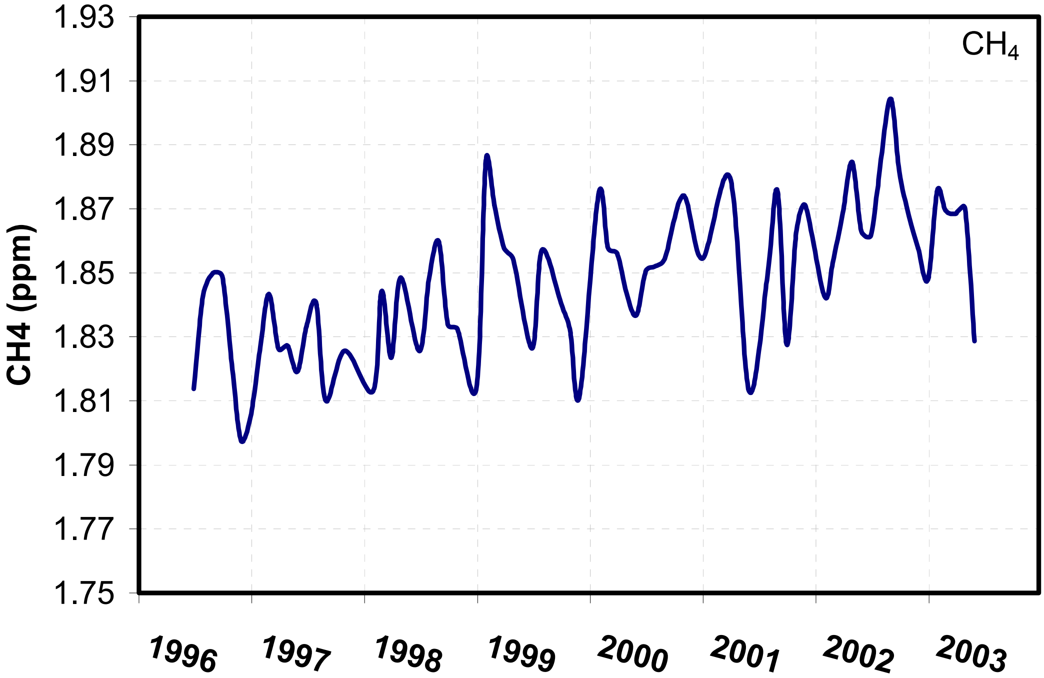

Figure 2: Record of CH_4 mixing ratio available from Kasprowy Wierch station. Monthly averaged data obtained through on-site gas chromatographic measurements were selected and smoothed.

7.7.2 Kraków AGH laboratory

Measurement of CO_2 and CH_4 atmospheric mixing ratio at University of Science and Technology in Kraków (50°N, 20°E, 300m a.s.l.) were initiated by Dr Bogdan Drozdowicz in year 1987. Gas chromatography technique was used from the beginning. This data together with stable isotope composition and radiocarbon activity were used to construct urban CO_2 balance. Since the beginning gas chromatograph in Kraków has been engaged in many other activities and continuous monitoring was no available, however routinely during one week in every month observations are performed. Methane concentration variations are frequently parallel to CO_2 concentration fluctuations – both strongly dependent on stability of the atmosphere. Figure 3 demonstrates typical variability of the CO_2 and CH_4 mixing ratios in Kraków urban environment.

Standard mixtures of CO_2, CH_4, SF_6, N_2O in synthetic air can be prepared in Kraków laboratory now on the requested level of concentration. In this way polish laboratory may produce and calibrate working standards. There is 7 cylinders calibrated in other European laboratories (Heidelberg, Germany and Paris, France) in possession of AGH group which serve as the laboratory primary standards for calibration of working standards and connection to the actually used NOAA scale.

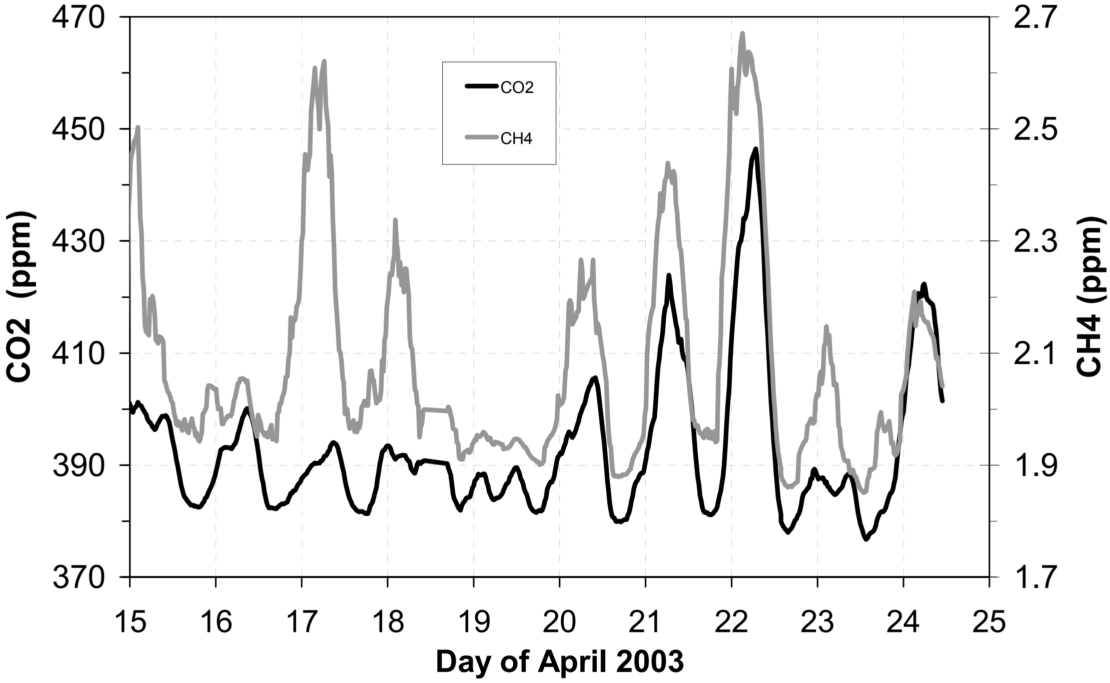

Figure 3: Examples of the short-term variability of CO_2 (black line) and CH_4 (grey line) mixing ratio recorded in Kraków air in April 2003.

7.7.3 Acknowledgements

The analytical equipment installed at the Kasprowy Wierch observatory was funded by the Polish-German Foundation (project No.573/93). The operation of the station was partly supported by State Committee for Scientific Research. Authors wish to thank crew of Kasprowy Wierch IMGW Meteorological Observatory for help maintaining scientific equipment and carrying the measurements.

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7.8 The Atmospheric CO_2 and greenhouse gas monitoring activities at Lutjewad, The Netherlands

R.E.M. Neubert, P.Weber, R. Gerritsma and H.A.J. Meijer

7.8.1 Station Lutjewad

During the last few years the Centre for Isotope Research (CIO) of Groningen University set up the new atmospheric measurement and sampling station Lutjewad (LUT) for CO_2, other Greenhouse gases and related tracers, on the northern coast of the Netherlands, at 6º 21' E, 53º 24' N, 1 m a.s.l. Though Lutjewad is at less than 10 km distance from Kollumerwaard, an air quality measurement station where earlier atmospheric research of the CIO was done (Zondervan and Meijer, 1996; Meijer and Neubert, 1998), we decided to put up a new station. Kollumerwaard is closer to natural gas winning and storage installations and could not be upgraded with a sampling tower. Lutjewad is situated directly on the sea dike. On the land side (to the south) the 60 m-tower is overlooking the perfectly flat rural landscape. Within this agricultural area the closest village is at two kilometres distance. On the seaside, sporadically flooded overgrown mud plains next to the dike pass into the Waddensea with its tidal flats. It stretches about six kilometres to the north where finally the North Sea begins. The spot on the coast was chosen in order to be able to sample air that can be charaterized as “Middle-European background”, with northern air masses, and air masses with continental “pollution” by anthropogenic and biogenic sources (and sinks) with southerly winds (see Figure 1).

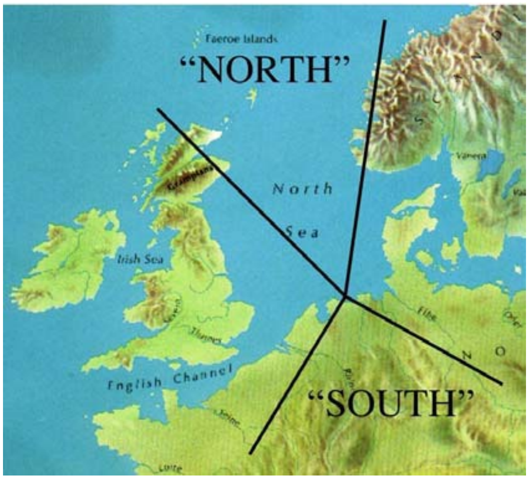

Figure 1: North-Western Europe with the position of Lutjewad at the central point of the chosen “North” and “South” sectors.

7.8.2 The tower equipment

Air intakes are fixed to the open metal frame tower at 7 m, 40 m and 60 m above ground, 1/2” dekabon tubings connect the tower underground with the laboratory in the building nearby. At every air intake height one sampling line is equipped with a Nafion membrane dryer in order to prevent the sample air from condensation of water vapour. This might occur especially in the underground part and would cause oxygen isotope exchange between CO_2 and water, thus adulterating the sample's stable isotopic signature (Gemery et al., 1996). The membrane dryer makes use of a counter-flow of dry gas to take up to 50% of the sample air's water vapour load. For this purpose we pump back the “exhaust” sample air to the tower after cryogenically drying in the building in an extended three-lines version of our flask autosampler (Neubert et al., 2004, see also below), and after flushing flasks or online instruments. As normally only small quantities are taken out of the sample air stream, the membrane dryer is fed with the same quantity of dry air of the same atmospheric composition as the actual sample, just delayed by twice the travel time in the tubing.

7.8.3 Meteorological instrumentation

All three air intake heights are equipped with basic meteorological instrumentation as given in Table 1. A detailed description can be found in Gerritsma and Neubert (2002).

Table 1: Meteorological instrumentation at Lutjewad.

Quantity measured at	ground	7 m	40 m	60 m
Temperature		x	x	x
Relative Humidity		x	x	x
Windspeed		x	x	x
Winddirection				x
Atmospheric Pressure		x		
Precipitation	x			

7.8.4 Wind distribution from 1-1-2001 until 31-12-2003

Figure 2 shows the distribution of the wind speed classes over 30° wind direction sectors at Lutjewad in 60 m height during the years 2001, 2002 and 2003, based on hourly means. The data are expressed as permil values of the total number of valid hourly means (26099 = 99.1 % data coverage). Wind speeds of less than 0.5 m/s in the hourly mean were summed up under “calm” conditions (rightmost column), as this is the minimum wind speed for accurate working of the windvane. Thus the next class, labeled “<3 m/s”, only contains hourly means between 0.5 and 2.99 m/s. As expected, the highest frequency as well as the highest wind speeds and the highest percentage wind speeds above 9 m/s were measured between 180° and 270°. Unfortunately the supposedly cleanest air from the North sector has the lowest frequency.

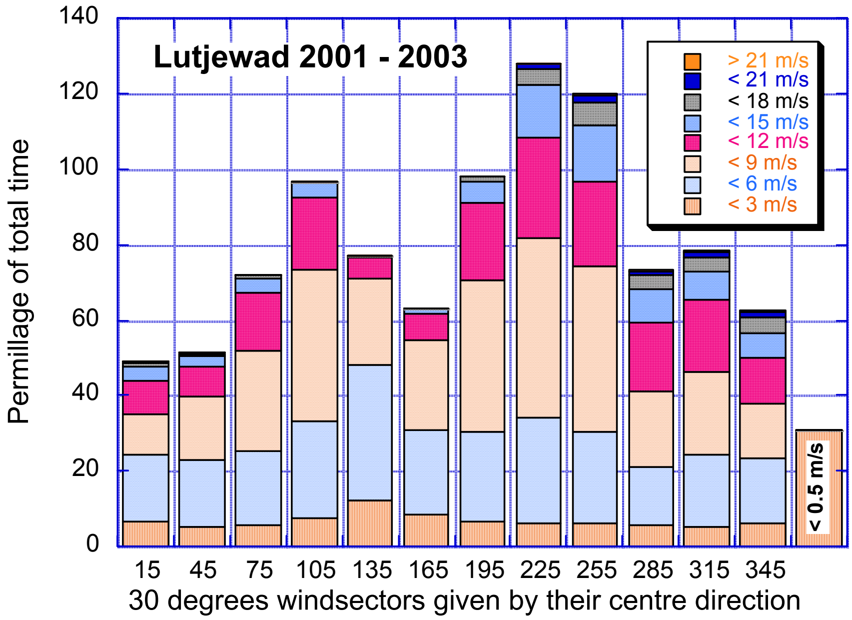

Figure 2: The frequencies of the wind classes (hourly means from 1-1-2001 until 31-12-2003) per 30° sector. All wind speeds lower than 0.5 m/s are subsumed under “calm” conditions (right-most bar).

7.8.5 Lutjewad Laboratory equipment

Flask sampling at Lutjwad for analysis at the CIO laboratory is done fully remote-controlled (via a modem/internet connection) using a double-triple drying system combined with a flask autosampler (Neubert et al., 2004). For each of the three sampling heights two glass coldtraps are immersed each into one of two dewar vessels containing a silicone oil based heat-/cool fluid. This fluid can be cooled down to below -50°C by means of an immersion cryogenic cooler, or heated to +40°C using a resistor at the bottom of the dewar. The two dewar vessels are used alternatingly: while the one is cooled, and water vapour being frozen out of the air streams, the other one is heated and the water is removed in a heated room air flow. The up to twenty flasks are flushed with dry air from a certain height one after the other (or in pairs) at prescribed intervals. Thus we always have a series of flasks containing the air of the last few hours or the last day (in e.g. hourly intervals) and then afterwards can decide, regarding the results of online measurements and meteorology, which flasks to remove from the filling cycle in order to preserve the air sample and take it to the CIO laboratory for analysis.

Our 2.5 litre flasks are fitted with two highvacuum valves (Louwers, Hapert, NL) with Viton o-rings, operated by homemade electric motor actuators. They are filled to atmospheric pressure in order to prevent the air sample from adulteration by differential permeation through the o-rings, most prominently visible in O_2/N_2 ratios (Sturm et al., 2004).

Separate lines are used for online instruments, as otherwise “old” air from the flasks would be measured after opening a flask in case of a branch-off behind the flask. A branch-off in front of the flasks cannot be installed as this would introduce a strongly temperature-dependent fractionation for O_2/N_2 ratios (Manning, 2001).

Finally, the air is pumped back up to the respective air inlets and used to pre-dry the incoming air by means of the membrane dryer.

The flask autosampler is used for the sampling of diurnal cycles (typically ten to sixteen flasks; Neubert et al., manuscript in preparation) or e.g. a weekly pair of flask samples. Flasks can be analyzed at the CIO laboratory for the concentrations of O_2 (i.e. O_2/N_2 ratios), CO_2, CH_4 and CO, stable isotopes and ^{14}C-AMS of CO_2.

Flask samples from Lutjewad show large variations and deviations in CO_2 concentration and O_2/N_2 ratios (Figure 3) as well as in CH_4 and CO concentrations (Figure 4) from a smooth curve, mainly because sampling could not always be done according to preferable meteorological conditions but rather had to follow operator presence, when the flask autosampler had not been installed yet (see figures 3 and 4). The open symbols correspond to diurnal cycles that were taken intentionally for their large day-night amplitudes (see Zondervan and Meijer, 1996).

CO_2, CH_4 and CO are given on the NOAA/CMDL scale, O_2/N_2 ratios are given on the local Groningen scale, zero being marked by cylinder 2534.

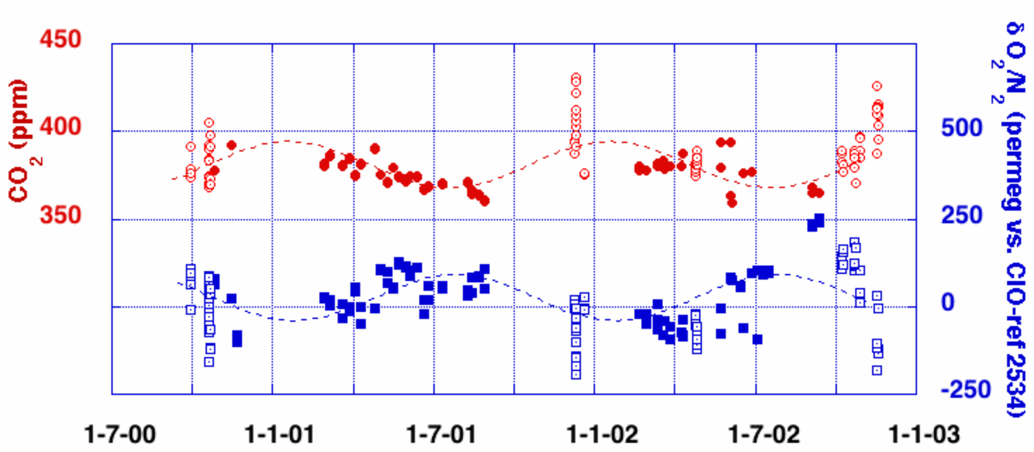

Figure 3: First Lutjewad flask results for CO_2 and O_2/N_2, open symbols correspond to diurnal cycles.

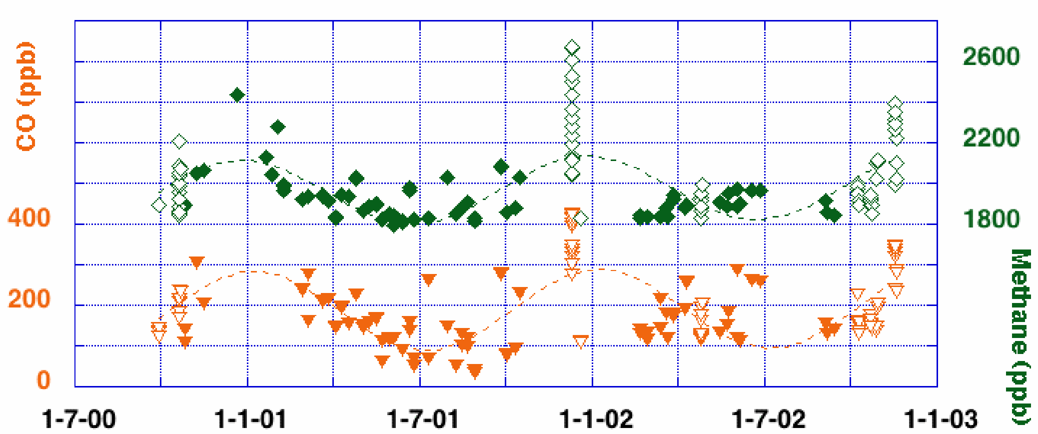

Figure 4: First Lutjewad flask results for CH_4 and CO, open symbols correspond to diurnal cycles.

7.8.6 CO_2 and methane concentration measurements

For the time being we apply an older model Chrompack 9000 gas chromatograph with a Haysep Q column for concentration measurements of CO_2 and CH_4. Unfortunately the station could not yet be equipped with a state-of-the-art gas chromatograph, but will be in the near future. Repeated and relatively large data-gaps are the consequence of the unreliable instrument in combination with the remote place of operation.

As an example, the CO_2-record of 2003 is given in figure 5. The lower limit more or less follows the background curve, during summer time undercut by outliers derived from CO_2 uptake. The typical diurnal variability is in the order of 20 ppm. Depending on the wind sector, low concentrations occur in winter (e.g. end of January, northern winds) as well as continuously rising CO_2 concentrations during several days, like in the second half of February.

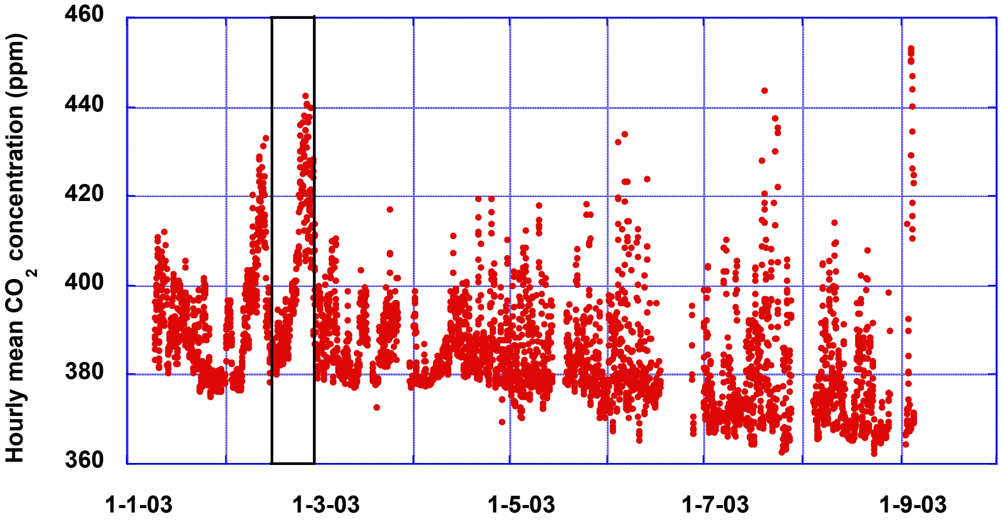

Figure 5: Hourly mean CO_2 concentration at Lutjewad 2003.

This latter period is magnified in figure 6 together with the hourly mean wind speed and wind direction at 60 m. During the whole period the wind came from clearly continental (south-) easterly directions with wind speeds up to 10 m/s.

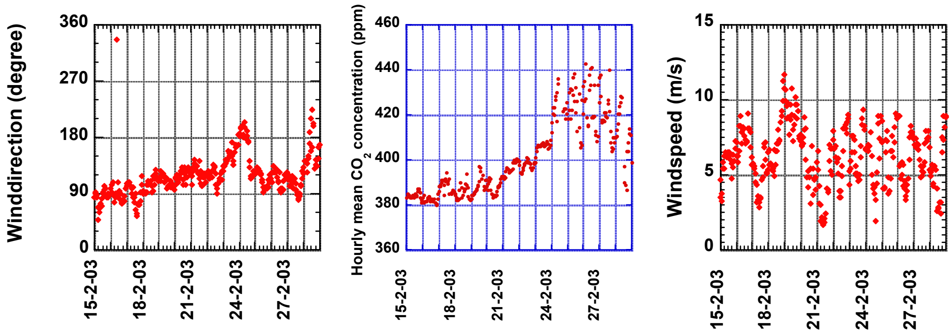

Figure 6: Hourly mean CO_2 concentration, wind direction and wind speed at Lutjewad, February 2003

A detailed air mass trajectory analysis and comparison with transport models will give more information about the origin of the CO_2. For the future it is strongly desirable to have an automatic sampling (or at least alarm) system that would take flask samples during times of persistently high concentrations, in order to get also the isotopic and ^{14}C information of the CO_2 heap.

7.8.7 Integrating CO_2 sampling by absorption in NaOH for $^{14}CO_2$ analysis

Integrating sampling of CO_2 for conventional ^{14}C analysis started at the CIO in the 1950's, taking monthly integrated samples at the television tower of Smilde (52°54'N, 6°24'E, 12 m asl), about 30 km south of Groningen (Meijer et al., 1995). The sampling is still going on, at a height of about 100 m above ground. During a certain period of time (up to one month), sample air is continuously led through a 1.5N NaOH solution, i.e. admitted to the sodium hydroxide through a glass frit at the bottom of a narrow column. During the travel up through the column, the CO_2 contained in the air bubbles is taken up quantitatively by the hydroxide. Later, back in the laboratory, the absorbed CO_2 can be driven out again by applying an acid, and after cleaning be measured in a proportional counter tube.

At Lutjewad we started a similar but extended sampling system in October 2000. Since then one continuous sampler is running 24 hours a day. In addition two more samplers are installed for special tasks. Until the end of 2001, one sampler was running only during the early afternoon hours (11.30 – 16.00 local time), when in general the best vertical mixing of the atmosphere provides the lowest CO_2 concentrations in the 'cleanest' air. The third sampler was running with 12 hours time shift, from 23.30 until 4.00 local time. This should give the highest percentage of local influences during eventual inversion events. This choice, however, was not inspired by scientific (or meteorological) reasons, but by the lack of the wind direction control that only could be added in the beginning of 2002. As expected, the ^{14}C activity of the three Lutjewad systems don't show much of a difference during 2001. This changes with the start of the winddirection dependent sampling. We chose a "clean air" sector to the North, i.e. wind arriving from between 310° and 15° (see Figure 1), which for straight trajectories would be equivalent to the North Sea including the west coast of Norway, and a Continental sector between 120° and 210°, both with a minimum sampling wind speed of 3 m/s. From the southwest we miss – again with presumed straight trajectories – the influence of large parts of the highly populated and industrialized western part of the Netherlands. However, under the prevailing meteorological conditions south westerly winds very frequently are stormy, thus diluting the sought after fossil fuel signature into clean marine air masses.

To depend on special wind conditions also means to experience greatly varying weekly and monthly sampling times and volumes for the north and south sector. Even with a higher air flow it is frequently not possible to get the minimum amount of CO_2 that is necessary for a counter tube analysis. In this case the extracted CO_2 from the hydroxide is transferred to the graphitization laboratory to produce targets for ^{14}C analysis by Accelerator Mass Spectrometry (AMS). In order to end up with the same precision of ±3‰, the samples are measured in threefold in at least two different batches.

In Figure 7 we can see the decreasing trend and seasonal cycles of the Smilde record. For the summer of 2001, Smilde / Lutjewad agrees well with Schauinsland / Jungfraujoch (Levin et al., 2003) around a $\Delta^{14}C$ of 80 ‰, while in the wintertime our stations are considerably more influenced by fossil fuel-derived CO_2, coming closer to, but not reaching, values as low as measured in the highly-populated Rhine-valley at Heidelberg (Levin et al., 2003). A detailed analysis will be published elsewhere.

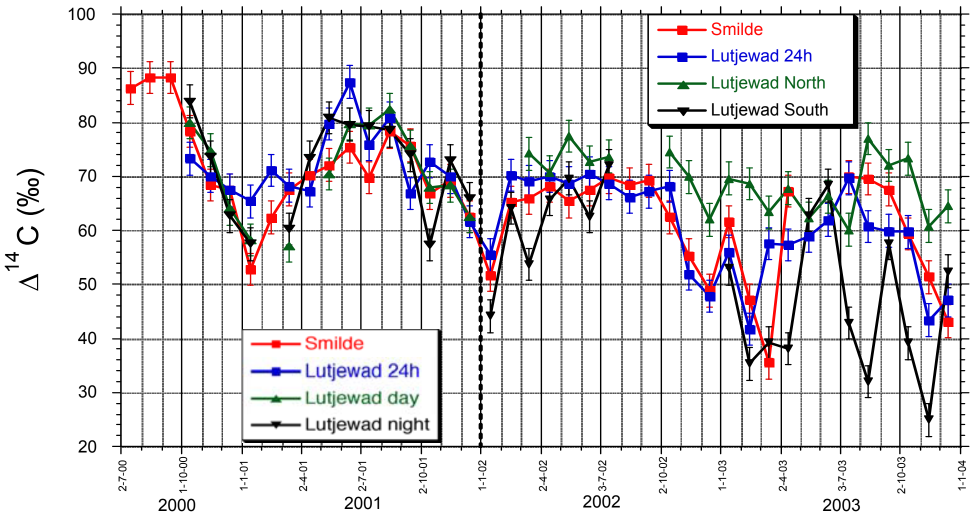

Figure 7: Atmospheric $^{14}CO_2$-activity at Smilde and Lutjewad. The sampling regime at Lutjewad changed at 1-1-2002 according to the legends.

7.8.8 Temporary instrumentation, future perspectives

In the summer of 2003, eddy-covariance equipment was run in the tower at 50 m height by Groningen University's Marine Biology department temporarily in combination with radiation instruments, and a first record of CO_2 flux data could be sampled (v. Heuven, 2004). New equipment for continuous eddy-covariance operation will be installed in 2005.

In 2005 a ^{222}Radon monitor will be installed in order to distinguish marine from continentally influenced air masses and get a measure for the nighttime inversion strength.

A state-of-the-art gas chromatograph, applying a FID for CO_2 and CH_4 and an ECD for SF_6 and N_2O concentration measurements, will also be installed in the beginning of 2005.

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7.9 Carbon Dioxide Measurement Programmes in Japan

Yukitomo Tsutsumi

7.9.1 Introduction

The JMA has been continuously measuring near-surface concentrations of greenhouse gases such as carbon dioxide (CO_2) at three stations: Ryori, Minamitorishima, and Yonagunijima. The locations, situations, and meteorology were reported in the last CO_2 Expert meeting report (WMO, 2003). JMA has also carried out a project to observe concentrations of greenhouse gases at altitudes of 8-13km by regular commercial flights between Japan and Australia in cooperation with the Japan Air Line Foundation, the Ministry of Land, Infrastructure and Transport, and the Japan Airlines. Furthermore, concentrations of greenhouse gases over the ocean and in sea water are regularly monitored by JMA research vessels in the western North Pacific. The observation sites and flight and cruise tracks were illustrated in Figure 1.

Such observations have been made systematically as a part of international frameworks such as the Global Atmosphere Watch (GAW) programme of the World Meteorological Organization (WMO). JMA also operates the WMO World Data Centre for Greenhouse Gases (WDCGG) to collect, archive, and analyze data of greenhouse gases in the world. The archived data can be accessed from all over the world through the Internet (http://gaw.kishou.go.jp/wdcgg_e.html), so that the data contributes to various studies for global distributions and trends in greenhouse gases, projections of their future concentrations, and understandings of the carbon cycle among the atmosphere, ocean, and biosphere.

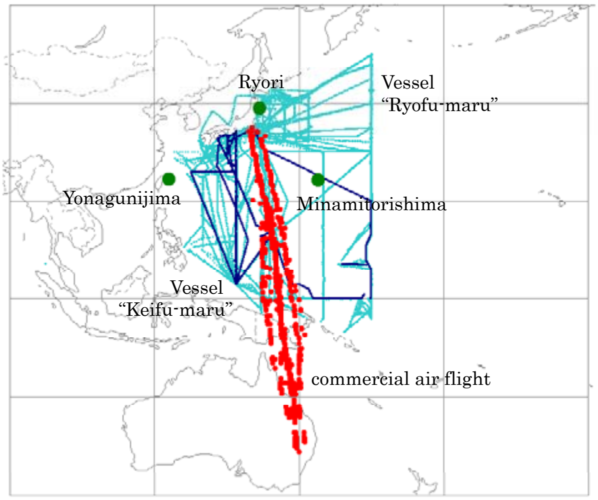

Figure 1: Observation sites (circles), sea routes for the research vessels (thin lines and faint lines) and air routes for the aircraft observation (thick lines).

7.9.2 CO_2 concentrations at the surface in Japan

Figure 2 shows monthly-mean atmospheric CO_2 concentrations and deseasonalized concentrations at Ryori, Minamitorishima, and Yonagunijima. The deseasonalized concentration is obtained by filtering out the seasonal variation. At all stations, the CO_2 concentrations increase with the seasonal variation from photosynthesis and respiration of the biosphere. The CO_2 concentration at Yonagunijima is, in general, higher than that at Minamitorishima while they are located almost the same latitude. This reflects influences of anthropogenic emissions throughout a year and biospheric emissions from autumn to the following spring from the Asian continent that is closely located upwind of Yonagunijima. The annual mean CO_2 concentrations in 2002 were 375.8 ppm at Ryori, 373.8 ppm at Minamitorishima, and 375.5 ppm at Yonagunijima. In comparison with the concentrations in the previous year, CO_2 increased by 2.4 ppm at Ryori, 2.0 ppm at Minamitorishima, and 2.0 ppm at Yonagunijima.

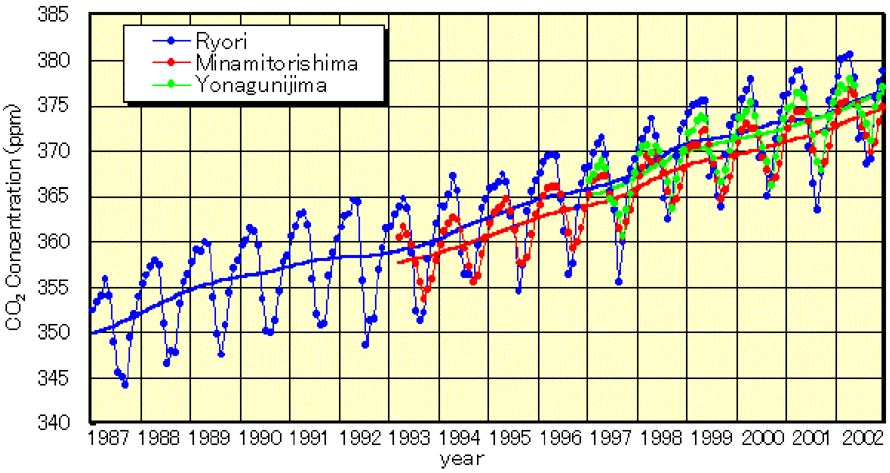

Figure 2: Time series of monthly-mean atmospheric CO_2 concentrations and deseasonalized concentrations at Ryori, Minamitorishima, and Yonagunijima.

7.9.3 High CO_2 growth rates at the surface in Japan during the El Niño (1997-1998)

As illustrated in Figure 3 a rapid increase of CO_2 growth rate from 1997 to 1998 and the following decrease are related with the El Niño event in 1997/1998. El Niño events have two opposite effects on the atmospheric CO_2 concentration. During an El Niño event, suppression of CO_2-rich ocean-water upwelling reduces CO_2 emissions from the ocean into the atmosphere in the eastern tropical Pacific. On the other hand, warmer and drier weather caused by an El Niño event strengthens CO_2 emissions from the terrestrial biosphere into the atmosphere by plant respiration, decomposition of organic soil, and depression of photosynthesis, particularly in the tropical regions. The superiority of the latter effect over the former brings about a net CO_2 increase in the atmosphere with several month delay (Keeling et al., 1989; Nakazawa et al., 1993; Dettinger and Ghil, 1998). Scarce precipitation that brought about droughts and frequent forest fires in Southeast Asia in 1997/1998 and the remarkable global mean high temperature observed in 1998 are considered to have strengthened CO_2 emissions from the terrestrial biosphere into the atmosphere (Watanabe et al., 2000).

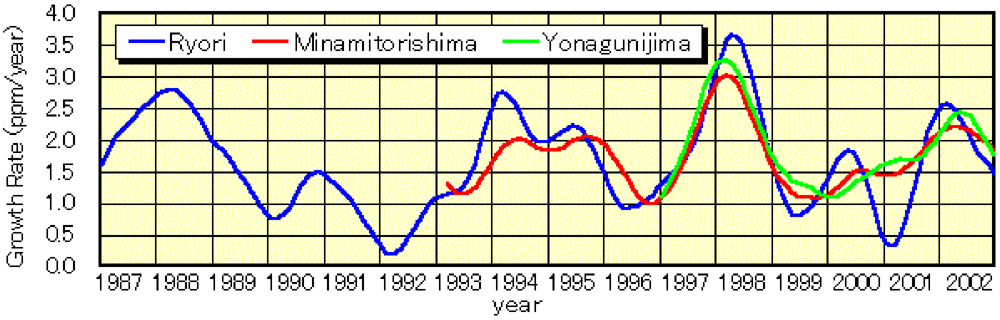

Figure 3: Time series of CO_2 growth rates at Ryori, Minamitorishima, and Yonagunijima.

7.9.4 Low CO_2 growth rates at the surface in Japan in 1992

Although an El Niño event occurred in 1992-1993, the growth rate decreased significantly (Figure 3). The decrease of CO_2 emission from the terrestrial biosphere, which was resulted from global cooling due to the eruption of Mt. Pinatubo, brought about the growth-rate decrease (Rayner et al., 1999). These inter-annual variations in CO_2 growth rate can be interpreted as fluctuations in the carbon cycle influenced by climate variations. It is necessary to clarify the carbon cycle system including the inter-annual variations for achieving an accurate prediction of global warming.

7.9.5 CO_2 concentrations in high altitudes (8-13km) over the Pacific

Figure 4 shows time series of the atmospheric CO_2 concentrations over the Northern and Southern Pacific at altitudes of 8-13km by regular commercial flights between Japan and Australia. This aircraft measurement has been conducted by the Meteorological Research Institute in JMA. The CO_2 concentrations increase with seasonal variations like those on the surface. The seasonal variations observed over the Northern Hemisphere also reflect those on the surface, but the amplitudes are smaller. In the Southern Hemisphere, the variations are complicated with double peak seasonality (Matsueda et al., 2002).

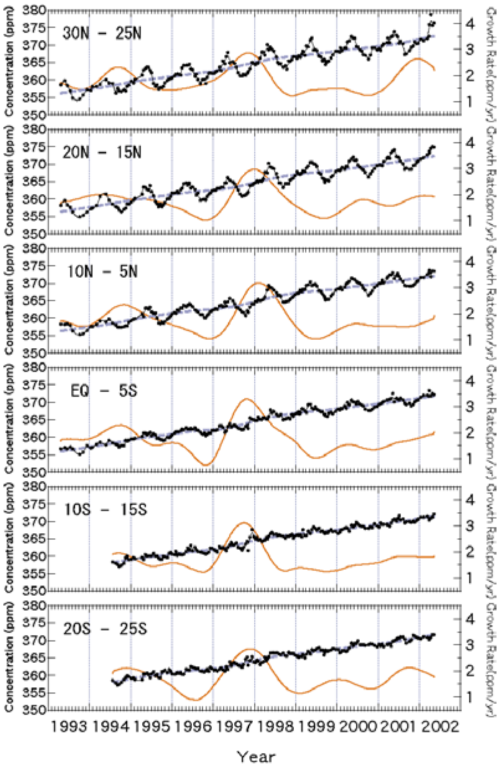

Figure 4: Time series of CO_2 concentrations (dots), fitting curves (black solid line), deseasonalized concentrations (blue dashed line), and growth rates (red solid line) averaged in each 5-degree latitudinal zone observed at altitudes of 8–13km. The samples used in this analysis were collected by a regular commercial flight between Japan and Australia.

7.9.6 Observation of oceanic CO_2 in the western North Pacific in 2002

JMA has conducted to observe oceanic CO_2 using a research vessel (Ryofu-Maru) at the western North Pacific since 1981. This observation was strengthened by adding another vessel (Keifu-Maru) in 2000. This two-vessels scheme enables us to make a seasonal observation along 137°E.

Here, partial pressure of atmospheric CO_2 (pCO_2air), partial pressure of oceanic CO_2 (pCO_2sea), and partial pressure difference between air and sea water (ΔpCO_2) are defined as follows:

$p\,CO_2\text{air} = (P\text{-}e)\cdot\chi CO_2\text{air}$,

$p\,CO_2\text{sea} = (P\text{-}e)\cdot\chi CO_2\text{sea}$,

$$\Delta p\ CO_2 = p\ CO_2\text{sea} - p\ CO_2\text{air}$$
$$= (P\text{-}e)\cdot(\chi CO_2\text{sea} - \chi CO_2\text{air}),$$

where P is atmospheric pressure, e is saturated water vapour pressure, χCO_2sea is concentration in sea water, and χCO_2air is concentration in the atmosphere.

Figure 5 shows the distributions of the CO_2 partial-pressure difference ($\Delta p\ CO_2$) between the seawater and the air in 2002 along the cruising tracks.

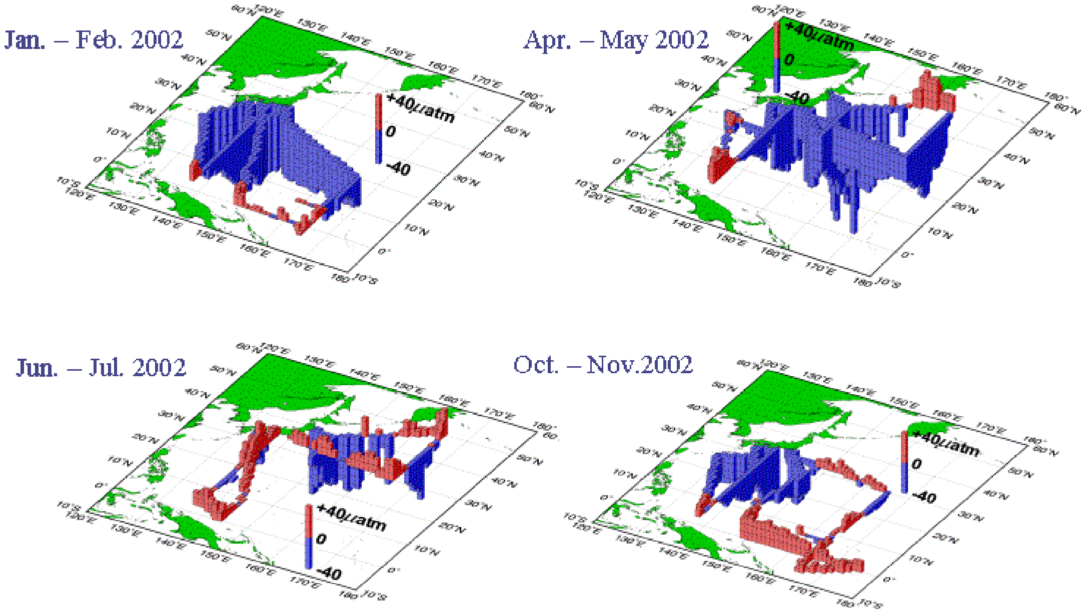

Figure 5: Distributions of the CO_2 partial-pressure difference ($\Delta p\ CO_2$) between the sea water and the air in 2002. Positive value means CO_2 emission from the ocean.

7.9.7 Annual variation of oceanic CO_2 at the surface in the tropics

From Figure 6 a large variation of oceanic CO_2 in the tropics reflects the variation of ocean condition by El Niño. During the El Niño periods of time (1982-1983, 1991-1993, 1997-1998), the concentrations of oceanic CO_2 were increased.

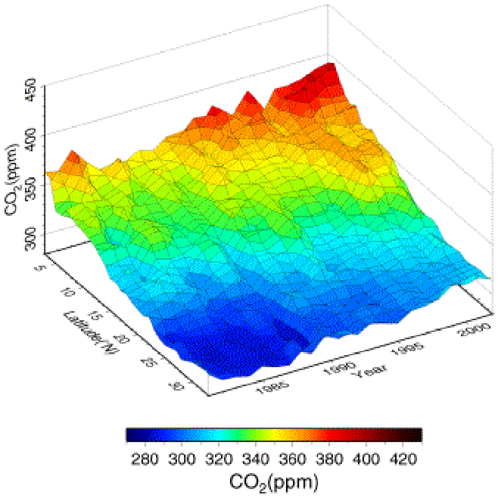

Figure 6: Annual variation of the latitudinal distribution of oceanic CO_2 in the Northern Hemisphere at the surface along 137°E from 1981 to 2002.

7.9.8 A trend of oceanic CO_2 at the western Pacific

JMA has periodically made the CO_2 observations along 137°E in winter since 1981. Figure 7 shows the long-term variation of atmospheric and oceanic CO_2 concentrations averaged between 3°N and 30°N along 137°E in January and February. In this region, the concentration of oceanic CO_2 is lower than that of atmospheric CO_2, suggesting that the ocean acts as a sink for atmospheric CO_2 in winter.

The concentration of the atmospheric CO_2 in this area has almost linearly increased at the growth rate of about 1.6 ppm/year from 1981 to 2002. Although the concentration of oceanic CO_2 has increased at a similar growth rate of about 1.5 ppm/year on average during the same period, the annual increasing rate has larger variability compared with the relatively monotonic increase in the atmospheric CO_2. This is due to the variations of the oceanic conditions.

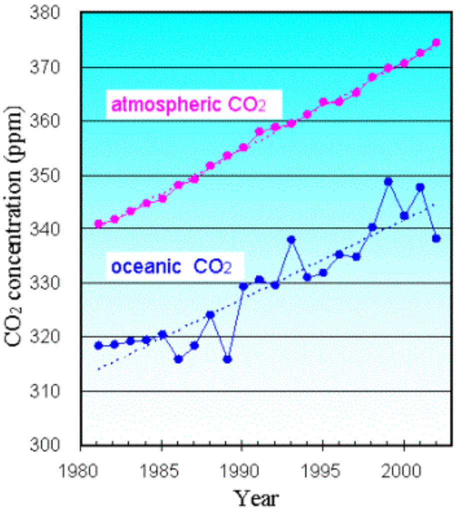

Figure 7: Time series of the concentration of air on the ocean's surface and oceanic CO_2 along 137°E (the average of 3°N–30°N) in winter (January–February) from 1981 to 2002.

7.9.9 Annual variations of oceanic CO_2 in the equatorial western North Pacific

The oceanic CO_2 concentration in the equatorial western North Pacific (156°E-165°E) in autumn has been always higher than the atmospheric CO_2, as demonstrated by Figure 8. However, the difference between the concentrations of oceanic CO_2 and atmospheric CO_2 reduced in October 1997 and October 2002 when the mature El Niño was observed.

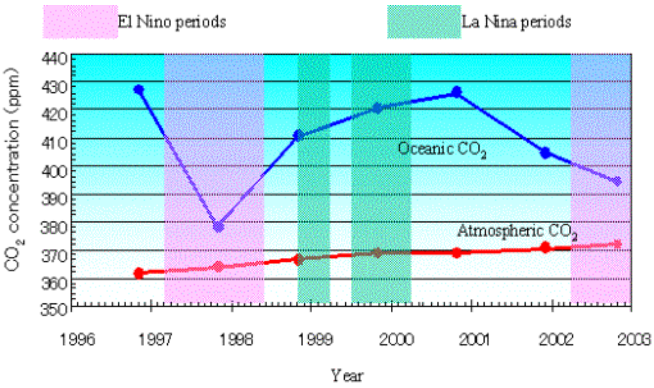

Figure 8: Time series of the concentration of air on the ocean's surface and oceanic CO_2 in the equatorial western North Pacific (the average of 165°E–156°E) in autumn (October–November) from 1997 to 2002. El Niño and La Niño events are indicated by shading.

7.9.10 Estimation of net exchange fluxes between the ocean and the atmosphere

In the subtropical western North Pacific, the concentration of oceanic CO_2 has closely correlated with the sea surface temperature (Inoue et al., 1995). Applying the empirical interpolation method based on this high correlation, the concentration of oceanic CO_2 and the air-sea partial pressure difference of CO_2 can be estimated in the season and the region of no observed CO_2 data (Murata et al., 1996). Furthermore, using the calculated air-sea partial pressure difference of CO_2 and the monthly mean wind speed distribution over the ocean, air-sea CO_2 exchange flux can be estimated. JMA has conducted the ship observations along 165°E on board the research vessel Ryofu-Maru since 1996, an estimation of the time series of CO_2 flux in the western North Pacific has become possible by using the observation results along 165°E in addition with those along 137°E. Figure shows the time series of the annual net CO_2 flux from 1996 to 2001 in the western North Pacific (11°N-30°N and 130°E-165°E). The ocean in this region acts as a source in summer and a sink in winter for the atmospheric CO_2. This region, however, acts as a net sink on a yearly base, because the absorption amount of CO_2 in winter is estimated to be greater than the emission amount in summer. The estimated annual net flux in this region has fluctuated between 30 TgC (30 x 10^{12} g carbon) and 85 TgC/year.

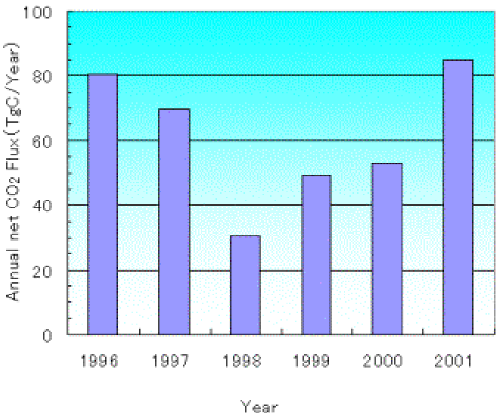

***Figure 9:** Time series of the net annual CO_2 flux in the subtropical region in the western North Pacific (11°N–30°N and 130°E–165°E) from 1996 to 2001. The unit is tera-gram (10^{12} gram) of carbon per year and positive means ocean uptake. The gas transfer formulation is based on Tans et al. (1990), and the gas transfer coefficient is calculated using surface-wind speed data from monthly-mean objective-analysis data (GANAL) Provided by Japan Meteorological Agency.*

7.9.11 CO_2 observation activities in other organizations in Japan

Activities in Tohoku University (Centre for Atmospheric and Oceanic Studies)

- Aircraft observations of GHGs over Japan
- Shipboard observations of GHGs over the Pacific Ocean
- Ground-based observations of GHGs in China, Japan, the Antarctic and the Arctic
- Observations of stratospheric of GHGs with balloons over Japan, the Antarctic and the Arctic
- Shipboard observations of oceanic CO_2 fluxes
- Gas analyses of Antarctic and Greenland ice cores

Activities in National Institute for Environmental Studies

- GHGs Monitoring at Hateruma and Cape Ochi-ishi
- Monitoring of GHGs along a north-south transect by volunteer ship
- Monitoring of the atmosphere-ocean carbon dioxide exchange by ship of opportunity
- Monitoring of greenhouse gases in Siberia by chartered airplane
- GHGs flux monitoring in Northern Forest

Activities in National Institute of Polar Research

- Studies of temporal and spatial variations of GHGs in the Antarctic and the Arctic
- Monitoring of GHGs at Syowa Station, Antarctica
- Monitoring of the atmosphere-ocean carbon dioxide exchange by "R/V SHIRASE" on her route to the Antarctic
- Analyses of ice core from "Deep Ice Coring Project at Dome Fuji, Antarctica"

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7.10 Climate Chemistry Studies of the Institute of Ocean Sciences in the North Pacific and Western Arctic

C.S. Wong, Institute of Ocean Sciences, Fisheries and Oceans Canada

7.10.1 Climate Chemistry Programmes

The Climate Chemistry Programme was initiated in 1969 as part of the Marine Science Directorate of the Pacific Region. Laboratory for atmospheric CO_2 monitoring was established for CO_2 collected on the weatherships between 1969 to 1981. An agreement was made between Dr. Bob Stewart, director of the Institute and Dr. Ken Hare, Director of Atmospheric Environment Service for the IOS laboratory to analyze atmospheric samples from Canadian WMO background stations at Alert, NWT, Sable Island, Nova Scotia and Cape St. James at Queen Charlotte Island, till AES established her own facilities. With funding from the Panel of Energy Research and Development of the Department of Natural Resources since 1981, the Laboratory has been designated by the Department of Fisheries and Oceans as a national Centre of Disciplinary Expertise for Ocean Climate Chemistry (COCC) with components of standard facilities and participation in international programs of GARP (Global Atmospheric Research Program). JGOFS (Joint Global Ocean Flux Study), WOCE (World Ocean Circulation Experiment), Global CO_2 Survey, SOLAS (Surface Ocean and Lower Atmosphere Study) and the GCP (Global Carbon Project), an IBGP Program sponsored by the International Oceanographic Commission of UNESCO. Its present scope of research and monitoring is in the Pacific Ocean and western Arctic.

7.10.2 Laboratory

The calibration laboratory has a cathetometer system capable of measuring pressure to 0.01 mm Hg in a chamber with temperature kept at 0.01ºC, and a fibre-quartz system for routine analyses, with inter-comparison with the system at the Scripps Institution of Oceanography. The gravimetric system consists of a balance capable of weighing gas cylinder of 100 kg to 0.1 g, a table balance capable of weighing small steel cylinder of 1 kg. to 0.001 g, and gas mixing system so that standards and working standards of CO_2, pCO_2 isotopic composition, freons and other GHGs can be prepared.

Analytical facilities include coulometric system for DIC (Dissolved inorganic carbon), TA (total alkalinity), pCO_2 by infrared/equilibrator and by sensors, pH. $^{13}C/^{12}C$ and $^{18}O/^{16}O$ by mass spectrometry, O_2/N_2 by mass spectrometry and by a fuel-cell system.

7.10.3 Field Projects

(1) Ships of opportunity: The oceanic CO_2 and isotope changes are being studied by sampling from cargo carriers: lumber carrier *M/V Skaugran* in great circle route between Japan and Vancouver; Japanese car carrier between Japan and Portland, USA; Canadian coastguard ship *CCGS Wifred Laurier* annually from Victoria to the Arctic.

(2) Atmospheric isotopic changes and O_2/N_2 changes. Sampling is being made at the international calibration station at Alert. O_2/N_2 study is being negotiated for BIOCAP biome towers at Campbell River, Vancouver Island, tundra site and boreal forest., and will be done on *JP Tully* along Line P (between Vancouver Island and Station P at 50ºN, 145ºW) and on the *CCGS Wilfred Laurier* in Alaskan Gyre, Bering Sea, Beaufort Sea and Canada Basin near Banks Island.

(3) Oceanic climate gases and tracers are being conducted in NE Pacific Ocean along Line P to measure changes and penetration of climate gases and tracers into the interior of the sub-arctic Pacific Ocean. The parameters include DIC, TA, surface pCO_2, CFC's, SF_6 and DMS.

(4) Fluxes of C, N, Si, Fe from upper ocean into deep ocean by moored sediment traps at Station P and other sites along Line P.

(5) Remote sensing of new production and air-sea CO_2 flux from space. SeaWifs ocean colour in combination with chlorophyll measurements from ships-of-opportunity and research ships and sediment trap carbon flux are used to assess oceanic new production and changes. Air-sea CO_2 flux is assessed from shipboard pCO_2 and wind data from satellite.

7.11 Update on the Canadian Atmospheric Greenhouse Gases Measurement Programmes

D. Worthy, A. Platt, R. Kessler, M. Ernst, C. Audette and S. Racki.

7.11.1 Introduction

Recommendations from the 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (this issue) expanded the measurement component list for global network comparability to include CH_4 (± 2 ppb), CO (± 2 ppb) and N_2O (± 0.2 ppb). The complete measurement component list can be found in the recommendations section. Recommendations from previous meetings for network comparability had only included $\delta^{13}C$-CO_2 (± 0.01‰) and CO_2 (± 0.1 ppm). In view on these recent changes, the aim of this report will be to summarize the current status of the CO_2, CH_4, CO and N_2O atmospheric measurement programmes in Canada, with a particular focus on data quality and network (interlaboratory) comparability.

7.11.2 Observational Sites

The Meteorological Service of Canada (MSC) currently operates a small network of stations (Figure 1). Alert, located on the northeastern tip of Ellesmere Island in the High Arctic reflects the long-range transport out of Europe and Siberia. The west coast station of Estevan Point is influenced by the North Pacific and transport out of Asia. Sable Island, 300 km off the east coast of Nova Scotia located in the Atlantic Ocean provides an excellent platform to assess the influence of anthropogenic and terrestrial emissions from the North American continent to the troposphere. Fraserdale, located in north central Ontario is strongly influenced by the eastern boreal forest and northern wetland regions around Hudson’s Bay. The western boreal forest region influences the Prince Albert station, located in a black spruce forest site near Prince Albert National Park SK.

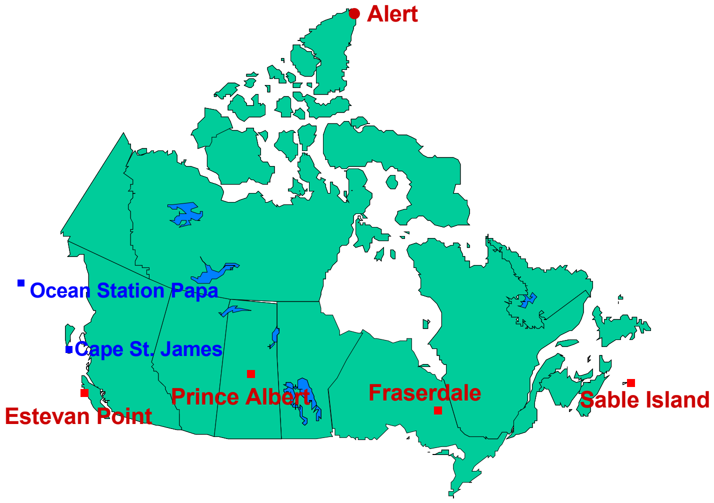

Figure 1: Location of Canadian baseline measurement sites. The measurements sites at Cape St. James and Ocean Station Papa are no longer in operation.

7.11.3 Measurement Programmes

A complete summary of the atmospheric greenhouse gas (continuous and flask) and stable isotope programmes carried out by MSC along with their respective start dates is outlined in Table 1. In view of the difficulty in achieving the WMO goal of ± 0.1 ppm for CO_2, a conscientious effort was made to implement flask-sampling programmes at sites with insitu measurement programmes. The dual flask and insitu programmes improve our capability to quality assess the data and monitor/evaluate systematic discrepancies. The flasks also provide multi-species and isotopic ratio analysis capability.

In order to evaluate and maintain inter-laboratory network comparability, a flask intercomparison programme (ICP) between NOAA/CMDL and MSC was implemented at Alert in 1999. An additional pair of NOAA 2.5 Litre flasks is sampled every week (total of 4 flasks). Two of the flasks are analyzed at MSC for CO_2, CH_4, CO, H_2, N_2O and SF_6 before being sent to NOAA for similar analysis. An ICP between CSIRO and MSC for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 was implemented at Estevan Point and Alert in 1997. Details and results on this programme can be found in *Huang et al.,* [2002] and *Langenfeld et al.,* [2003]. In 2002, the CSIRO/MSC ICP programme was expanded to include CO_2, CH_4, CO, H_2 and N_2O. In 2004, flask ICP programmes will be initiated at Alert for GHGs (and eventually for CO_2 isotopes as well) between MSC and the Max Planck Institute in Jena Germany and between MSC and the University of Heidelberg, Germany.

Table 1: GHG and Isotope Measurements carried out by MSC.

Station	Location	Type	Species	Sampling Frequency	Sampling Record
Alert, NU	82°27'N, 62°31'W	*Flask*	CO_2,	*weekly*	*1975-1998*
		Flask	$\delta^{13}C$ & $\delta^{18}O$	weekly	1997 - present
				bi-weekly	1997 - present
		Flask	CO_2, CH_4, CO, N_2O, SF_6	weekly	1998 - present
				bi-weekly	2000 - present
		Insitu	CO_2, CH_4,	Hourly	1988 - present
			CO	Hourly	1995 - present
			N_2O and SF_6	Hourly	2000 - present
Cape St. James, BC	52°, 130°W	*Flask*	CO_2,	*weekly*	*1979-1992*
Estevan Point, BC	49°35'N, 126°22'W	*Flask*	CO_2,	*weekly*	*1992-1998*
		Flask	$\delta^{13}C$ & $\delta^{18}O$	weekly	1997 - present
				bi-weekly	1997 - 2001
		Flask	CO_2, CH_4, CO, N_2O, SF_6	weekly	1998 - present
Sable Island, NS	43°56'N, 60°01'W	*Flask*	CO_2,	*weekly*	*1979 -1998*
		Flask	$\delta^{13}C$, $\delta^{18}O$, & CO_2, CH_4, CO, N_2O, SF_6	weekly	2003 - present
		Insitu	CO_2, CH_4, CO, N_2O, SF_6	Hourly	2003 - present
Fraserdale, ON	49°53'N, 81°34'W	Flask	$\delta^{13}C$, $\delta^{18}O$, & CO_2, CH_4, CO, N_2O, SF_6	8 Intensive campaigns	1998 - 2000
		Flask	$\delta^{13}C$, $\delta^{18}O$, & CO_2, CH_4, CO, N_2O, SF_6	weekly	2002 - present
		Insitu	CO_2, CH_4,	Hourly	1990 - 1996, 1998 -
			N_2O	Hourly	1998 - present
			CO and SF_6	Hourly	2002 - present
Prince Albert, SK	53°59'N,105°7'W	*Flask*	$\delta^{13}C$, $\delta^{18}O$, & CO_2, CH_4, CO, N_2O, SF_6	weekly	2002 - present
(BERMS-OBS)		*Flask*	$\delta^{13}C$, $\delta^{18}O$, & CO_2, CH_4, CO, N_2O, SF_6	intensive campaigns	2002 & 2003
		Insitu	CO_2, CH_4, CO, N_2O, SF_6	Hourly	2002 - present

7.11.4 Atmospheric CO_2:

The hourly averaged insitu CO_2 measurements and corresponding CO_2 flask measurements from Alert, Fraserdale, Sable Island and Prince Albert are shown in Figure 2. Time records only include periods when both insitu and flask samples are available. All CO_2 measurements are directly traceable to the international absolute WMO mole fraction scale maintained by the WMO Central Calibration Laboratory (CCL) at the NOAA/CMDL in Boulder. The in-house suite of primary tanks is calibrated at NOAA approximately every 2 years. Specific details on scale maintenance, recent WMO round robin results and on the insitu calibration and measurement protocols can be found in Worthy et al, [2003].

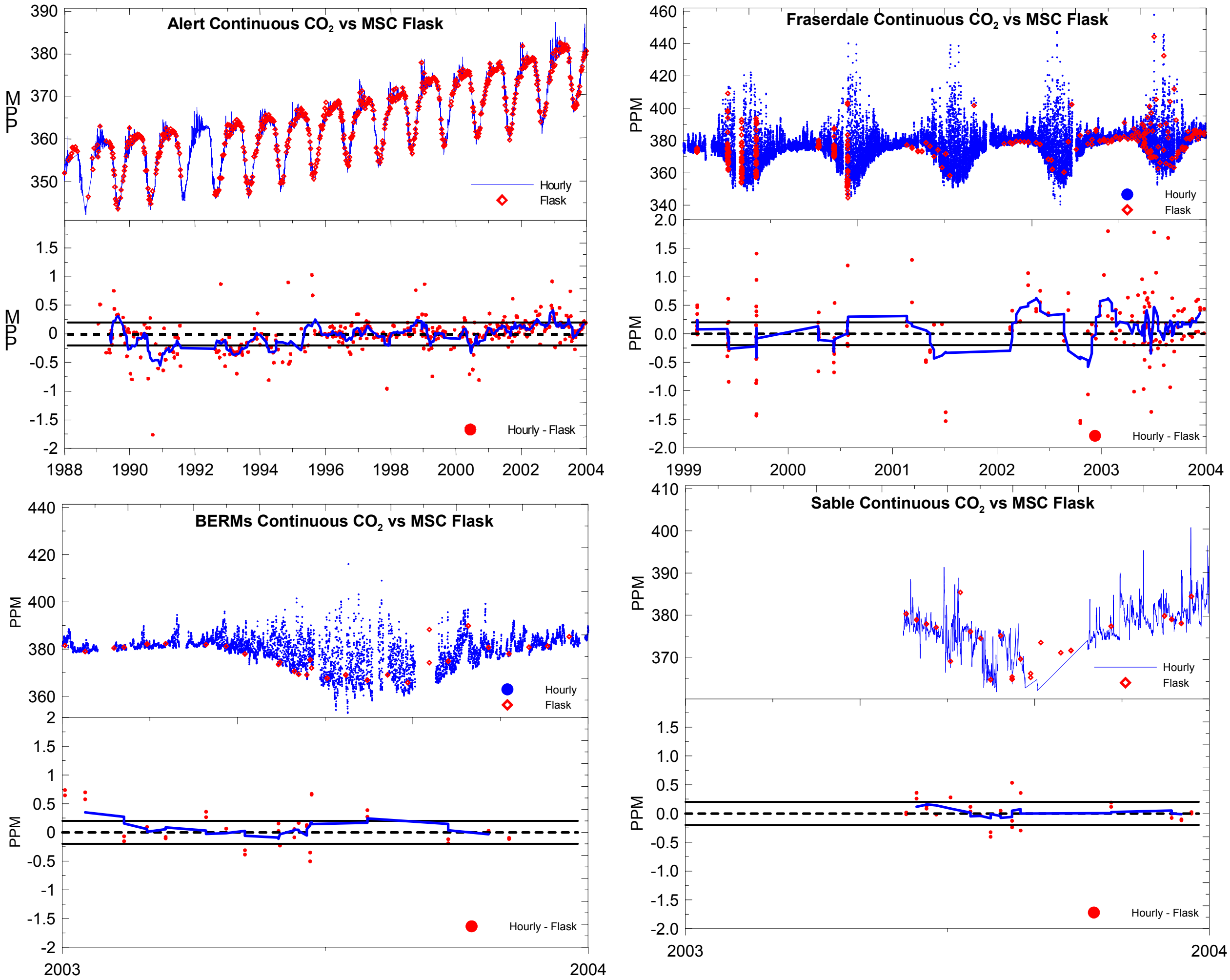

Figure 2: Hourly averaged insitu and weekly CO_2 mixing ratios at Alert, Fraserdale, Sable Island and Prince Albert. Time records only include periods when both Insitu and flask samples are available. The bottom panel displays the difference of the flask with the matching insitu hourly average value (Insitu – flask). The three lines on the bottom panel represent the zero, +0.2 and –0.2 ppm levels.

At Alert, the flask vs. insitu comparison for *CO_2* results in an average difference of **0.01±0.37ppm (n=573).** Since 1996, a similar offset of near zero is observed but with a reduced uncertainty of 0.22 ppm. An evaluation of the CO_2 flask programme as well as a history on the types of flasks utilized at Alert can be found in *Hudec and Trivett*, [1995] and in *Worthy et al.* [2003].

At Fraserdale, 8 intensive flask-sampling campaigns for diurnal isotope studies were conducted at Fraserdale between 1998 and 2000 [*Huang et al.*, 2003]. In order to extend the study, in 2002, an automated flask sampling system was built and installed at Fraserdale [*Ernst et al.*, 2003] for long-term trend analysis (in view of hoping to better understand the relationship of the regional terrestrial ecosystem to the global carbon cycle). Each week, a single flask is sampled prior to sunrise (diurnal maximum) followed by the sampling of a single flask in the late afternoon (diurnal minimum). The system can hold up to 8 flasks and is fully automated and if necessary, can be remotely programmed. The flask vs. insitu comparison for CO_2 at Fraserdale from all samples shows a mean difference of **0.11±0.85 ppm (n=274).** Most of the variability can be attributed to sampling during diurnal maximum when atmospheric variability in CO_2 is extremely high. When only the afternoon values are used, the mean difference is similar at 0.09 ppm but the variability reduces sharply to ± 0.41 ppm.

At Prince Albert, continuous measurement programmes for CO_2 as well as for CH_4, CO, SF_6 and N_2O began in May 2002. A bi-weekly flask-sampling programme for GHGs and isotopic analysis for ^{13}C and ^{18}O in CO_2 was also added. Unfortunately start-up problems were encountered with the CO_2 system resulting in an official start up date in January 2003. For flask sampling, a separate sample line is teed into to the main ambient sample line after the cryogenic moisture trap. The local operator samples two flasks in parallel. Initially, sampling tended to occur in the morning before local noon but the flask sampling protocol was changed to collect the samples in the late afternoon when the boundary layer should be well mixed. The flask vs. insitu comparison for CO_2 at Prince Albert from all samples shows a mean difference of **-0.02±0.39 ppm (n=58**).

At Sable Island, continuous measurement programmes for CO_2 as well as for CH_4, CO, SF_6 and N_2O began in June 2003. A separate sampling case with pump and drying cartridge had been used to collect flask samples but after installation of the continuous monitoring equipment, flasks were sampled using a sample line teed into the main dried ambient sample line (similar to that done at Prince Albert). The local operator samples two flasks in parallel each week. No time restrictions for sampling are given. The flask vs. insitu comparison for CO_2 at Sable Island from all samples shows a mean difference of **0.03±0.21 ppm (n=38**).

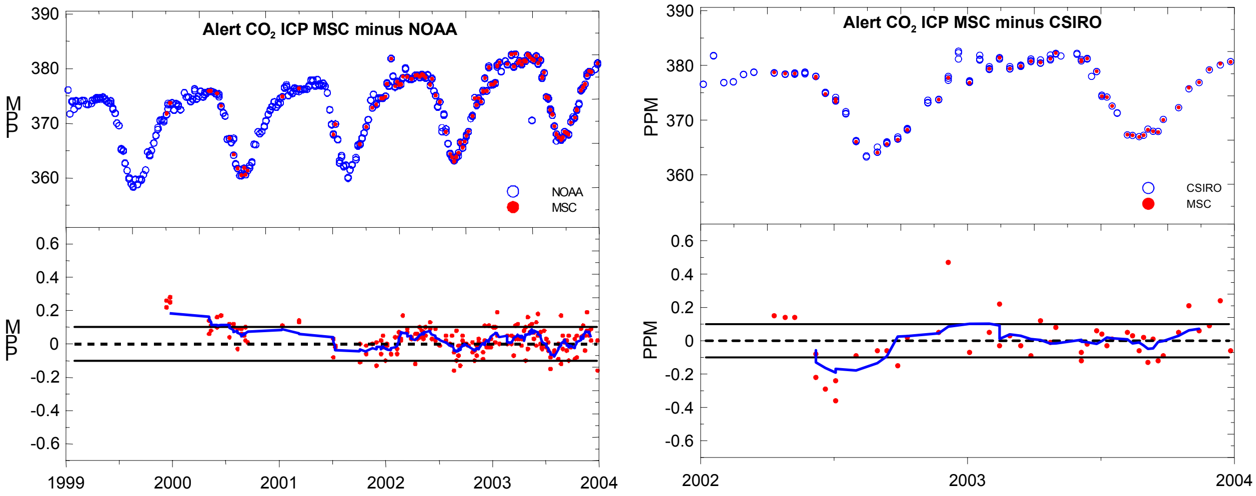

Figure 3: A comparison of individual flask analysis between MSC and NOAA and MSC and CSIRO. The bottom panel shows the differences (MSC minus NOAA and MSC - CSIRO). The three lines represent the zero, +0.1 and –0.1 ppm levels.

Network comparability has typically been assessed based on round robin standard tank intercomparisons. Although a good first measure, it's been shown that consistent laboratory tank intercalibrations do not necessarily translate to similar comparisons on flasks [*Masarie et al*., 2001]. Flask ICP programmes provide a "truer" measure of network comparability in that analytical capabilities come into play as well. Figure 3 shows the ICP flask intercomparison values for CO_2 between NOAA/CMDL and MSC and CSIRO and MSC. The comparison data results in a mean difference of 0.04 ± 0.19 ppm (n=234) for the MSC/NOAA ICP and a mean difference of –0.003 ± 0.16 ppm (n=46) for MSC/CSIRO. Both ICP programmes appear to indicate all 3 laboratories, on average, meet the 0.1 ppm WMO network comparability objective. It's important to note that in order to maintain these network comparability levels, it's imperative that ICP programmes continue to run on an on-going basis.

7.11.5 Atmospheric CH_4:

The hourly averaged insitu CH_4 measurements and corresponding CH_4 flask measurements from Alert, Fraserdale, Sable Island and Prince Albert are shown in Figure 4.Time records include only periods when both insitu and flask samples are available. The historic and current measurement procedures along with the equipment and processing routines applied at all four sites have been previously reported. [*Worthy et al.,* 1999] The MSC CH_4 measurement scale is propagated from a Standard Reference Material cylinder purchased from the National Institute for Standards and Technology (NBS SRM-1658a, 913± 10 ppb) in 1985. In 1986, three large steel cylinders previously used in the CO_2 programme were adopted as secondary standards for the methane programme. These 3 standard tanks are still in use today. The MSC CH_4 scale has also been compared with the CH_4 scale utilized at NOAA/CMDL via several inter-calibration experiments. The CH_4 mixing ratios determined by MSC are a factor of 1.0151 higher than those determined by NOAA/CMDL. Further details on the CH_4 calibration scale and inter-calibration results can be found in Worthy et al. [1998].

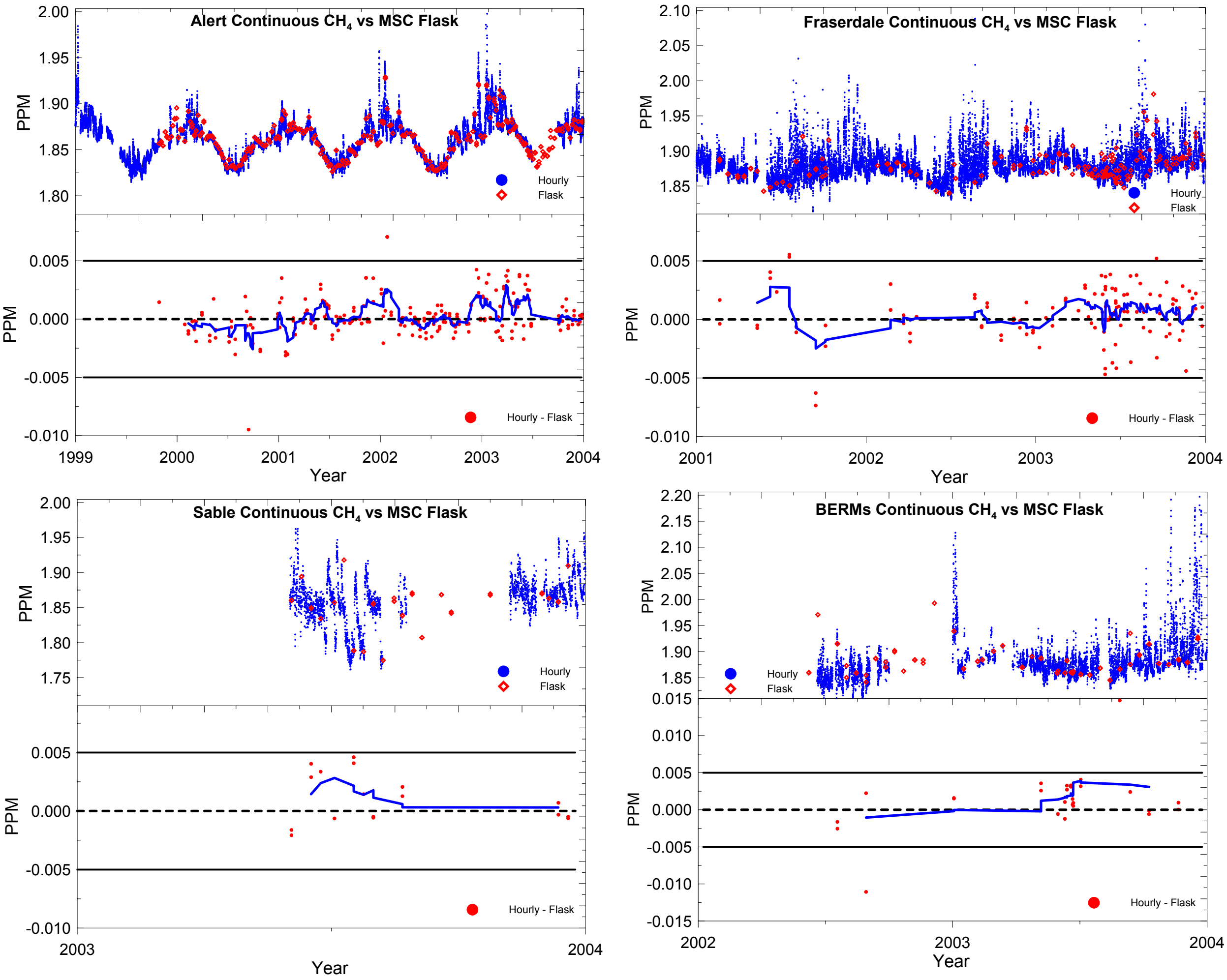

Figure 4: Hourly averaged Insitu and weekly CH_4 mixing ratios at Alert, Fraserdale, Sable Island and Prince Albert. Time records include only periods when both Insitu and flask samples are available. The bottom panel displays the difference of the flask with the matching insitu hourly average value (Insitu – flask). The three lines on the bottom panel represent the zero, +5 and –5 ppb levels.

The comparison of the flasks and continuous data results in a mean difference of **0.04±2.7 ppb (n=262)** for Alert, **1.4±2.7 ppb (n=135)** for Fraserdale, **-2.8±1.6 ppb (n=18)** for Sable Island and **0.91±3.7 ppb (n=29)** for Prince Albert. All 4 sites indicate good agreement. Figure 5 illustrates the ICP flask intercomparison results for CH_4 between NOAA/CMDL and MSC and CSIRO and MSC. All MSC data has been adjusted to the NOAA/CMDL CH_4 measurement scale. The comparison data results in a mean difference of **0.38 ± 2.2 ppb (n=235)** for the MSC/NOAA ICP and a mean difference of **1.5 ± 3.4 ppv (n=46) ppb** for MSC/CSIRO ppb. The ICP programmes appear to indicate that all 3 laboratories, on average, meet the 2 ppb WMO network comparability objective.

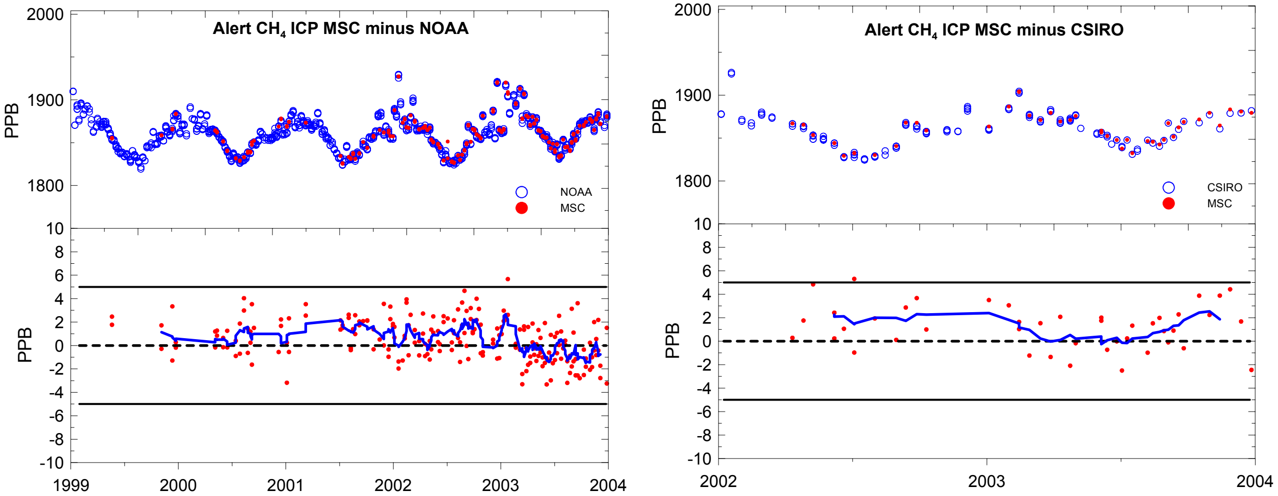

Figure 5: Comparison of individual flask analysis between MSC and NOAA and MSC and CSIRO. The bottom panel shows the differences (MSC minus NOAA and MSC - CSIRO). The three lines represent the zero, +05 and –5 ppb levels.

In addition to the ICP flask programmes being used to assess network comparability levels, in May 2004, the GAW World Calibration Centre audited the CH_4 and CO programmes at Alert. Five tanks with various levels of CH_4 and CO mixing ratios were evaluated first on the calibration system in Toronto and then a few weeks later on the insitu CH_4 and CO GC instruments in Alert. The CH_4 results, listed in Table 2, are preliminary because the tanks require an end point calibration. Nonetheless, it appears that on average, the results will be within the 2 ppb WMO network comparability value.

Table 2: GAW Station Audit results for Methane. Data are reported in ppb on the NOAA/CMDL measurement scale. Numbers in parenthesis represent the 1σ value.

Tank SN	**Toronto Evaluation**	**Alert Evaluation**	**Preliminary GAW Assigned Value**	**Difference**
030701-1	1901.15 (0.6)	1900.50 (1.3)	1896.0	4.50
030701-2	1738.80 (0.5)	1736.77 (1.4)	1736.3	0.47
030701-3	1753.80 (0.9)	1753.82 (1.3)	1753.3	0.52
FF01477	1779.10 (0.5)	1779.43 (1.1)	1777.9	1.53
FF30491	1821.30 (1.4)	1821.30 (1.1)	1820.5	0.80

7.11.6 Atmospheric CO

The hourly averaged insitu CO measurements and corresponding CO flask measurements from Alert, Fraserdale, Sable Island and Prince Albert are shown in Figure 6. The Toronto CO flask system “officially” came on line in February 2003 and thus, the time records in Figure 6 only show data starting in 2003, even though many of the continuous data records begin earlier**.** The automated continuous CO measurements at Alert are made using a commercial RGA3 Reduction Gas Analyzer. The automated continuous CO measurements at Fraserdale, Prince Albert and Sable Island are made using FID methodology by converting the CO to CH_4 via a Nickel catalyst.

An RGA3 Reduction Gas Analyzer is also used in the central laboratory facility in Toronto for both gas standard calibrations and flask analysis. Detailed descriptions of the insitu measurement systems including sampling and calibration protocols and data reduction procedures are described in the 1998 and 2002 Baseline Summary Reports [Worthy et al., 1999 and 2003].

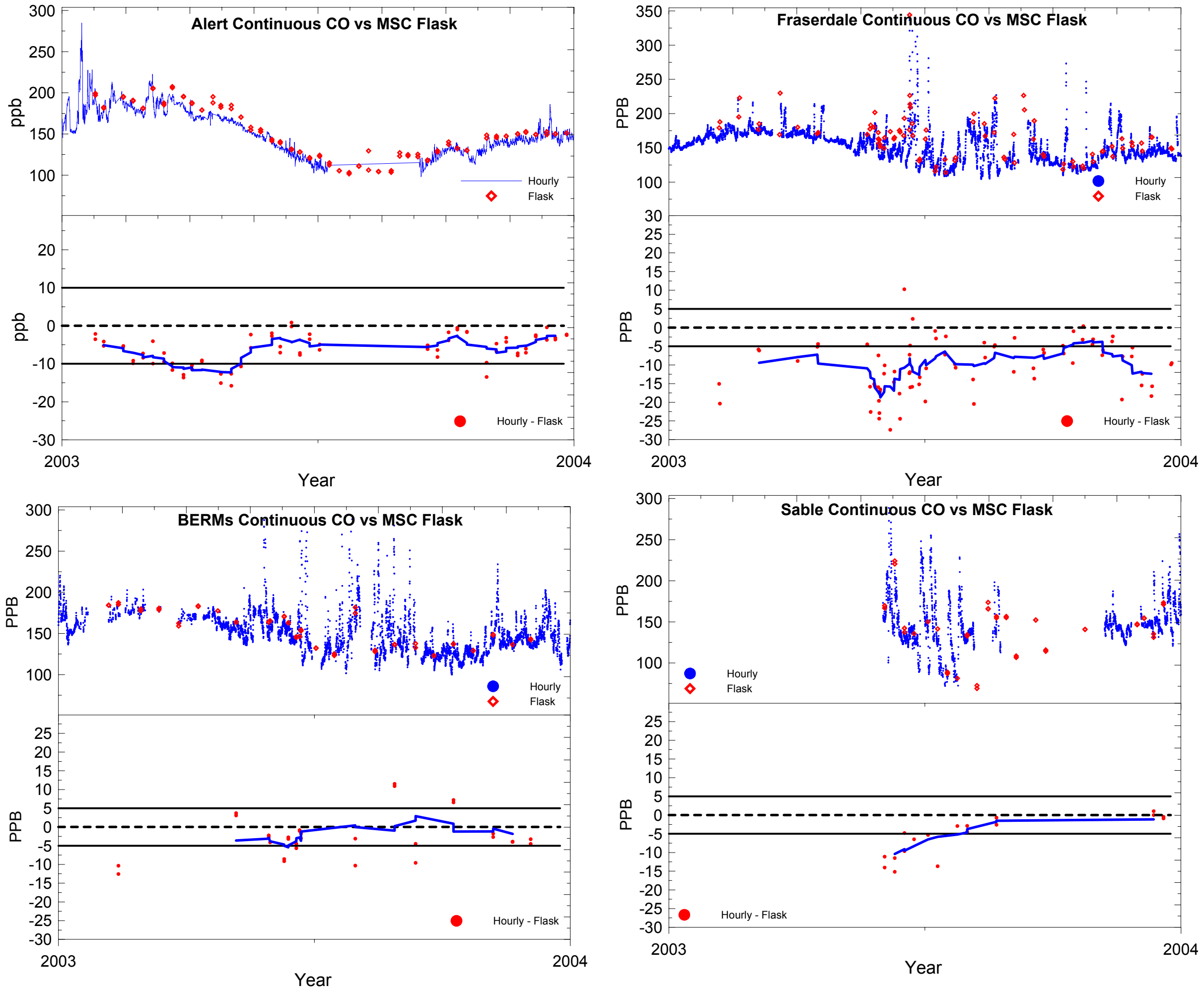

Figure 6: Hourly averaged Insitu and weekly CO mixing ratios at Alert, Fraserdale, Sable Island and Prince Albert. Time records only include periods when both Insitu and flask samples are available. The bottom panel displays the difference of the flask with the matching insitu hourly average value (Insitu – flask). The three lines on the bottom panel represent the zero, +5 and –5 ppb levels.

The CO measurement scale is based on a set of six 29.5 L aluminium cylinders purchased in 1993 from Scott Marin located in California. The cylinders span the concentration range of 50 ppb to 300. The cylinders have been calibrated at the NOAA/CMDL calibration facility (the WMO assigned holder of the international CO scale) in 1993, 1998 and 2003. All calibration values have been adjusted/updated to recent scale changes applied by NOAA/CMDL to their CO measurement scale.

The comparison of the flasks and continuous data (Figure 6) results in a mean difference of **–5.3±2.8 ppb (n=28)** for Alert**, -12.1±7.5 ppb (n=42)** for Fraserdale, -8.9±6.9 ppb (n=18) for Sable Island and **–5.8±7.1 ppb (n=31**) for Prince Albert. These values obviously do not meet the assigned 2 ppb GAW CO precision requirements, however, the large discrepancies between the flask and insitu values (with the flasks being higher) and large variability can be attributed to the Viton O-rings used in the flask stopcocks. Viton is known to cause CO out-bleeding.

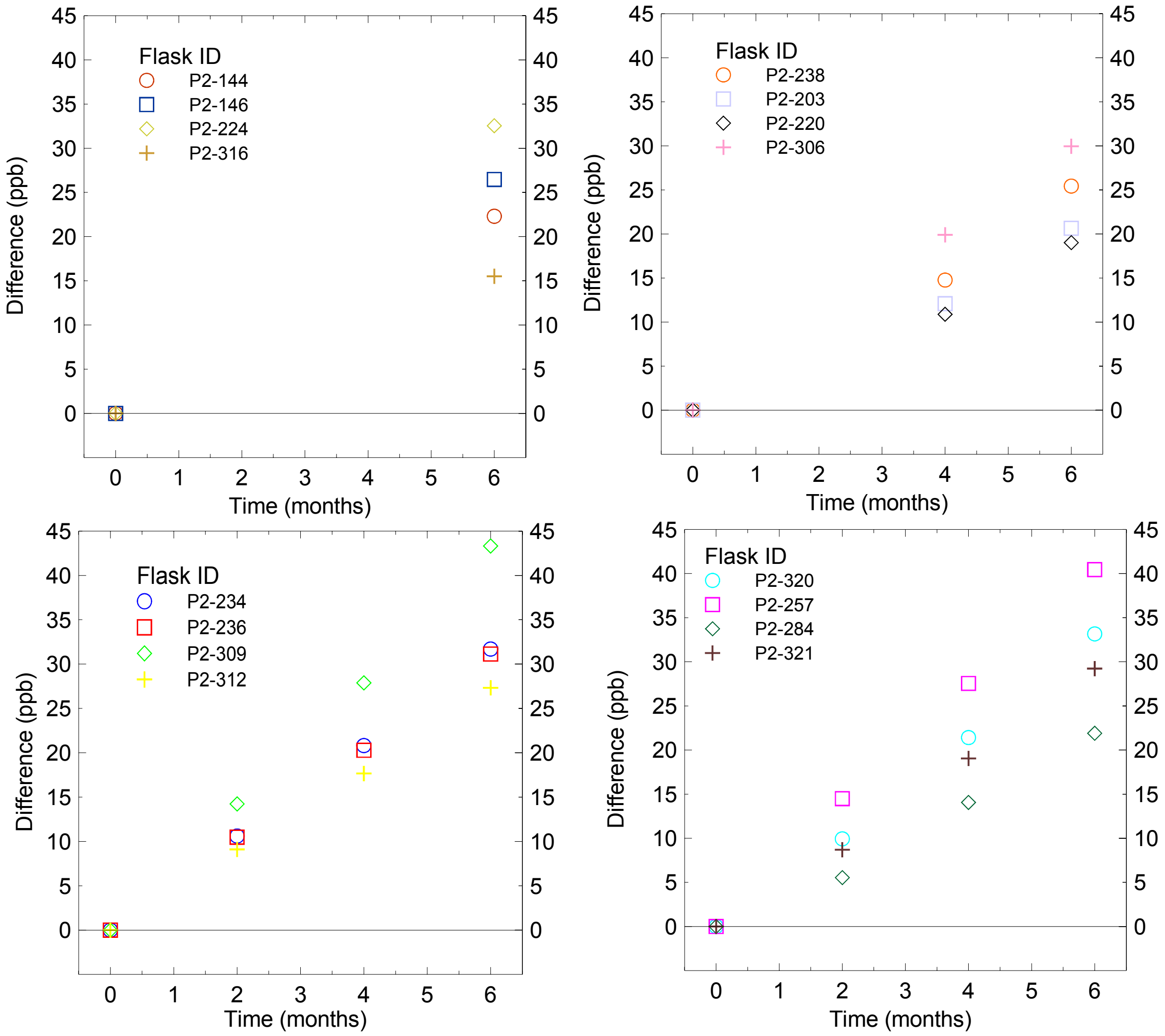

Figure 7: Flask storage test results for CO. Each flask was filled with dry calibration gas and analyzed immediately to assign an initial concentration level. The 16 flasks were then divided into 4 subsets of 4 flasks each. These subsets of flask were then analyzed at different times and frequencies over the 6-month period.

The Viton problem for CO is clearly evident in Figure 7**.** A series of flask storage tests were conducted over a 6-month period using 16 standard MSC double stopcock flasks. Each flask was filled with dry calibration gas and analyzed immediately to assign an initial concentration level. The 16 flasks were then divided into 4 subsets of 4 flasks each. These subsets of flask were then analyzed at different times and frequencies over the 6-month period. Some subsets were analyzed in 2-month intervals (for a total of 4 analyzes) while some flasks were stored longer before conducting a 2nd analysis. Figure 7 clearly shows the CO concentration in each flask increasing. The drifts are typically on the order of 5 ppb to 10 ppb per month. Considering the assigned network capability requirement of 2 ppb, these flasks are obviously not suitable for high precision CO measurements. MSC is currently evaluating options on replacing these o-rings

Figure 8 illustrates the ICP flask intercomparison results for CO between NOAA/CMDL and MSC and CSIRO and MSC. As noted earlier, the MSC-NOAA ICP is conducted using the standard 2L NOAA type flask. The MSC-CSIRO ICP is conducted using MSC type flasks and is of course subject to CO drifting problems. The comparison data results in a mean difference of **–6.5** ± **4.0 (n=66)** ppb for the MSC/NOAA ICP and a mean difference of **2.93** ± **5.3 ppv (n=46)** ppb for MSC/CSIRO ppb. The ICP programmes indicate that network comparability for MSC does not meet the 2 ppb WMO network comparability objective. This is a further example of how acceptable comparisons on tanks do not necessarily translate to similar comparisons on flasks. For instance, the recent Alert WMO GAW audit results for CO (Table 3) show much better agreement and on average, meet the 2 ppb network agreement level.

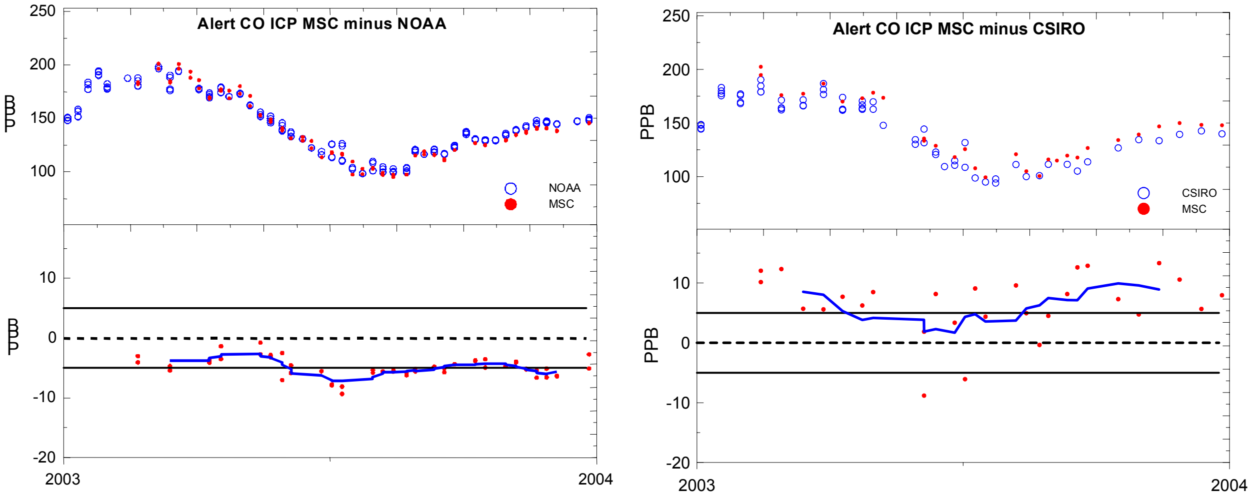

Figure 8: A comparison of individual flask analysis for CO between MSC and NOAA and MSC and CSIRO. The bottom panel shows the differences (MSC minus NOAA and MSC - CSIRO). The three lines represent the zero, +05 and –5 ppb levels.

Table 3: GAW Station Audit results for Carbon Monoxide. Data are reported in ppb on the NOAA/CMDL measurement scale. Numbers in parenthesis represent the 1σ value. The GAW results are preliminary and possibly subject to adjustment.

Tank SN	Toronto Evaluation	Alert Evaluation	Preliminary GAW Assigned Value	Difference
030701-1	51.28 (1.34)	49.66 (0.49)	53	3.3
030701-2	116.85(0.34)	116.29 (0.9)	117	0.7
030701-3	72.06 (0.13)	71.05 (0.56)	73	2.0
FF01477	196.02 (0.84)	196.73 (1.9)	196	0.7
FF30491	157.94 (0.53)	157.65 (1.0)	160	2.4

7.11.7 Atmospheric N_2O:

The hourly averaged Insitu N_2O measurements and corresponding N_2O flask measurements from Alert, Fraserdale, Sable Island and Prince Albert are shown in Figure 9. Startup problems on the system at Sable Island resulted in an initial start time of November 29th 2003, as opposed to June 3rd when the CO, CH_4 and CO_2 programmes came on-line. The automated continuous measurements of N_2O at Alert and Fraserdale are made using Agilent 6890 gas chromatographs employing ECD methodology. At Sable Island and Prince Albert, Hewlett Packard model 5890 gas chromatographs are used. Detailed descriptions of the insitu measurement systems including system specifications, sampling and calibration protocols and data reduction procedures are described in the 1998 and 2002 Baseline Summary Reports [Worthy et al., 1999 and 2003].

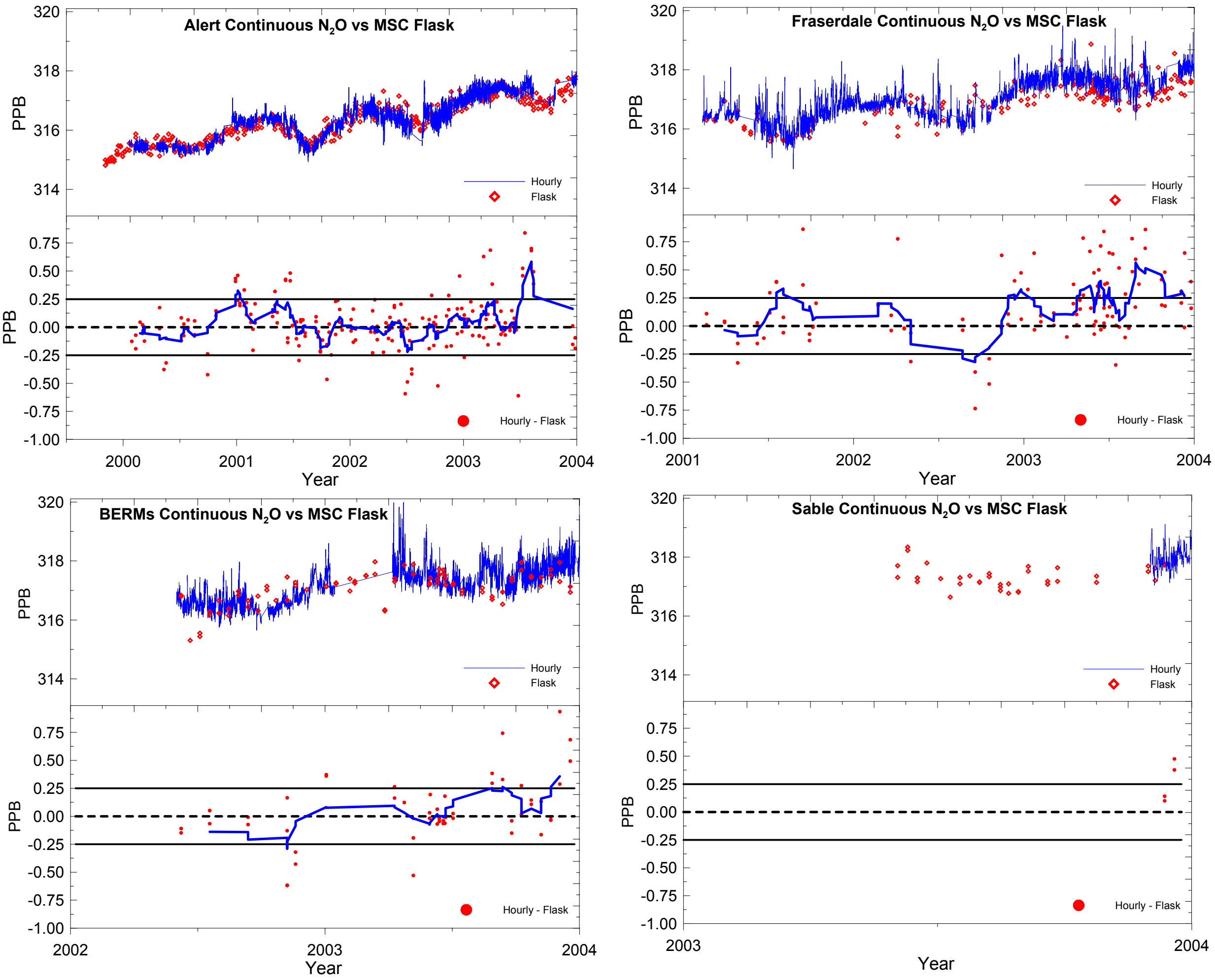

Figure 9: Hourly averaged Insitu and weekly N_2O mixing ratios at Alert, Fraserdale, Sable Island and Prince Albert. Time records only include periods when both Insitu and flask samples are available. The bottom panel displays the difference of the flask with the matching insitu hourly average value (Insitu – flask). The three lines on the bottom panel represent the zero, +0.25 and –0.25 ppb levels.

The N_2O reference scale is propagated from a standard gas cylinder provided by the NOAA/HATS group in Boulder Colorado. The data reported here have not yet been adjusted for instrument non-linearity. The ECD detection technique is significantly non-linear and preliminary non-linearity analyses have been done (~ 0.2 ppb/ppb) but the data will not be adjusted until the non-linearity has been thoroughly evaluated against a suite of calibrations tanks with various concentration levels. As recommended (as listed in the recommendation section), six standard tanks from Scott Marin in California spanning the concentration range of 280 to 330 ppb have been recently purchased. These gas tanks are currently being calibrated at the central calibration facility for N_2O at NOAA/CMDL. All data will be corrected/adjusted for scale and non-linearly. For the time being, all flask and insitu N_2O data are currently computed relative to a single point calibration.

The comparison of the flasks and continuous data (Figure 9) results in a mean difference of **0.08±0.4 ppb (n=213)** for Alert**, 0.33±0.44 ppb (n=115)** for Fraserdale**, 0.43±0.36 ppb (n=5)** for Sable Island and **0.16±0.55 ppb (n=55**) for Prince Albert. The values for all 4 sites are either within or close to the assigned GAW 0.2 ppb N_2O precision requirement. The implementation of correct calibration curves on all insitu systems and the Toronto flask and calibration system should improve these flask-insitu intercomparisons results.

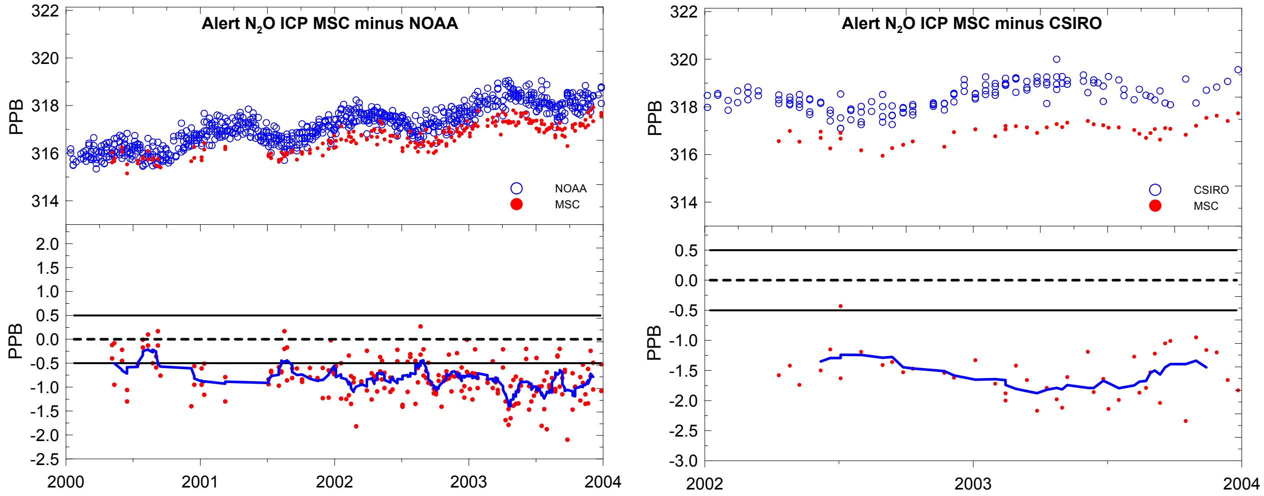

Figure 10: A comparison of individual flask analysis for N$_2$O between MSC and NOAA and MSC and CSIRO. The bottom panel shows the differences (MSC minus NOAA and MSC - CSIRO). The three lines represent the zero, +0.5 and –0.5 ppb levels.

The results for N$_2$O from the flask intercomparison programme between NOAA/CMDL and MSC at Alert show the effect of the non-linearity. The offsets for the MSC-CSIRO are due to scale differences between the 2 respective laboratories. The effect of non-linearity on the CSIRO-MSC ICP is not obvious because the duration of the study is small.

7.11.8 Summary

The aim of this report was to provide an update on the status of the flask and continuous CO$_2$, CH$_4$, CO and N$_2$O measurement programmes and to assess the quality and accuracy of these data in view of the recently assigned WMO recommended network precision requirements. Sampling and calibration protocols have been described in detail in previous reports. The results of the multiple flask programmes (ICP and insitu inter-comparisons) gives us greater confidence in the accuracy of our measurements and shows that it is possible to meet the WMO objective within our own programme and between laboratories for CO$_2$ and CH$_4$. Replacement of the Viton O-rings in the MSC dual stopcock flasks is required for adequate CO analysis. Nevertheless, the flask ICPs with NOAA indicates discrepancies larger than 2 ppb. Further investigative work will be required to improve the CO programme. We're confident that implementation of calibration curves on the individual ECDs at each site, including on the flask and calibration system in Downsview will markedly improve the N$_2$O programme and that the 0.2 ppb network precision requirement will be met.

7.11.9 Acknowledgements

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7.12 CO_2, CH_4, CO Monitoring & Research Programmes at the China GAW Baseline Observatory, Mt. Waliguan, China

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7.12.1 Introduction

The China GAW Baseline Observatory, Mt. Waliguan (CGAWBO, 36°17'N, 100°54'E, 3810m asl) is located on the Tibetan Plateau in Western China. It is a part of China's commitment to the World Meteorological Organization's (WMO) Global Atmospheric Watch (GAW) program. The CGAWBO was officially opened in September 1994. With the exception of occasional re-construction activities (1998-2000), the observatory has been fully operational. It is an established site within the GAW network (the only baseline station in continental Asia) for long-term measurements of greenhouse gases, ozone, physical and meteorological parameters (Wen et al., 1993, 1994; WMO, 2001, 2003; Zhou et al., 1998a, 2003b, 2004d).

7.12.2 Site and experiment

Mt. Waliguan is a remote site away from major anthropogenic sources. The general area is covered in sparse vegetation. The immediate surroundings are grassy with no tree growth. Figure 1 shows a topographical map with a radius of 100km; the triangles represent high mountains (height in meters above sea level). The meteorological data indicate a typical continental plateau climate. It is relatively windy and dry with a yearly precipitation of 300mm (mostly during summer). The yearly mean temperature is -1.5°C (Wen et al., 1994; Zhou et al., 2003b, 2004d). Figure 2 shows wind roses during the period of 1994-2000. Predominant wind directions have a significant seasonal change, from WSW in winter (D, J, F) to ESE-ENE in summer (J, J, A).

Figure 3 shows the main building and facilities of the CGAWBO. Situated on the northwest hilltop of Mt. Waliguan, the area of the observatory is about 8 hectare, which is contained with a fence, in order to exclude livestock. There is an observational area 100m east of the main building. An 89m tower, erected 20m east of the main building, is used to measure certain meteorological parameters at different levels (10m, 20m, 40m, 80m heights) and to obtain air samples from the 80m height for the in-situ CO_2, CH_4 and CO measurements. The first floor of the main building contains living quarters, kitchen and bedrooms. The laboratories with the measurement instruments are located on the second floor. The main laboratory with the in-situ CO_2, CH_4 and CO monitoring systems is maintained at a temperature of 18±2°C.

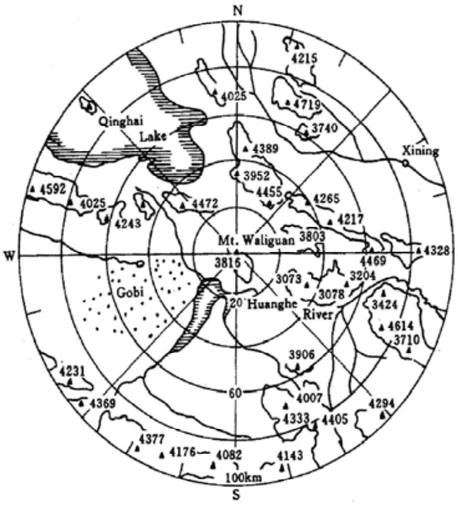
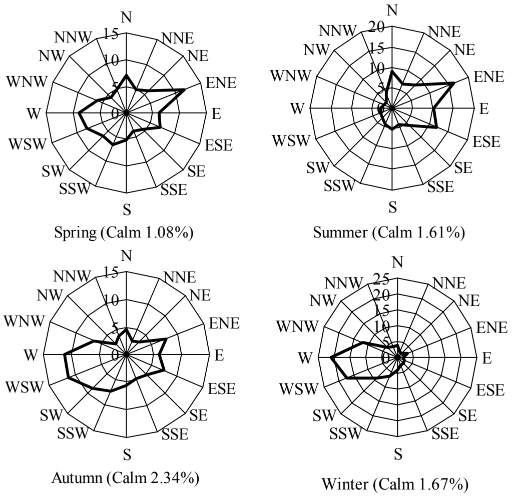


Figure.1: Topographical map (within 100km distance).



Spring (Calm 1.08%)

Summer (Calm 1.61%)

Autumn (Calm 2.34%)

Winter (Calm 1.67%)

Figure 2: Wind rose (1994-2000).

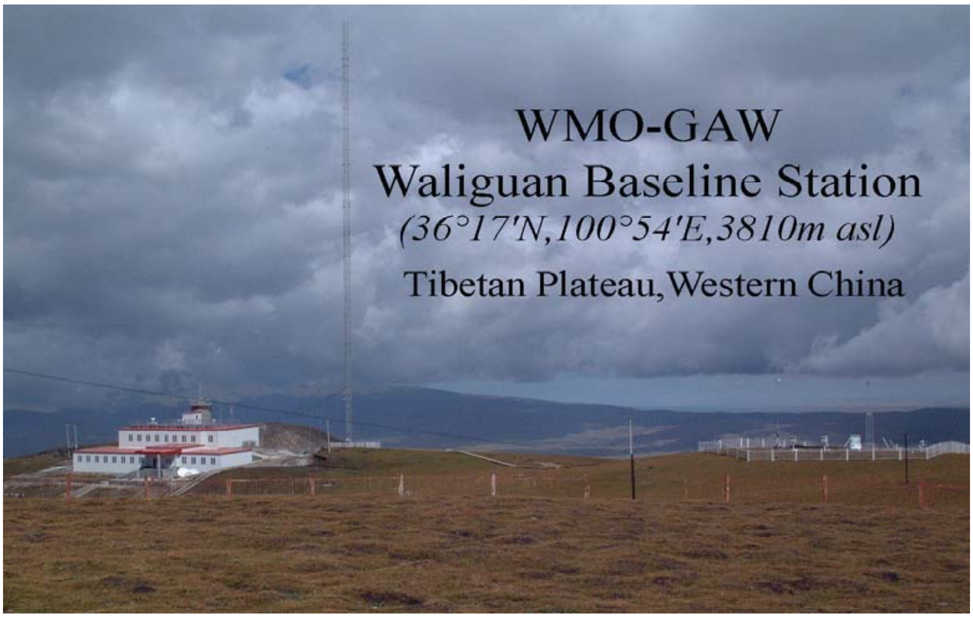


Figure 3: Main building and facilities of the CGAWBO.

The in-situ CO_2 mixing ratio is measured using a Licor6251 NDIR system (~1994-08, continuously), originally built at NOAA-CMDL, USA under a GAW “twinning” arrangement. The in-situ CH_4 and (2nd) CO_2 mixing ratio is measured by an HP5890 GC-FID system (~August 1994, 64 ambient injections per day) and the in-situ CO mixing ratio is measured by an RGA-3 system (~November 1997, 14 ambient injections per hour). Both systems were originally built at MSC, Canada under a GAW "twinning" arrangement.

Three groups of standard gas cylinders (provided by CMDL and MSC, for the NDIR, GC-FID, RGA-3 analytical systems, respectively) are used to calibrate the instruments' responses. Detailed descriptions of the systems' performances have been previously written (see references Wen et al., 1993; Zhou et al., 1998a, 2001a, 2001b, 2003b, 2004d).

As a part of the NOAA-CMDL Cooperative Air Sampling Network, discrete air samples are collected in glass flasks approximately weekly at Mt. Waliguan and returned to the CMDL and CU/INSTAAR laboratories for analysis. Measurements of CO_2, CH_4, CO, H_2, $\delta^{13}C$ and$\delta^{18}O$ of CO_2 started from 1990, N_2O and SF_6 from 1997, and $\delta^{13}C$ of CH_4 from 2002. As of July 2003, more than 600 pairs of air samples were collected. Data obtained at Mt. Waliguan by the in-situ and discrete measurements are being used in the NOAA-CMDL Cooperative Atmospheric Data Integration Project and are also available from the CMDL, CDIAC, and WDCGG database (CMDL, 2002; Globalview, 2001, 2003; Masarie and Tans, 1995; WMO, 2001, 2003).

7.12.3 Programme status and results

7.12.3.1 In-situ CO_2 measurement programme

Figure 4 and Figure 5 show daily CO_2 measurements and standard deviations at Mt. Waliguan. CGAWBO (CMA Central Lab in Beijing) joined the WMO Round-robin CO_2 inter-comparison organized by NOAA-CMDL for the periods of 1995-1997 and 1999-2000. The CO_2 concentration differences from NOAA-CMDL (CMA minus NOAA, ppm) were -0.07 (low), -0.01 (medium) and -0.02 (high) in December 1995, -0.08 (low), -0.20(medium) and -0.13 (high) in September 1999, respectively (see http://gaw.kishou.go.jp/wcc/co2/co2comparison.html for further details).

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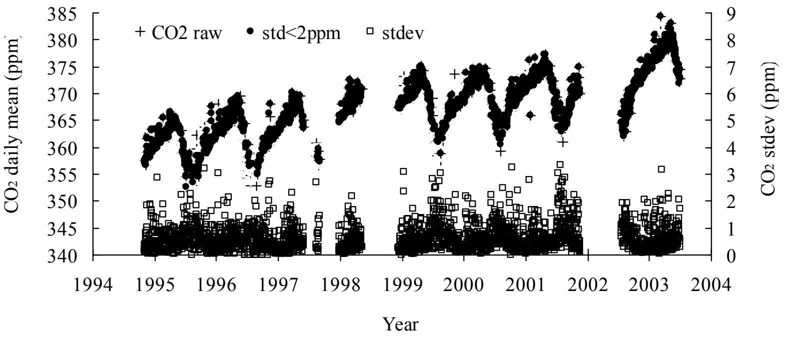

Figure 4: In-situ CO_2 daily average and standard deviation by hourly mean.

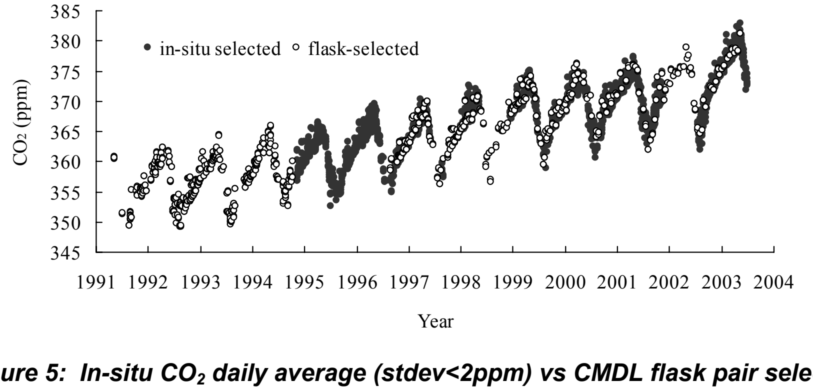

Figure 5: In-situ CO_2 daily average (stdev<2ppm) vs CMDL flask pair selected.

The most recent calibration of the CMA CO_2 primary standard cylinders (X93) was performed at SIO in January 1994. A re-calibration of the CMA CO_2 primary standards by NOAA-CMDL during the period of 2001-2002, could not be completed because of overseas transportation and customs problems, due to the age of the cylinders (almost 10 years old). A new set of five primary standards have been purchased by CMA, from NOAA-CMDL. The CMA will be participating in the 2002-2004 (and future) WMO Round-robin activities. Dr. Lingxi Zhou from CMA-CAMS serves as the referee and handles measurement results from the WMO Round-robin participants. A CMA (China) and NIES (Japan) periodic "Melon" or "Sausage" standard gas inter-comparison program on the GHGs and related tracers is under discussion.

7.12.3.2 In-situ CH_4 and in-situ CO measurement programmes

Figure 6 and Figure 7 show hourly CH_4 and CO measurements at Mt. Waliguan. Inter-comparison of CH_4 measurements among JMA, KMA and CMA (Asian area) was performed in the year 2001 and organized by the WMO-WCC under JMA, Japan (http://gaw.kishou.go.jp/wcc/ch4/comparison.html). The in-situ CH_4 monitoring system at CGAWBO was upgraded directly afterwards and the raw data haven't been analyzed since then. The system calibration and the in-situ CH_4 data processing will be conducted soon. The CGAWBO CH_4 calibration factor (propagated from MSC, Canada) is 1.0151 higher than that of the NOAA-CMDL scale (Global-view CH_4, 2001; Worthy et. al., 1998, Zhou et al., 1998a). All of the scientific outcomes of the CH_4 data obtained at Mt. Waliguan (Zhou et al., 1998a, 1998b, 2001a, 2004a, 2004b, and in this issue) have been reported on the NOAA-CMDL CH_4 scale.

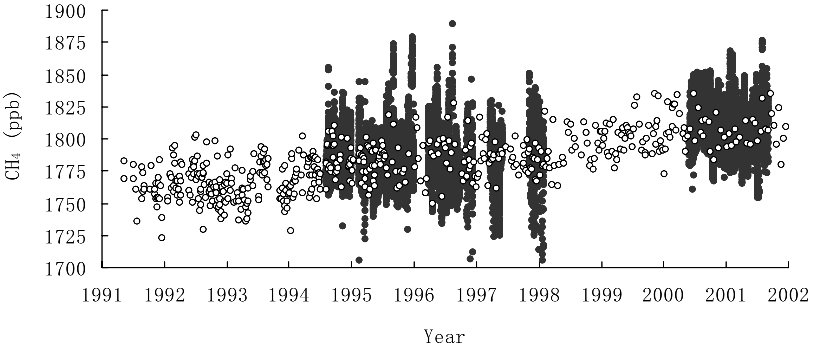

Figure 6: In-situ CH_4 hourly means (stdev<10ppb) vs CMDL flask pair selected.

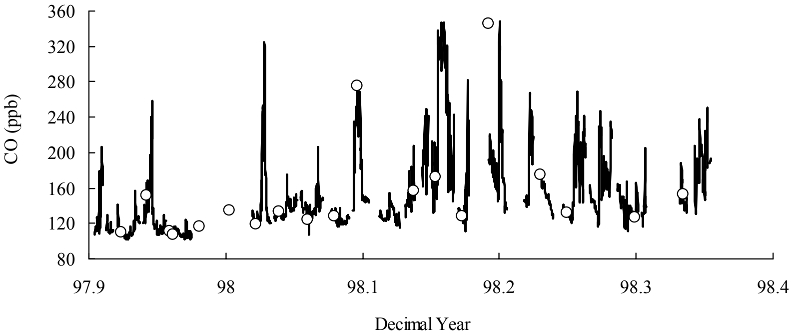

Figure 7: In-situ CO hourly averages vs NOAA-CMDL flask pair selected.

WLG RGA-3 = 0.98xCMDL scale (CO in ppb from the 4 CMDL transfer standards of the WCC)+6.6ppb

A system performance audit for surface O_3, CO and CH_4 was performed at Waliguan by the WMO-WCC under the Swiss Federal Laboratories for Materials Testing (EMPA) in September 2000 (Zhou et al., 2001a, 2001b, 2004c). Due to the building re-construction and the RGA-3 instrument malfunction at CGAWBO, in-situ CO measurements at Mt. Waliguan were interrupted frequently, and ultimately stopped in May 2002. An attempt to re-start the CO system in December 2003, with help from the WMO-AREP-Environment Division, was unfortunately not successful. Presently, EMPA is providing technical support and spare parts and will perform a second audit (for surface O_3, CO, CH_4) at Mt. Waliguan in the autumn of 2004.

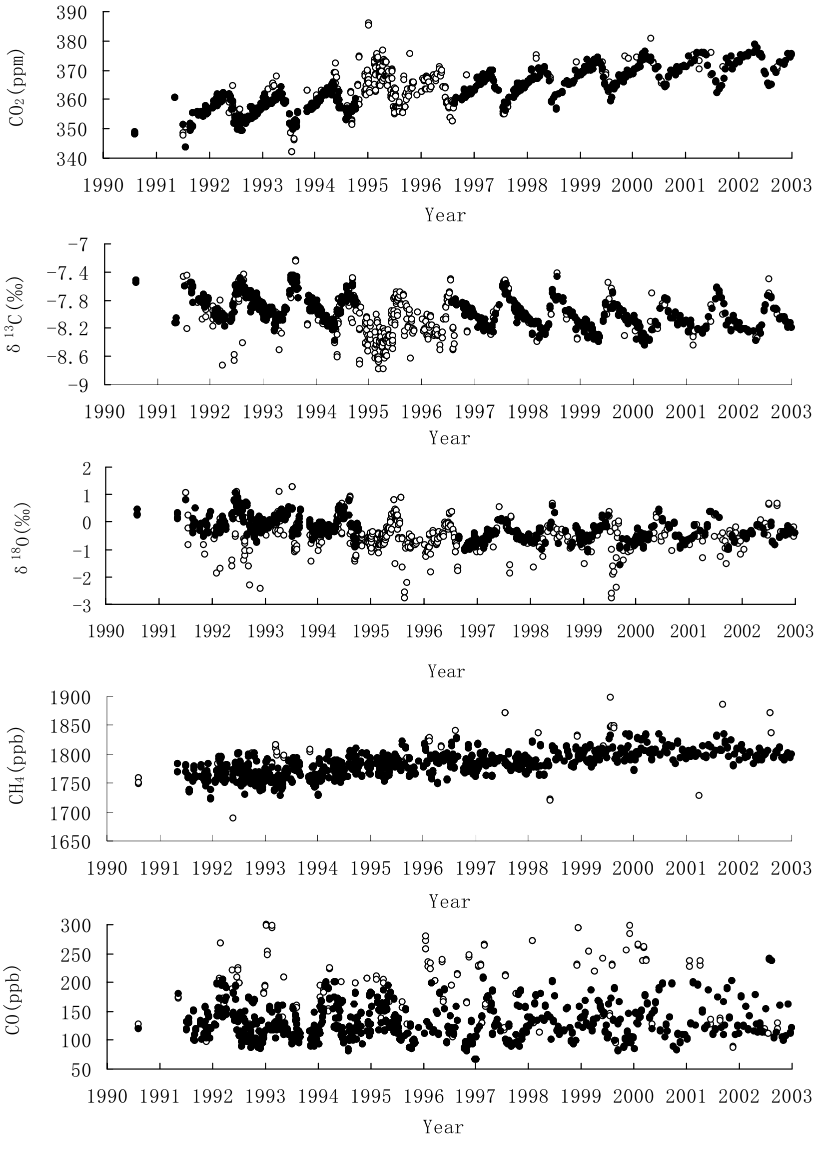

Figure 8: Time series by discrete air samples (NOAA-CMDL Cooperative Air Sampling Network).

7.12.3.3 Discrete air samples measurement programme

Figure 8 shows time series of the CO_2 and stable isotopes ($\delta^{13}C$,$\delta^{18}O$), CH_4 and CO by discrete air samples collected at Mt. Waliguan and analyzed by CMDL and CU-INSTAAR. Open circles are raw, unflagged data and filled circles are selected data (CMDL, 2002). For further analysis and discussion (inter-comparisons of in-situ and discrete measurements; average seasonal cycle, long-term trend, source-sink impact, etc, at Mt. Waliguan) see other studies (Wen et al., 1993, 1994; Zhou et al., journal papers published during 1998-2004).

7.12.4 Acknowledgments

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ANNEX A

12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques
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ANNEX A2

PREVIOUS MEETINGS OF THE WMO EXPERTS IN CO_2 MEASUREMENT

The first meeting of the Experts on Carbon Dioxide Measurement was held in La Jolla, California, Unites 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 CO_2 monitoring programmes, which has ensured that CO_2 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:

	LOCATION	DATE	PUBLICATION
1.	La Jolla, California, USA	3-7 March 1975	4*
2.	Geneva, Switzerland	8-11 September 1981	6†
3.	Lake Arrowhead, California, USA	4-8 November 1985	39†
4.	Gaithersburg, Maryland, USA	15-17 June 1987	51†
5.	Hilo, Hawaii, USA	24-26 March 1988	‡
6.	Lake Arrowhead, California, USA	14-19 October 1990	77‡
7.	Rome, Italy	7-10 September 1993	88†
8.	Boulder, Colorado, USA	6-11 July 1995	121†
9.	Aspendale, Australia	1-4 September 1997	132†
10.	Stockholm, Sweden	23-26 August 1999	
11.	Tokyo, Japan	25-28 September 2001	148†
12.	Toronto, Canada	15-18 September 2003	161†

* Number of reports in the WMO Executive Panel-I/Document 5, 13.3.1975.

† Number of reports in the WMO Atmospheric Environment and Research Programme/GAW Report Series.

‡ Elliot, W.P. (ed.) (1989) The statistical treatment of CO_2 data reports. NOAA Technical memorandum ERL ARL-173.

ANNEX A3

12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques
Toronto, Canada, 15-18 September 2003

Agenda

Monday, September 15

8:00-9:00am	**Registration**
	Opening session
9:00am	Information update for preparation and organization of the meeting
9:10am	Welcome address by MSC (Whelpdale Douglas, Canada)
9:20am	The Global Atmosphere Watch Programme: Challenges Of A Global Atmospheric Composition Measurement System (BARRIE Leonard, WMO)
9:40am	TBA (BRAND Willi, IAEA)
9:50am	**Break**
	CO_2 measurements
10:10am	Consistency of JMA CO_2 standard gases (TSUTSUMI Yukitomo, Japan)
10:30am	The WMO Mole Fraction Scale for CO_2 (TANS Pieter, USA)
11:10am	***Discussion***
12:30pm	**Lunch**
1:30pm	Making Quality Measurements without a Data Management Strategy (MASARIE Ken, USA)
2:10pm	The MSC Insitu GHG Data Management Strategy (WORTHY Doug, Canada)
2:30pm	**Break**
2:50pm	An update on what we have learned from operation of LOFLO CO_2 analyser
3:10pm	Terrestrial and Atmospheric Carbon Observing System (TACOS)-Infrastructure (CIAIS/MNNING/LEVIN, Europe)
3:30pm	A Calibration and Intercomparison Scheme for Continuous, Multi-species Measurements from a Network of Tall Towers in Europe (MANNING Andrew, Germany)
3:50pm	***Discussion***
4:30 - 5:30pm	**Poster Session**
	The Network for Background CO_2 Measurement in Italy [ID#: 1] (ARTUSO, Florinda et al, Italy)

The New Zealand CO_2 and O_2 Measurement Programme at Baring Head [ID#: 2]
(BRAILSFORD Gordon, New Zealand)
Global Atmosphere Watch Activities of the South African Weather Service [ID#3]
(BRUNKE Ernst, South Africa)
Trans European flights.[ID#:4]
A study of the CO-CO_2 relationships near Paris (car and aircraft) [ID#: 5]
(CIAIS, Philippe, France)
Simultaneous Study of Hydrogen, Carbon Monoxide, Methane, Carbon Dioxide and Ozone at Baie Saint-François wetland, Québec [ID#: 6] (CONSTANT Philippe, Canada)
Measurements of soil CO_2 flux [ID#: 25] (GARCIA,Richard, USA)
Status of CO_2 Monitoring and Research in Hungary [ID#:7] (HASZPRA Lلszlĺ, Hungary)
National report: Finland [ID#: 8] (HATAKKA Juha, Finland)
Stable Isotope Research Program at MSC [ID#;9]
Isotope Measurements of Organic and Inorganic Carbon (OC/EC) in Aerosols [ID#:10]
Stable Carbon Isotopic Composition of Ethane and Benzene in the Arctic Troposphere [ID#:11] (HUANG Lin et al., Canada)
The Ochsenkopf tower monitoring station [ID#: 12] (JORDAN Armin, Germany)
Results of long-term measurements of CO_2 content in the atmospheric column at the Issyk Kul station (Russia) [ID#: 13] (KASHIN Felix, Russia)
The greenhouse gas measurement program of SNU in Korea [ID#: 14]
(Kim Kyung-Ryul, Korea)
Long-term monitoring of $^{14}CO_2$ in the atmosphere budgeting fossil fuel CO_2 over Europe [ID#:15]
(LEVIN Ingeborg, Germany)
National Report (Poland) [ID#: 16] (NECKI Jaroslaw, Poland)
National Report (Netherlands) [ID#:17] (NEUBERT, Rolf, Netherlands)
TBA [ID#: 18, 19] (NISBET Euan, United Kingdom)
The Network for Background CO_2 Measurements in Italy [ID#: 1] (SANTAGUIDA Riccardo, Italy)
The Australian national report [ID#:20] (STEELE Paul, Australia)
Carbon Dioxide Measurement programs in the Japan Meteorological Agency [ID#:21]
(TSUTSUMI, Yukitomo, Japan)
Greenhouse Gases Monitoring and Research at GAW Station, China [ID#:22] (ZHOU Lingxi, China)
National report and data quality [ID# 23, 24] (WORTHY Doug, Canada)

Tuesday, September 16

Isotopes in CO_2

8:30am Isotopic analysis of CO_2 in air samples:
State of the art and requirements for a new CO_2-in-air standard (BRAND Willi, Germany)
9:10am Inter-comparison of Isotopic Values for CO_2 Using Some Reference Materials (MUKAI Hitoshi, Japan)
9:30am The role of carbonate standard in traceability maintenance for isotope measurements of CO_2
(HUANG Lin, Canada)
9:50am N_2O Influence On Stable Isotope Measurements of Atmospheric CO_2
(SIRIGNANO Carmina, Netherlands)

10:10am **Break**

10:30am ***Discussion***

12:30pm **Lunch**

1:30pm Carbon and Oxygen Isotopes of Greenhouse Gases in the NOAA Network (WHITE James, USA)
1:50am An update on the "CLASSIC" experiment (STEELE Paul, Australia)

2:10pm	Isotopic analysis of CO_2 from air samples in glass flasks	(BRAND Willi, Germany)
2:30pm	Progress in d13C in CO_2 measurements at DFO	(CHRISTIAN James, Canada)
2:40pm	***Discussion***	
4:10pm	**Break**	
4:30 - 5:30pm	**Poster session - Second Viewing**	

Wednesday, September 17

	Sampling Strategies	
8:30am	Aircraft and Ground-based Measurements of Continental CO_2 Sources and Sinks	(WOFSY Steven, USA)
9:10am	An Overview of the Comprehensive Global CO_2 Network and its Potential Future	(BUTLER James H., USA)
9:30am	A Major Expansion of the CMDL Measurement Program	(CONWAY Tom, USA)
9:45am	The Carbo-Europe Atmospheric CO_2 Sampling Strategy	(CIAIS Philippe, Europe)
9:55am	Flask-sampling strategy by MSC	(HUANG Lin, Canada)
10:05am	**Break**	
10:25am	High-precision and High-accuracy CO_2 Mixing Ratio Measurements at Flux Towers: The Virtual Tall Towers Approach	(DAVIS Kenneth J., USA)
10:45am	Usefulness of Long-term, High-frequency CO_2 Concentration Measurements at a Continental Site	(CHEN J., Canada)
11:05am	***Discussion***	
12:00pm	**Lunch**	
1:00pm	The CARIBIC B767 aircraft CO_2 observations	(BRENNINKMEIJER Carl, Germany)
1:20pm	Frequent aircraft vertical profiling as a tool for the studies of the small-scale (synoptic and mesoscale) CO2 variability in the atmospheric boundary layer	(SHASHKOV Alexander, Canada)
1:40pm	***Discussion continuing***	
2:30pm	***Picture taking***	
2:40pm	**Break**	
	Other tracers (O_2/N_2)	
3:00pm	Atmospheric Oxygen Measurements: Results and Analytical Issues	(KEELING Ralph, USA)
3:40pm	An intercomparison of standard air for measurements of the atmospheric O_2/N_2 ratio among Tohoku University, Princeton University and National Institute for Environmental Studies	(NAKAZAWA Takakiyo, Japan)
4:00pm	O_2/N_2 storage aspects and open split mass spectrometric determination	(BRAND Willi, Germany)
4:20pm	Progress in O_2/N_2 measurements at DFO	(CHRISTIAN James, Canada)
4:30 - 5:30pm	***Discussion***	

Thursday, September 18

	Other tracers (CO, CH_4 and N_2O) & New Techniques	
8:30am	Global N_2O Measurements: Challenges and Perspectives	(SCHEEL Eckhart)
9:10am	The united effort in monitoring global CO	(BRENNINKMEIJER Carl, Germany)
9:50am	The CMDL Gravimetrically-Prepared Methane Mole Fraction Scale	(DLUGOKENCKY Ed, USA)
10:10am	Isotopic Analysis of CH_4 and CO_2 in London Air Using Micromass Trace Gas	(LOWRY David, United Kingdom)
10:30am	Methane Monitoring consortium in the European Union, Russia (including the Ob River gasfields) and Norway/Spitsbergen.	(NISBET Euan, United Kingdom)
10:35am	**Break**	
10:55am	***Discussion***	
12:00pm	**Lunch**	
1:00pm	Analyzer for CO_2 and O_2 on Jungfraujoch, Switzerland	(LEUENBERGER Markus, Switzerland)
1:20pm	Results of Simultaneous Measurements of CO_2, CH_4 and CO Contents in the Surface Air and in the Atmospheric Column at the Obninsk (Moscow region)	(KASHIN Felix, Russia)
1:40-2:40pm	***Discussion***	
2:40pm	**Break**	
3:00 - 5:30pm	**Finalizing the recommendations**	
7:30pm	Banquet at Hart-House, University of Toronto	

Friday, September 19

Excursion to Niagara Falls

Meeting programme (more information)

September 15

Session	**Key note speakers**	**Chairs**	**Discussion Topics**
CO_2 ***Data Management***	Pieter Tans Ken Masarie -	D. Worthy/L. Huang	- Precision and accuracy targets for our measurements - Traceability maintenance - What is the optimal balance between accuracy and precision of CO_2 measurements, and between number of sites and frequency of CO_2 measurements when attempting to quantify terrestrial CO_2 budgets? - Data Quality assessment
September 16			
Isotope in CO_2	Wiili Brand	J.White/L. Huang	- New International CO_2-in-air Standard - Traceability maintenance - Can we make precise and accurate isotope measurements via the only one primary standard? - How useful are continuous flow isotopic data for understanding greenhouse gases in the atmosphere? - On-line (optical) measurements of ^{13}C in CO_2
September 17			
Sampling Strategy	Steven Wofsy	J. Miller/B. Stephens	- New Measurement Strategies and Methods - The Long Term Comprehensive Global CO_2 Network and Its Relation to the Baseline CO_2 Network Of GCOS - Links to FluxNet
Other trace gases O_2/N_2	R. Keeling	Andrew Manning	- Protocols for Handling Calibration Gases - O_2/N_2 calibration and possible intercomparision.
September 18			
N_2O	Euckerk	Harro A.J. Meijer	- Fast response instrumentation for trace gases (CH_4, N_2O..)
CO	Carl A. M. Brenninkmeijer		- Why is flask-CO increasing with time?
New techniques		Harro A.J. Meijer	- Permeation problems - "Cheap" CO_2 detectors - LOFLO CO_2 analyser - inexpensive ($5-10K) but slightly less accurate (0.3-0.5 ppm) CO_2 measurement systems for regional continental networks - Instrumentation requirements for global CO_2 network
Recommendation		Ingeborg Levin	

ANNEX A4

MEASUREMENT SITES

		Method of CO_2 Concentration Analysis		*Additional Isotopic Measurement*		
Station	Operated by	In Situ	Flasks	^{13}C	^{18}o	^{14}C
Alert	MSC	MSC	MSC	MSC	MSC	IUP-HD
			CSIRO	CSIRO	CSIRO	
			NOAA	UCB	UCB	
			SIO	SIO	SIO	
			IOS	IOS		IOS
			MPI	MPI	MPI	
			IUP-HD	IUP-HD	IUP-HD	
Ascension Island	USAF		NOAA	UCB	UCB	
Assekrem	ONM		NOAA	UCB	UCB	
Amsterdam Island	CFR	CFR	CFR	CFR	CFR	
Anmyeondo	KMA	KMA				
Baltic Sea	MIR		NOAA	UCB	UCB	
Barbados	UBr		NOAA	UCB	UCB	
Baring Head	NIWA	NIWA	SIO	SIO	SIO	NIWA
Barrow	NOAA	NOAA	NOAA	UCB	UCB	
			SIO	SIO	SIO	
Begur	UBa		CFR	CFR	CFR	
Bermuda	BBSR		NOAA	UCB	UCB	
Bobabeb	DRFN		NOAA	UCB	UCB	
Brotjacklriegel	UBA	UBA				
Cabauw	KNMI/ECN	ECN		ECN		ECN/UU
Cape Grim	BoM/CSIRO	CSIRO	CSIRO	CSIRO	CSIRO	
			NOAA	UCB	UCB	IUP-HD
Cape Kumakahi	NOAA		NOAA	UCB	UCB	
			SIO	SIO	SIO	
Cape Ochiishi	NIES	NIES				
Cape Point	SAWS	SAWS				
Cape Rama	PRL/IAEA		CSIRO	CSIRO	CSIRO	
Cape St. James	MSC		MSC			
Charles Point	CSIRO/NTU		CSIRO	CSIRO	CSIRO	
Christmas Island	SIO		SIO	SIO	SIO	
Cold Bay	NOAA		NOAA	UCB	UCB	
Constanța	RMRI		NOAA	UCB	UCB	
Crête	UC		CFR	CFR	CFR	
Crozet	CFR	CFR	CFR	CFR	CFR	
Deuselbach	UBA	UBA				
Eastern Island	DMC		NOAA	UCB	UCB	
Estevan Point	MSC		MSC	MSC	MSC	
Fraserdale	MSC	MSC	MSC	MSC	MSC	
Fundata	INMH	INMH				
Garmisch	FAU		FAU			
Gozo Island	MEM		NOAA	UCB	UCB	
Grifton	WITN		NOAA	UCB	UCB	
Guam	NOAA		NOAA	UCB	UCB	
Halley Bay	BAS		NOAA	UCB	UCB	
Hateruma Island	NIES	NIES				
Hegyhatsal	HMS		NOAA	UCB	UCB	
Heidelberg	IUP-HD	IUP-HD	IUP-HD	IUP-HD	IUP-HD	IUP-HD
Izaña	INM	INM	NOAA	UCB	UCB	IUP-HD
Jubany	DNA/PNRA	DNA/PNRA	NOAA	UCB	UCB	
Jungfraujoch	UBe		CFR	UBe	UBe	IUP-HD
Kaashidhoo	SIO		NOAA	UCB	UCB	
Kasprowy Wierch	AGH	AGH	SIO			
Key Biscayne	NOAA		NOAA	UCB	UCB	
Kollumerwaard	KEMA/CIO	KEMA*	CIO	CIO	CIO	CIO
Kosan	KMA/SNU		KMA/SNU	KMA/SNU	SIO	SNU
K-puszta	HMS	HMS				
La Jolla	SIO		SIO	SIO	SIO	

Lampedusa Island	ENEA		ENEA			
Lin-an	CAMS		CAMS			
Longfengshan	CAMS		CAMS			
Lutjewad	CIO	CIO		CIO		
Mace Head	CFR/UCG/ISC		CFR	CFR	CFR	
Mahe Island	SBS		NOAA	UCB	UCB	
Mauna Loa	NOAA	NOAA	NOAA	UCB	UCB	
	SIO	SIO	SIO	CSIRO	CSIRO	
Macquarie Island	CSIRO	CSIRO	CSIRO	CSIRO	CSIRO	IUP-HD
Mawson	CSIRO	CSIRO	CSIRO	CSIRO		
Minamitorishima	JMA		JMA			
Mould Bay	NOAA		NOAA	UCB	UCB	
Monte Cimone	IMS	IMS				
Mt. Waliguan	CAMS	CAMS	NOAA	UCB	UCB	
Neuglobsow	UBA	UBA*				
Neumayer	AWI		IUP-HD	IUP-HD	IUP-HD	IUP-HD
Niwot Ridge	NOAA		NOAA	UCB	UCB	
Ny Ålesund	MISU/NILU	MISU	NOAA	UCB	UCB	
Ocean Station M	NMI		NOAA	UCB	UCB	
Ochsenkopf	MPI-BGC	MPI-BGC				
Orléans	CFR		CFR	CFR	CFR	
Palmer Station	NSF		NOAA	UCB	UCB	
Park Falls	WECB		NOAA	UCB	UCB	
Plateau Assy	Kazhydromet		NOAA	UCB	UCB	
Plateau Rosa	ENEL	ENEL	ENEL			
Point Arena	PALK		NOAA	UCB	UCB	
Portsall	CFR		CFR	CFR	CFR	
Prince Albert	MSC	MSC	MSC	MSC	MSC	
Puy de Dôme	CFR	CFR	CFR	CFR	CFR	
Ryori	JMA	JMA				
Sable Island	MSC	MSC	MSC	MSC	MSC	
Saclay	CFR	CFR				
Sary Taukum	Kazhydromet		NOAA	UCB	UCB	
Sammaltunturi	FMI	FMI	NOAA	UCB	UCB	
Samoa	NOAA	NOAA	NOAA	UCB	UCB	
	SIO	SIO	SIO	SIO	SIO	
Sand Island	NOAA		NOAA	UCB	UCB	
Schauinsland	UBA	UBA	IUP-HD	IUP-HD	IUP-HD	IUP-HD
Schimücke	UBA	UBA*				
Sede Boker	WIS		NOAA	UCB	UCB	
Shangdianzi	CAMS		CAMS			
Shemya Island	USAF		NOAA	UCB	UCB	
Shetland Islands	CSIRO		CSIRO	CSIRO	CSIRO	
Sonnblick	OUBA		OUBA			IUP-HD
South Pole	NOAA/NSF	NOAA	NOAA	UCB	UCB	
	CSIRO		CSIRO	CSIRO	CSIRO	
		SIO	SIO	SIO	SIO	
Syowa	NIPR	NIPR/TU	TU	NIPR	TU	NIPR
			NOAA	UCB	UCB	
Tae-ahn Peninsula	KNEU		NOAA	UCB	UCB	
Terceira Island	IM		NOAA	UCB	UCB	
Teriberka	MGO		MGO			
Tromelin	MF		CFR	CFR	CFR	
Tsukuba	JMA	JMA				
Ulaan Uul	HMRI		NOAA	UCB	UCB	
Ushuaia	SMN		NOAA	UCB	UCB	IUP-HD
Utah	NOAA		NOAA	UCB	UCB	
Vestmannaeyjar	IMO		NOAA	UCB	UCB	
Waldhof	UBA		UBA			
Wank	FAU		FAU			
Westerland	UBA	UBA	IUP-HD	IUP-HD	IUP-HD	IUP-HD
Yakutsk	NIES	NIES*				
Yonagunijima	JMA	JMA				
Zingst	UBA	UBA*				
Zugspitze	DWD	UBA	FAU			

** Gas Chromatograph*

ABBREVIATIONS

AGH	University of Mining and Metallurgy, Poland
AWI	Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany
BAS	British Antarctic Survey, United Kingdom
BBSR	Bermuda Biological Station for Research, United Kingdom
BoM	Bureau of Meteorology, Melbourne, Australia
CAMS	Chinese Academy of Meteorological Sciences, Beijing, China
CFR	Centre des Faibles Radioactivités, Gif-sur-Yvette, France
CIO	Centrum voor IsotopenOnderzoek, Groningen University, Netherlands
CSIRO	Commonwealth Scientific and Industrial Research Organisation, Aspendale, Australia
DMC	Dirección Meteorológica de Chile, Chile
DNA	Dirección Nacional de l’Antartida, Argentina
DWD	Deutscher Wetterdienst, Germany
DRFN	Desert Research Foundation of Namibia, Namibia
ECN	Netherlands Energy Research Foundation, Petten, Netherlands
ENEA	Ente per le Nuove Tecnologie, l’Energia e l’Ambiente, Italy
ENEL	Italian Electric Energy Company, Italy
FAU	Fraunhofer Institute für Atmosphärische Umveltforschung, Garmisch-Partenkirchen, Germany
FMI	Finnish Meteorological Institute, Finland
Kazhydromet	Main Administration on Hydrometeorology, Kazakhstan
KEMA	The Electricity Companies Joint Research Institute, Netherlands
KMA	Korea Meteorological Administration, Republic of Korea
KNMI	Royal Netherlands Meteorological Institute, Netherlands
KNUE	Korea National University of Education, Rep. of Korea
HMRI	Hydrometeorological Research Institute of Mongolia, Mongolia
HMS	Hungarian Meteorological Service, Hungary
IAEA	International Atomic Energy Agency
IM	Instituto de Meteorologia, Portugal
IMO	Icelandic Meteorological Office, Iceland
IMS	Italian Meteorological Service, Roma, Italy
INM	Instituto Nacional de Meteorología, Madrid, Spain
IOS	Institute of Ocean Sciences, Canada
IUP-HD	Institute für Umweltphysik, University of Heidelberg, Germany
JMA	Japan Meteorological Agency, Tokyo, Japan
LMCE	Laboratoire de Modélisation du Climat et de l’Environnement, Gif-sur-Yvette, France
MGO	Main Geophysical Observatory, St. Petersburg, Russian Federation
MEM	Ministry for the Environment, Malta
MF	Météo-France, France
MIR	Morski Instytut Rybacki, Poland
MISU	Department of Meteorology, Stockholm University, Sweden
MPI	Max-Planck-Institut für Biogeochemie, Germany
MSC	Meteorological Service of Canada, Toronto, Canada
NIES	National Institute for Environmental Studies, Tsukuba, Japan
NILU	Norwegian Institute for Air Research, Kjeller, Norway
NIPR	National Institute of Polar Research, Tokyo, Japan
NIWA	National Institute of Water and Atmospheric Research, New Zealand
NMI	Norwegian Meteorological Institute, Norway
NOAA	National Oceanic and Atmospheric Administration, USA
NSF	National Science Foundation, USA
NTU	Northern Territory University, Darwin, Australia
ONM	Office National de la Météorologie, Algeria
OUBA	Österreichisches Umweltbundesamt, Wien, Austria
PALK	Point Arena Lighthouse Keepers, USA
PNRA	Programma Nazionale de Richerche in Antartide, Italy
PRL	Physical Research Laboratory, Ahmedabad, India
RMRI	Romanian Marine Research Institute, Romania
SBS	Seychelles Bureau of Standards, Seychelles

SIO	Scripps Institution of Oceanography, La Jolla, USA
SMN	Servicio Meteorológico Nacional, Argentina
SNU	Seoul National University, Republic of Korea
TU	Tohoku University, Sendai, Japan
UBA	Umweltbundesamt, Berlin, Germany
UCB	University of Colorado, Boulder, USA
UCG	University College of Galway, Ireland
UG	University of Guam, USA
USAF	United States Air Force, USA
UBa	Universitat de Barcelona, Spain
UBe	University of Bern, Switzerland
UBr	University of Bristol, United Kingdom
UC	University of Crete, Greece
UU	State University Utrecht, Netherlands
WECB	Wisconsin Educational Communications Board, USA
WIS	Weizmann Institute of Science, Israel
WITN	WITN Television, Grifton, North Carolina, USA

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1. Final Report of the Expert Meeting on the Operation of Integrated Monitoring Programmes, Geneva, 2-5 September 1980.

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5. Report of the WMO/UNEP/ICSU Meeting on Instruments, Standardization and Measurements Techniques for Atmospheric CO_2, Geneva, 8-11; September 1981.

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12. Report on the Mount Kenya Baseline Station Feasibility Study edited by Dr. Russell C. Schnell.

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

15. Provisional Daily Atmospheric Carbon Dioxide Concentrations as Measured at BAPMoN Sites for the Year 1981, May 1983.

16. Report of the Expert Meeting on Quality Assurance in BAPMoN, Research Triangle Park, North Carolina, USA, 17-21 January 1983.

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28. Report of the Meeting of Experts on the Eastern Atlantic and Mediterranean Transport Experiment ("EAMTEX"), Madrid and Salamanca, Spain, 6-8 November 1984.

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).

30. Report of the Ad-hoc Consultation on Quality Assurance Procedures for Inclusion in the BAPMoN Manual, Geneva, 29-31 May 1985.

31. Implications of Visibility Reduction by Man-Made Aerosols (Annex to No. 14) by R.M. Hoff and L.A. Barrie. October 1985 (WMO TD No. 59).

32. Manual for BAPMoN Station Operators by E. Meszaros and D.M. Whelpdale. October 1985 (WMO TD No. 66).

33. Man and the Composition of the Atmosphere: BAPMoN - An international programme of national needs, responsibility and benefits by R.F. Pueschel, 1986.

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35. Provisional Daily Atmospheric CO_2 Concentrations as Measured at BAPMoN Sites for the Year 1983. December 1985 (WMO TD No. 77).

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37. Air-Sea Interchange of Pollutants by R.A. Duce. September 1986 (WMO TD No. 126).

38. Summary Report on the Status of the WMO Background Air Pollution Monitoring Network as at 31 December 1985. September 1986 (WMO TD No. 136).

39. Report of the Third WMO Expert Meeting on Atmospheric Carbon Dioxide Measurement Techniques, Lake Arrowhead, California, USA, 4-8 November 1985. October 1986.

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64. Report of the consultation to consider desirable locations and observational practices for BAPMoN stations of global importance, Bermuda Research Station, 27-30 November 1989.

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83. Report on the Global Precipitation Chemistry Programme of BAPMoN (WMO TD No. 526).

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152. Current Activities of the Global Atmosphere Watch Programme (as presented at the 14th World Meteorological Congress, May 2003). (WMO TD No. 1168).

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