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THE INTEGRATED GLOBAL GREENHOUSE GAS OBSERVATIONS AND ANALYSIS SYSTEM: WMO-GAW

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The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) was established in 1989 (http://www.wmo.int/gaw). A major focus is global coordination of atmospheric chemistry research and analysis to address outstanding problems related to climate change. GAW is a partnership of managers, scientists and technical experts from ~80 countries. It is coordinated by the WMO Secretariat in Geneva under the advice of expert groups in the WMO Commission for Atmospheric Sciences (CAS). The international greenhouse gas measurement community that meets at this 15th meeting has been sponsored by WMO since 1975. They are representatives of nationally funded measurement projects that constitute the WMO/GAW Global Atmospheric CO2 & CH4 Monitoring Network which is the one and only comprehensive greenhouse gas network of the Global Climate Observing System (GCOS). High level representatives from nations to the United Nations Framework Convention on Climate Change have approved and support this international instrument.

Today we are at a critical point in Earth system management in which carbon management will play a key role. We are in a position to combine atmospheric observations with global atmospheric carbon cycle models driven by the global analyses of numerical weather prediction centres to develop a carbon tracking tool that can address the question, “what is the net release and uptake of CO2 between the Earth’s surface and the atmosphere on a monthly basis for regions of interest around the world. The power of this tool is determined by the effectiveness of the atmospheric observing system and the atmospheric inversion models used to convert these observations into estimates of sources and sinks. In the next 5 years, major advances are expected in observing system technology in all sectors. Atmospheric CO2 observations from the Earth’s surface, aircraft, and satellites are coordinated by all parties through the GAW network. Recommendations from this group on data requirements constitute a dynamic rolling review critical to design of future systems.

In this paper, we describe the architecture of the WMO-GAW global network and the links to regional research, analysis and assessment that drives it.

Observation System Requirements to Support Greenhouse Gas Management Strategies

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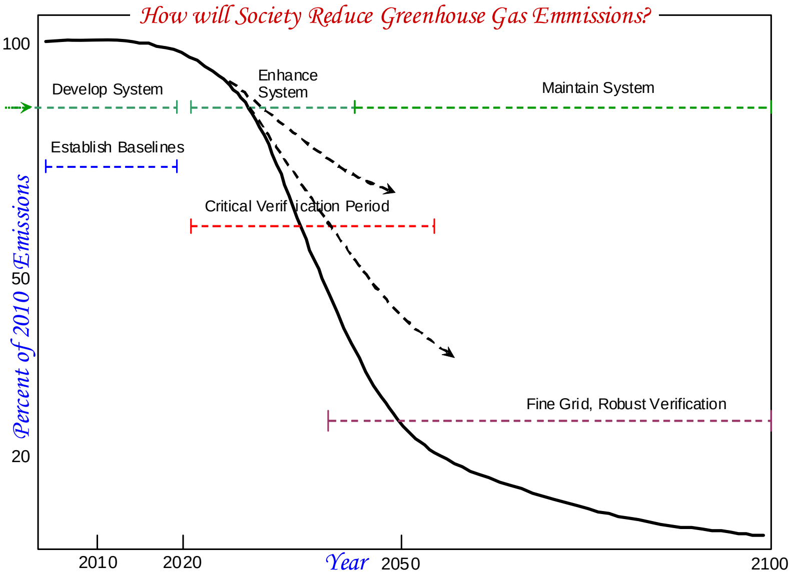
Over the course of three decades, scientists have come together at these meetings to address issues related to improving measurements, ensuring quality control, managing data, identifying emerging challenges and opportunities, and enhancing communication among participants. During that time, the questions we sought to address evolved with increasing information and a growing challenge for society – that of how to understand and address increasing CO_2 and other greenhouse gases in the atmosphere. From these meetings, we have been able to set measurement guidelines appropriate to questions as they evolved. Ensuring high quality, coordinated measurements is a core requirement for developing any network of observations designed to address global issues.



Today, society will soon accelerate efforts to reduce greenhouse gas emissions in a variety of ways. There will be international treaties, national policies, and regional strategies applied to a number of economic, social, and environmental sectors. Some will work better than others and some will not work at all. Providing independent, globally coherent information will give considerable strength to these treaties, policies, and strategies. The closest thing the world has to a globally consistent greenhouse gas observation network is WMO's Global Atmospheric Watch and the scientists who support it. So, the question before us is, "How do we provide the best information to support these efforts and how would this affect measurement guidelines and sampling strategies?" Measurement techniques and systems are evolving fast, and likely will be evolving even faster in the future. Yet, if appropriate constraints are not placed on them, we run a huge risk of society making decisions on poorly coordinated data. The challenge to us today is to think about the requirements for such a system of diverse measurements (e.g., flasks, towers, FTIRs, satellites) if we are to provide a coherent story over decades. At some point we must derive a set of guidelines that will allow an integrated system of measurements to supply the information that society will need to succeed in this effort.

The TCCON network for the calibration of greenhouse gas column data and satellite validation

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CO_2 is the most important anthropogenic greenhouse gas. The oceans and terrestrial ecosystems currently act as sinks for atmospheric CO_2 and absorb approximately half of the anthropogenic emissions (IPCC, 2007). Inverse models have been used to infer the geographical distribution of these sinks from atmospheric measurements. Until recently inverse modeling studies were solely based on a network of in-situ boundary layer measurement stations. This approach is limited by the sensitivity of the sink estimates to vertical transport and by the sparse spatial coverage of the sampling sites. Column measurements are not sensitive to vertical transport and therefore provide complementary information to the in situ measurements.

Column measurements of greenhouse gases of sufficient precision are now available from ground-based solar absorption measurements using FTIR-spectrometers and from space-borne sensors measuring reflected sunlight. Space-borne sensors provide global coverage and the first satellite dedicated to greenhouse gas measurements (JAXA-GOSAT) has been successfully launched in January 2009.

The ground-based quality control of the satellites cannot be based on in situ measurements alone, since the satellites measure a weighted column integral while the in situ measurements are of a single point. Even aircraft profiling, which can deduce a part of the column integral are slow compared to the snapshot character of satellite measurements. Ground-based solar absorption FTIR-spectrometry can measure the same column integrals as the satellite but do so at a fixed point, making it amenable to direct comparison with aircraft. For the validation of satellites the Total Carbon Column Observing Network (TCCON) was founded in 2004. TCCON is a network of ground-based Fourier Transform Spectrometers recording direct solar spectra in the near-infrared spectral region. The observation and retrieval will be performed in a strictly coordinated way and TCCON will provide a critically maintained and long timescale record for identification of temporal drift and spatial bias in the calibration of the space-based sensors. The TCCON network will not only allow studying CO_2 and CH_4, but in addition many other trace gases of interest can be observed.

Ground-based solar absorption FTIR-spectrometry is becoming a vital component in the global atmospheric observing system for greenhouse gases and co-located column and surface in situ measurements will become abundant constraints on carbon cycle processes. We will present observations performed using the ground-based absorption spectrometry from different sites of the TCCON network. Collocated in-situ observations together with column data and model results will be presented and discussed for the different sites.

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Verifying the emissions of non-CO_2 GHG of NW Europe using the European network of tall towers

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According to the official bottom-up estimates of anthropogenic emissions of CH_4 these emission have recently been substantially reduced in most European countries due to e.g. measures in landfill management and industry. The global average atmospheric concentration of methane in parallel hardly increased in the last ten years, in contrast to the period before, but this decrease in growth rate can be attributed to other causes as well.

An increased density network of high precision and high frequency observations of atmospheric concentration of methane in the planetary boundary layer using tall towers has developed in Europe since 2004, in addition to the existing global and European surface network. The data from this network will allow us to derive independent estimates of the emissions of CH_4 and other non-CO_2 GHG's in NW Europe. The precision of the emission estimates is most limited by the uncertainties associated with the transport models used and most propably by the still limited spatial resolution of the network. Ancillary tracers measured in this network like ^{222}Rn and SF_6 allow for further independent emission estimates or multi-tracer model verification and improvements.

In this presentation the first results of observed CH_4 concentrations from the improved network will be presented along with the first results for emission verification using the network.

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A brief update of the WMO X2007 Scale for CO2-in-air will be presented, together with the uncertainty associated with the propagation of the WMO scale.

Data assimilation techniques allow us to put together different data sets in an atmospheric transport model, in-situ measurements at the surface and from aircraft, satellite retrievals of mole fractions averaged over the atmospheric column, flux measurements, and prior estimates of fluxes supported in part by yet more data. We have to decide how to weigh one set of information versus another. Data assimilation has a formal framework for weighing different information but in practice it is quite arbitrary. It is made more difficult because errors of modeled transport may cause data to be systematically misinterpreted. It is our job to ensure that data are directly comparable, without any model intervention, including satellite retrievals.

The societal relevance of our work is increasing rapidly. We need to measure the response of the carbon cycle to climate change, and atmospheric measurements can, and will, be used for verifying emissions reductions. How much is a 0.1 ppm systematic error worth?

RECENT HISTORY OF CO_2 STANDARD GASES IN JMA

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The Japan Meteorological Agency (JMA) has maintained its CO_2 standard gases since 1986 to obtain high-quality observational data sets from JMA’s three GAW Global and Regional stations: Minamitorishima, Ryori and Yonagunijima. The primary standard gases were calibrated against the standards of the WMO Central Calibration Laboratory (CCL) before taking over from and after taking over to a different set of primary standard gases to ensure a consistent calibration scale that is traceable to the WMO scale for a long period of time. The standard gases are sent to the WMO World Calibration Centre (WCC) every a couple of years and the most recently JMA’s fifth-generation set of primary standard gases were calibrated at the NOAA/ESRL in 2008 to assign concentrations on the WMO-X2007 scale.

JMA calibrates its primary standard gases with different generations of standard gases to ensure historical consistency in JMA’s calibration scale when taking over to different generations. JMA also validates stability in the concentration of standard gases in a generation, through a regular calibration of standard gases with the others in the set. All these calibration data are stored in a database for recalculating concentrations in a case of revisions in the WMO calibration scale. JMA has reexamined the calibration data to create a consistent calibration scale of its primary standard gases throughout the whole history, which is expressed as the WMO-X2007 scale.

This presentation will describe the history of JMA’s standard gases since the start of maintenance in 1986, in particular in the past 10 years, a long-term stability of the standard gases, and consistency of the calibration scale with the proven scales of the Meteorological Research Institute and the WMO CCL, based on an analysis of data taken from past calibrations and intercomparisons.

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A new CO_2 calibration scale based on gravimetric one-step dilution cylinders in National Institute for Environmental Studies – NIES 09 CO_2 Scale

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Since 1995, National Institute for Environmental Studies (NIES) had been employing the CO_2 calibration scale based on 10 CO_2-in-air standard gases in 10L aluminum cylinders prepared by gravimetric 3-step dilution method [Machida et al., 2009]. The internal stability has been kept well from 1995 to 2009. Based on the results from Round-Robin 1995/1996, differences in the CO_2 between WMO scale and NIES 95 scale varied from –0.02 to +0.12 ppm in a range between 343 and 372 ppm. Since the range of the NIES 95 cylinders for atmospheric measurement are only between 320 and 390 ppm, higher concentration cylinders are needed to detect the future CO_2 levels precisely.

To extend the NIES scale for atmospheric CO_2 to higher than 390ppm, we employed a new CO_2 scale based on cylinders prepared gravimetric method in one-step dilution. The one-step dilution method has two advantages: (1) reduction of dilution steps can reduce the uncertainty associated with mass determination and gas handling processes, and (2) independently prepared cylinders can reduce the systematic error [Tohjima et al., 2006]. In 2007, 10 standard gases with CO_2 mole fractions of 250, 340, 360, 380, 390, 400, 410, 430, 450 and 530 ppm were prepared. Averaged mass of diluted air was determined by measuring $N_2/O_2/Ar$ ratios using GC. The mass of CO_2 was calculated by measuring stable isotope ratios of CO_2. The residuals from the cubic fit of corrected mole fractions and NDIR responses were less than ±0.03 ppm.

We found the CO_2 stability in recent manufactured almimum cylinders was worse than before. Thus CO_2 mole fractions in these cylinders were succeeded to old matured CO_2-in-air cylinders which are expected to be stable for a long time. After confirming no certain drift in succeeded cylinders, we determined CO_2 mole fractions in one-step dilution cylinders as NIES 09 CO_2 scale.

CO_2 mole fractions of NIES 09 scale are within 0.3 ppm from NIES 95 scale in a range between 360 and 380 ppm and higher by 0.05 ppm at 390ppm. NIES 09 scale was compared with WMO X2007 scale by re-calculating past inter-comparison results (Figure 1). In this comparison, the differences in the apparent CO_2 mole fraction caused by the difference in the isotope compositions between industrial and natural CO_2 are corrected according to Tohjima et al. [2009]. NIES 09 scale is lower than WMO X2007 scale by about 0.07 ppm around 360 ppm but differeces are small between 380 and 400 ppm.

Cucumber data are provided by courtesy of Andrew Manning and Armin Jordan.

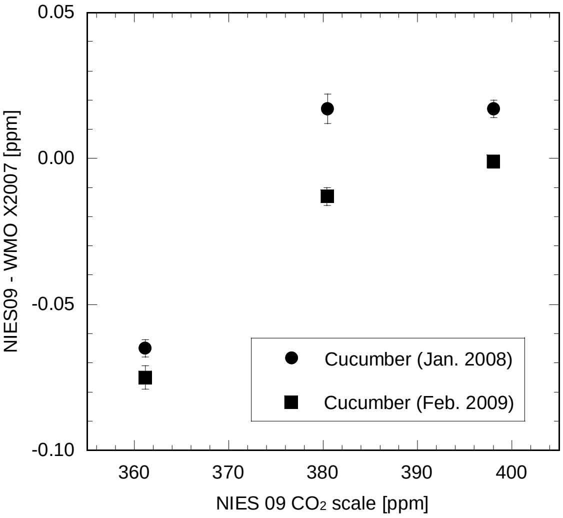

Figure 1. Difference of CO_2 mole fraction scale between NIES 09 and NOAA X2007.

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LINKING ISOTOPOLOGUE SPECIFIC MEASUREMENTS TO EXISTING INTERNATIONAL MOLE FRACTION SCALES

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Single line spectroscopic techniques, such as wavelength scanned-cavity ringdown spectrometry, (WS-CRDS) are likely to begin operating alongside current atmospheric measurement techniques like non-dispersive infrared (NDIR) in global networks, and ultimately may replace NDIR. However, this transition presents some calibration challenges as the two techniques do not measure exactly the same atmospheric components. WS-CRDS measures just a single isotopologue, for instance the dominant CO_2 isotopologue, $^{12}C^{16}O^{16}O$, whereas NDIR instruments generally use a narrow band pass filter to target the $^{12}C^{16}O^{16}O$ fraction, plus some unspecified portion of the $^{13}C^{16}O^{16}O$ component of total CO_2.

For NDIR instruments, the unspecified portion of the $^{13}C^{16}O^{16}O$ isotopologue measured is known to cause errors when calibration or reference gases vary in their isotopic composition from the measured atmosphere (Lee, Yoo et al. 2006). This problem will only be exacerbated by single line spectroscopic techniques. One possible remedy is to require all reference gases have universal isotopic composition, set at current atmospheric composition.

However, from a metrology perspective, since single line spectroscopic techniques make isotopologue specific measurements, we argue that calibration strategies for these instruments should also be isotopologue specific. This approach necessitates linking isotopologue specific measurements to current international mole fraction calibration scales and poses some challenges. This presentation will outline two calibration strategies devised to form these links. The first uses isotopically pure gas mixtures to create 'in-house' primary standards, which are linked to existing calibration scales by gas chromatography (GC) measurements. This approach assumes that the GC technique is isotopologue independent. The second strategy uses isotope ratio mass spectrometry measurements to decompose the total CO_2 of existing calibration gases into its three major isotopologues. For both strategies, the WS-CRDS instrument is then calibrated to the $^{12}CO_2$ fraction of the calibration gas.

Reference

Lee, J.-Y., H.-S. Yoo, et al. (2006). "Effect of carbon isotopic variations on measured CO_2 abundances in reference gas mixtures." Journal of Geophysical Research **111**(D05302): 1-8.

World Calibration Centre for Carbon Dioxide: Supporting the Quality of the Global Observation System

Jörg Klausen, Christoph Zellweger, Brigitte Buchmann

After many years of repeated requests by individual GAW stations to include CO_2 in their portfolio, WCC-Empa has been accepted by the governing body of GAW to act as the WCC-CO_2 (audits) with global responsibility. The mandate of WCC-CO_2 (audits) is to conduct system and performance audits at Global GAW stations worldwide. The presentation will give an overview of the concept of WCC-CO_2 and its implementation. The process of transferring the WMO scale to travelling standards, the scope of a system audit addressing the entire measurement chain, as opposed to only looking at results, and the procedure of a performance audit with travelling standards will be discussed. The steps involved in the generation and treatment of inter-comparison data, and the structure of an audit report and recommendations will be presented.

Nitrous Oxide: Are We Making Progress?

Brad Hall, Geoff Dutton, Ed Dlugokencky

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NOAA has served as the WMO/GAW Central Calibration Laboratory (CCL) for nitrous oxide (N_2O) since 2003. In recent years the reproducibility of N_2O calibrations has improved from about 0.5 ppb to 0.2 ppb. Despite improvements in calibration, some difficult issues remain, such as difficulties in transferring the WMO-06 scale to other labs, sampling issues that may lead to offsets between instruments, and possible drift associated with the CCL secondary standards. I will report on ongoing comparison studies, efforts to assess scale stability, and improvements in data management.

Preparation of nitrous oxide (N_2O) in air standard being traceable to SI by gravimetric method

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It is noted that there is difference between nitrous oxide (N_2O) scales which laboratories maintain. In the fourth WMO Round-Robin intercomparison (Zhou et al., 2009), N_2O scale of NIES is 0.6-0.7 nmol/mol lower than that of NOAA in a range between 309 and 316 nmol/mol. National Metrology Institute of Japan (NMIJ) developed standards of N_2O in air in order to elucidate cause of this difference. The substance fractions and expanded uncertainties of five standards developed are 303.57±0.13, 312.77±0.19, 326.44±0.20, 338.20±0.20, 343.73±0.23 nmol/mol. The substance fractions were determined from the gravimetric method (ISO 6142:2001), which is one of primary preparation methods traceable to the International System of Units (SI). The expanded uncertainties were determined by evaluating multiplying combined standard uncertainties and coverage factor (k =2), corresponding to an estimated confidence interval of approximately 95 %. The standards developed were measured by NIES for comparison with NIES-standards prepared by gravimetric method in a range from 252 to 402 nmol/mol.

Three processes were conducted in order to prepare the reliable standards. First, purities of N_2O, N_2, and O_2 used as a raw material were determined by analyses using GC-TCD, GC-MS, and FT-IR. In particular, N_2O concentrations (about 20 pmol/mol) in the dilution gases of O_2 and N_2 were determined using GC-MS with a preconcentration system. Consequently, N_2O concentration in O_2 and N_2 was negligible. Second, the five standards were independently prepared using electric balance calibrated by mass pieces traceable to SI. Atmospheric concentration level was obtained by 4-step dilution as shown in Figure 1. Amount of filled raw material was measured on an hour after setting up a cylinder in order to achieve adsorption-absorption equilibrium of atmospheric components to cylinder surface. Finally, we verified the concentration of standards for each step by calibration curve from their analyses using FT-IR or GC-ECD. The relative deviations of gravimetric values from calibration curve were less than 0.1% for all standards of each dilution steps.

The result of analysis by NIES revealed that the responses of NMIJ-standards were consistent with calibration curve obtained by measurement of NIES-standards (a range from 303 to 344 nmol/mol) using GC-ECD. The deviation between gravimetric values of NMIJ-standards and the value calculated from the calibration curve of NIES standards fell within 0.20 nmol/mol. This consistency indicates that the values of NIES-standerds are reliable. NMIJ has also participated in international comparison of ambient level N_2O (CCQM-K68) among national metrology institutes.

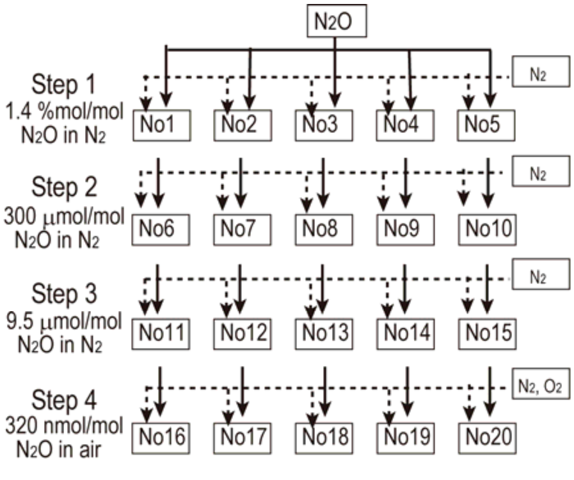

Figure 1 Schematic diagram of preparation for N_2O standards by our gravimetric method

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REPORT OF THE WCC-N_2O

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The World Calibration Centre for N_2O (WCC-N_2O) has been established as a central GAW facility according to requirements of the GAW Strategic Plan 2001–2007 (WMO/GAW Report No. 142). Its overall goal is the improvement of N_2O data quality and comparability. The WCC-N_2O (http://imk.fzk.de/wcc-n2o/) is hosted by the Forschungszentrum Karlsruhe, IMK-IFU, and its activities are conducted under supervision and through funding by the Quality Assurance/Science Activity Centre (QA/SAC) Germany, operated by the German Environment Agency (UBA). Among the major tasks of the WCC-N_2O are the development of quality control procedures, conducting audits at stations and intercomparison experiments as well as providing training and technical advice to GAW station personnel. The WCC-N_2O is linked to the GAW standard scale maintained by the Central Calibration Laboratory (CCL) for N_2O. This presentation reports primarily on activities of the WCC-N_2O since the 14th Experts Meeting in 2007.

Extensive comparisons of standards were conducted in the laboratory of the WCC-N_2O. A noteworthy experiment was the participation in a round-robin experiment initiated by a group of National Metrology Institutes (NMI), which provides a link to their N_2O scale. The eight highest-ranking standards of the WCC-N_2O, which establish the link to the GAW N_2O scale, were recalibrated by the GAW CCL in early 2009. The results confirmed the assigned mole fractions of the standards.

Two audits were conducted at global GAW stations (September 2007 and November 2008). Another audit took place at an associated laboratory in December 2008. Results of these audits are shown and discussed.

Editing work on the Measurement Guidelines (MGs) for N_2O has been finalized. The MGs for N_2O are part of a WMO/GAW report containing Data Quality Objectives (DQOs) and Measurement Guidelines for both CH_4 and N_2O. The report is available from the GAW web site. Further activities of the WCC-N_2O comprised contributions to four GAWTEC courses (2007 – spring 2009) in the form of nine lectures.

IS IT TIME FOR A WMO HYDROGEN CALIBRATION SCALE?

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Several long-term time series of atmospheric H_2 observations have been published describing seasonal cycles and latitudinal gradients for this tracer. While the H_2 concentrations have risen during the 1980s no further long-term trend was observed in the past two decades, suggesting that the source and sink processes are in balance. However, a changing climate will probably have an impact and influence processes that are part of the hydrogen cycle. Scenarios of introducing hydrogen as a major new energy carrier also suggest that the levels of atmospheric hydrogen might change.

The ability to detect such changes in H_2 mixing ratios or shifts of spatial gradients is dependent on consistent long-term measurements. Yet, inconsistencies in published data sets have been identified that are significant with respect to the atmospheric variability[1]. Sources for these discrepancies include unstable reference gas mixtures and diverse calibration scales generated using different methods. As scale offsets have not always been constant data from different sources have been difficult to compare. This restricts the use of atmospheric concentration data for inverse model calculations, which require harmonized data sets.

The global observational network for H_2 measurements has been expanded within the EuroHydros project. In the absence of a WMO calibration scale for H_2 part of this project was devoted to calibration of these measurements. In the course of this work a new calibration scale has been set up (MPI2009). The scale is based on 13 standard gas mixtures of H_2 in air with the concentrations ranging from 140-1220 ppb. The mixing ratios in these standards have been determined by comparing them to a suite of 50 reference gases produced with the previously described method for precise mixing of gases[2,3]. An assessment of the limitations of this method and the precision of the GC-RGA measurement yields in an accuracy estimate of better ±0.5% for the scale. In addition, various types of containers have been tested for their properties in maintaining stable H_2 mixing ratios.

The relationship of the MPI2009 scale to the scales used in the NOAA and the AGAGE networks (NOAA2008[4] and CSIRO94[5], respectively) has been evaluated. During two intercomparison campaigns in 2008 and 2009 a consistent offset of 7 ± 1 ppb has been observed relative to the NOAA2008 scale over the range of 400-650 ppb . A larger offset of 17 ± 2 ppb has been established relative to the CSIRO94 scale. However, a long-term intercomparison effort since 2002 has revealed that the inter-laboratory offset between CSIRO and MPI-BGC has been very stable over time. This might allow a retrospective harmonization of the records.

This cooperation between major measurement groups might serve as a starting point to establish a common calibration scale, which has been itemized as one of the goals in the WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015.[6]

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QUALITY ASSURANCE AND QUALITY CONTROL OF WDCGG DATA

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The WMO World Data Centre for Greenhouse Gases (WDCGG) has been operated by the Japan Meteorological Agency (JMA) since 1990 as one of the World Data Centres established in the framework of the Global Atmosphere Watch (GAW) programme. The WDCGG archives observational data reported from stations worldwide and provides global analysis for major greenhouse gases.

The reported data are in principle quality-controlled, selected, averaged and formatted by the contributors in accordance with the Data Submission and Dissemination Guide published as GAW Report No. 174, prior to submission to the WDCGG. The WDCGG also invites the contributors to report metadata to describe the data, which can be submitted or edited on the web. Upon reception of data or metadata, the WDCGG performs a basic quality check in terms of format, realizability and consistency. Questionable data are reported back to the contributors for review by the principal investigators (PIs).

As for the WDCGG's analytical products, data are selected according to the criteria described in the Technical Report of Global Analysis Method (GAW Report No. 184) for CO_2, CH_4 and N_2O. The criteria include aspects of traceability or comparability to the GAW Primary Standards, long-term continuity of data availability and geographical consistency to smoothed meridional distributions. Selection is made objectively based on predefined thresholds to identify observation sites that provide suitable data for global analysis.

This presentation will describe the WDCGG's procedures of a basic quality check on the reception of data, as well as more advanced screening based on statistical analysis of data. It will also review the results of data selection when the WDCGG produced global analyses of observations up to 2007 published for WMO Greenhouse Gas Bulletin No. 4 in November 2008 and WDCGG Data Summary No. 33 in March 2009, which overviews the usability of the archived data sets of the WDCGG.

Reference:
World Meteorological Organization, 2007: World Data Centre for Greenhouse Gases Data Submission and Dissemination Guide, WMO-GAW Report 174, 35 pp.
Tsutsumi, Y., K. Mori, T. Hirahara, M. Ikegami and T. Conway, 2009: Technical Report of Global Analysis Method for Major Greenhouse Gases by the World Data Center for Greenhouse Gases, WMO-GAW Report 184, 13 pp.

Overview of comparisons of non-CO_2 trace gas measurements between AGAGE and NOAA at common sites

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Three dimensional model studies that calculate emissions often require more data than from only one individual network's group of stations, therefore it is important to be able to accurately merge atmospheric trace gas data sets from different laboratories and networks, which may use different calibration scales. To facilitate this, on-going comparisons of *in situ* data with independent flask and/or *in situ* data collected at common sites are useful as they are sensitive diagnostic tests of data quality for the laboratories involved, and they provide a basis for merging these data sets with confidence.

For the past 9 years up to 300 comparisons of non-CO_2 greenhouse gases (more than 30 species) have been carried out twice yearly and presented at meetings of Advanced Global Atmospheric Gases Experiment (AGAGE) scientists and Cooperating Networks. The majority of these comparisons are between AGAGE *in situ* and NOAA flask data from the Halocarbons and other Atmospheric Trace Species (HATS) and Carbon Cycle Greenhouse Gas (CCGG) groups at NOAA/ESRL. The five common measurement sites are: Cape Grim, Australia; Cape Matatula, American Samoa (includes some NOAA *in situ* data); Ragged Point, Barbados; Trinidad Head, USA; and Mace Head, Ireland.

In this presentation the comparison methodology will be outlined and results from selected comparisons will be shown. A brief summary of the overall level of agreement between AGAGE and NOAA data will be given. An outline of an improved mechanism on how to summarise/disseminate the results will also be given.

NEW CAPABILITIES FOR INTERPRETING COMPARISON DATA

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Comparison experiments are an integral part of the NOAA ESRL atmospheric measurement program for several reasons. First, comparisons between atmospheric observations made using independent methods help us detect experimental problems within our program. Second, comparisons with observations derived from other laboratories are critical to assessing the level at which our measurements are comparable with those of the larger measurement community. Finally, ongoing comparisons provide a more complete appraisal of our true measurement uncertainty that in many applications may be more useful than our reported measurement repeatability. The burden is on us to clearly state the level of our internal consistency and to provide defensible justification for combining ESRL data with data from other laboratories. It is for this reason that ESRL participates in nearly 20 comparison experiments in collaboration with other projects and laboratories. The usefulness of each comparison varies widely and depends in part on experimental design, comparison frequency, and level of automation. In many instances we simply do not have sufficient information to make useful assessments. For example, comparisons based solely on results from WMO round robin experiments provide only a snapshot every 3 to 4 years of how well two laboratories are able to measure air from a high-pressure reference cylinder and infer from this our ability to maintain and propagate the WMO Mole Fraction Scale. This information establishes comparability but says nothing about potential measurement biases associated with gas handling that can often vary over time. In other instances, we may have sufficient information but it is not always readily and easily available. Here we present a web-based interactive atmospheric data comparison tool that improves our ability to interpret data generated from the many ESRL comparison activities. As an example, we are now able to compare ESRL and Environment Canada (EC) measurements of 1) the same air in high-pressure cylinders, e.g., WMO Round Robin experiment; 2) same air in weekly flask samples collected at Alert; 3) bimonthly air samples from the CarboEurope Sausage experiment; and 4) EC in situ data and either ESRL or EC weekly flask data from the EC stations at Alert and Lac LaBiche. These results can then be easily compared with results from comparison experiments with other laboratories; this capability greatly improves our ability to narrow possible causes for observed differences. The restricted web application accesses a database that is automatically updated when new comparison data become available. Production graphs and statistical summaries are automatically prepared for most standard comparisons; all historical results are archived and continue to be readily available. An interactive component provides ESRL and collaborating researchers direct access to the database to create custom comparison plots and summaries.

WMO ROUND-ROBIN INTER-COMPARISON: PROGRESS AND A NEW WEBSITE

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The purpose of the WMO Round-robin reference gas inter-comparison would be NOT to distribute calibration scales, but rather to determine the precision of the current practice of international calibrations. As recommended by the WMO/IAEA Meeting of Experts, all participating labs are urged to contribute the results of all systematic investigations of gas handling protocols and materials, whether the results were positive or negative. The protocol of the fifth inter-comparison started in early 2009 was similar to that used for the previous ones held during 1991-1992, 1995-1997, 1999-2000 and 2002-2007. However, reporting content details are emphasized:

Report to Lingxi Zhou (Referee): when reporting results please also include 1) One or more references to publications or reports describing their measurement procedures, and which standard scale they are on. 2) Instrument type and model. 3) Date of analysis start and end. 4) Cylinder numbers with trace gas concentration average and 1 SD [n-1] if multiple analysis. 5) If you do send cross calibration results by different "Instrument type and model" deployed in one Lab for one species, report this separately as two distinct reports, compared only to the three inter-comparison tanks. Denote them clearly via location, use, instrument type. 6) We are mostly interested in the point where the calibration scale is transferred to the rest of your lab (propagate, traceability), not necessarily each field measurement system.

Report to Duane Kitzis (Logistical planning): please send the following as you complete them 1) Date cylinders are unpacked. 2) Pressure when conditioning regulators. 3) Final tank pressures when removing regulators. 4) Date shipped out to the next laboratory.

A new website function and design open for discussion: Protocol; guideline; direction; Demo video; easily add account and password; log each entry; cylinder tracking; auto email reminder; statistics and custom graph plot; update of responsible person from each participating lab; results submission and update before/after deadline; search and visualization of the previous RR results; new participant application; and so on.

- *Peterson, J., P. Tans, and D. Kitzis, 1999, "CO2 Round-Robin Reference Gas Inter-comparison" in Report of the Ninth WMO Meeting of Experts on CO2 Concentration and Related Tracer Measurement Techniques, Australia, 1 - 4 September 1997, edited by R. Francey, WMO, Geneva.*
- *Zhou, L.X., D. Kitzis, P. Tans, 2009, Report of the Fourth WMO Round-Robin Reference Gas Inter-comparison, 2002-2007, WMO/GAW Report No. 186, pp. 40-43.*

What have we learnt from global intercomparison programmes and what should we do next?

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The World Meteorological Organization has specified an "inter-laboratory comparability" of ±0.1 ppm and ±1 per meg for background atmospheric CO_2 and O_2 measurements respectively. This means that any given two laboratories (or field stations) measuring the same air sample should strive to obtain values within ±0.1 ppm CO_2 (or ±1 per meg O_2) of each other. Intercomparability goals also exist for the other major greenhouse gases and greenhouse-related tracers. Several intercomparison programmes, focussed on CO_2, have existed for many years quantifying (and improving) such comparability between the few major greenhouse gas analysis laboratories around the world. No overarching programme existed, however, for assessing comparability between field stations or for O_2 measurements. Oxygen measurements further suffer from the non-existence of a common international calibration scale. The “GOLLUM” (Global Oxygen Laboratories Link Ultra-precise Measurements) and “Cucumber” intercomparison programmes were established to address these deficiencies. Each programme continuously circulates trios of high pressure cylinders of air of known concentrations to field stations and laboratories.

We present 4 years of results from these programmes, where we quantify the CO_2 and O_2 comparability from 22 participating European field stations and 16 international laboratories. Results of other tracers are also presented. By highlighting concentration offsets, the programmes have assisted in improving the analytical procedures and thus the precision and accuracy at some stations. Comparability between any two given stations or laboratories is not constant over time, thus the programmes run indefinitely, and emphasis is given to rapid circulation between participants and for each station/laboratory to build up a time-history of comparability. In addition to continuing the programmes and improving technical aspects of the measurements, next steps must consider quantitative adjustments to existing atmospheric concentration data, thus allowing one to merge formerly disparate datasets. This would lead to spatially and temporally denser datasets which would be invaluable to many aspects of carbon cycle science, for example by reducing uncertainty in atmospheric inverse models used to quantify global and regional carbon sinks.

Evaluating CarboEurope/IMECC Quality Control Activities: Do intercomparison results help us to further improve our measurements?

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D. Worthy, M. Ernst, L. Huang (EnCan)
A. C. Manning, A. Etchells (UEA)

Within CarboEurope and IMECC a set of intercomparison tools has been established that vary in terms of frequency, precision and the number of participants. An update of results from these various intercomparisons will be presented and evaluated for different species.

Main purpose of these exercises is to assess the degree of consistency of atmospheric monitoring data that have been generated by different laboratories. Offsets in analytical results derived by different laboratories may arise from various types of systematic errors with any component involved in the analytical process. This includes calibration standards, flask properties, the analytical method, and instrument performance.

The different tasks contain complementary but also redundant information. The combination of these independent ICP results has revealed differences in offsets between two given labs depending on the sort of exercise. On the one hand, these inconsistencies indicate the limit of the significance of these data. However, such discrepancies may also help to identify the limiting factor of the analytical procedure at the participating labs.

For several tracers including CO and N_2O concentration dependent offsets are apparent between laboratories that may arise from inhomogeneous calibration scales or concentration levels that exceed the calibrated range of some participants. Scale differences that are stable in time give the prospect of future calibration updates that allow a harmonization of the respective data sets.

It appears that additional meta-information is vital for the interpretation of the intercomparison data. This includes information on the calibration scale (including version numbers), calibrated ranges, the working standard associated to a measurement, and consequent flagging in cases of known problems at given laboratories (e.g. drifting working standards).

A precondition for the success of any intercomparison is regular data submission and the subsequent release of results. The regularity of this reporting and data release has been perturbed in the past. A major challenge remains a convenient but error-free way for data reporting and revision.

Uses and Limitations for Isotopes of Carbon Dioxide and Methane

J.W.C. White, C. B. Alden, B.H. Vaughn, S.E. Michel, J. Winokur, and V. Claymore

On global to broad latitudinal scales, C13 of CO2 provides a valuable check on fluxes of carbon between the atmosphere and the ocean versus the land. As scales shrink, and as observation networks become more dense, C13 of CO2 becomes more useful as a tracer of other aspects of t he carbon cycle. For example, the balance between photosynthetic and respiratory fluxes can influence the C13 of CO2 as these fluxes interact with the atmosphere on different time scales, photosynthesis being immediate and modern, while respired carbon can be decades old, a process known as isotope disequilibrium. As the C13 of atmospheric CO2 is changing with time, this means that even a balanced cycle of photosynthesis and respiration will generate an isotopic flux. Also, the degree to which plants fractionate during photosynthesis can change and leave its imprint on the atmosphere. Here we present initial results from models that assume a known ocean flux and use CO2 concentration and isotopes to infer time histories of disequilibrium and of isotope fractionation during photosynthesis.

On global to broad latitudinal scales, O18 of CO2 is thought to track the balance between photosynthesis and respiration, as these processes have quite different isotopic signatures. One of the uncertainties in the past has been the influence of isotope exchange between CO2 and H2O on the walls of flasks. We present here a new approach to eliminating data that have been compromised by oxygen exchange as well as a new release of the NOAA-INSTAAR data set.

The fluxes of methane to the atmosphere are arguably the least understood and most dynamic of the greenhouse gases. Isotopes (C13 and D) can help constrain this complex system. We will present an overview of the methane isotope records (C13 and D) in the NOAA-INSTAAR data base and discuss the implications for methane fluxes.

Isotope exchange between CO2 and O3 in the stratosphere: atmospheric and laboratory measurements

Thomas Röckmann, Robina Shaheen and Christoph Janssen

Isotope measurements of stratospheric CO_2 show strong enrichments in both ^{17}O and ^{18}O relative to tropospheric CO_2. The relative enrichments do not follow the mass dependent fractionation relation $\delta^{17}O \sim 0.52\ \delta^{18}O$, but enrichments in ^{17}O are much stronger than in ^{18}O, resulting in an oxygen isotope anomaly that is characterized by $\delta^{17}O \sim 1.65*\delta^{18}O$. The isotope anomalies of stratospheric and mesospheric CO_2 offer a potential tracer of upper atmosphere dynamics and the corresponding anomaly in O_2 can be used as a tracer of terrestrial gross carbon fluxes on decadal to millennial time scales. CO_2 inherits the anomaly via photo-induced isotope exchange with stratospheric O_3, which itself carries a strong oxygen isotope anomaly. However the details of the exchange process are not satisfactorily understood. Laboratory experiments show that the isotope equilibrium point between CO_2 and O_2 mediated via O_3 and $O(^1D)$ is a fundamental property of the exchange system that can be used to derive three-isotope slopes in different environments. The isotope anomaly of O_3 shows a strong temperature dependence, which explains to leading order the temperature dependence in the isotope exchange equilibrium point. Simultaneours measurements of O_3 and CO_2 in a photochemical equilibrium experiment indicate that no mass independent fracitionation is involved in the chemistry of the intermediate CO_3^* complex.

High precision CO2 isotope analyses of air samples from the free tropical troposphere and upper troposphere-lowermost stratosphere region: The CARIBIC project

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The project CARIBIC (http://caribic-atmospheric.com), aims to study atmospheric chemistry and composition by regularly measuring many compounds in the free tropical troposphere and the upper troposphere-lowermost stratosphere (UT/LMS) around the globe by using a commercial aircraft. During CARIBIC-1 (flights from Germany to mainly India, South Africa and the Caribbean), CO2 isotopic composition was measured on cryogenic extracts from large air samples of ~250 l STP (1999 to 2002). CO2 isotope analysis was continued during CARIBIC-LUFTHANSA (2007 to 2008). The new instrument container operates onboard a Lufthansa A340-600 (Frankfurt, Germany) with monthly flights from Frankfurt to remote destinations, collecting 28 air samples in glass flasks for laboratory analyses. High quality isotope measurements were performed at JRC-IRMM (Geel, Belgium) by using a new CO2 extraction line. Particular focus was on the traceable calibration as well as on the quality of d18O(CO2) data. The fact that CARIBIC-1 and CARIBIC-2 data (CO2 and d13C(CO2)) corrected for the known trend agree with each other and demonstrate the same features independently proves the quality of the previous and recent measurements. About 500 air samples analysed from June-2007 to Jan-2009 together with CARIBIC-1 data (about 350 samples, mostly d13C(CO2)) give a reliable data set for the free troposphere and the UT/LMS region in the Northern Hemisphere. The new data, trends and tracer-tracer correlations will be presented, with the focus on understanding the effects responsible for the distribution of signals observed. 13C values show at times extremely compact relationships with CO2 mixing ratios. 18O values show little if any latitudinal gradient and an increase across the tropopause.

A Report of $\delta^{13}C$ & $\delta^{18}O$ Measurements in NBS19 and NBS18 pure CO_2: Traceability Uncertainty in CO_2 Isotope Measurements

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** In alphabetical order by primary contact at each lab*

One of the major causes for the differences in CO_2 isotope measurements (i.e., $\delta^{13}C$ and $\delta^{18}O$) from inter-comparison exercises, including WMO Round Robin, Cucumber, Sausage and real flasks ICP at Alert, is the uncertainty of individual primary anchors on the VPDB scale. Due to this uncertainty, the applications of isotope measurements in quantifying the relative changes of sources/sinks in atmospheric CO_2 have been limited. It is likely that this uncertainty mainly originates from carbonate-CO_2 productions and/or isotope ratio mass spectrometer (IRMS) analysis. Measuring $\delta^{13}C$ & $\delta^{18}O$ compositions of NBS19 and NBS18 in pure CO_2 ampoules (which are made from one lab, Environment Canada) could be used as an independent approach to assess the uncertainty of individual primary anchors on the VPDBCO_2 scale.

Based on the calibration record over the last 10 years, the uncertainty for making those pure CO_2 ampoules from NBS19 and NBS18 carbonates at the Stable Isotope Research Laboratory, CRD/ASTD, Environment Canada, is ~ 0.02 ‰ and ~ 0.05 ‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively. A large number of NBS19 and NBS18 pure CO_2 ampoules were made through individual reactions via acid digestion with 100% H_3PO_4 at 25°C in the lab during the period of 2007 – 2008 and were sent, as individual packages (three NBS19 and three NBS18 ampoules in each package), to 14 international laboratories within ten countries for this inter-comparison exercise (most of the labs are involved in WMO/GAW activities). Suggested measurement protocol and data report format were also sent to the participating teams. The objective of this exercise was to address the uncertainty issue of individual primary anchors on the VPDBCO_2 scale, which may play an important role in high precision isotopic measurements of the atmosphere CO_2 in flask samples.

13 out of 14 labs from nine countries have reported their results, which include the raw data (δ^{45} and δ^{46}) and the final processed $\delta^{13}C$ and $\delta^{18}O$ data via using individual primary anchors (one lab reported only the final data). The results show that:

- the mean values of standard deviations (for $\delta^{13}C$ and $\delta^{18}O$) in individual NBS19CO_2 and NBS18CO_2 packages from the 13 labs are < **0.02‰** in $\delta^{13}C$ and < **0.05** ‰ in $\delta^{18}O$, implying that the mean uncertainties caused by the duplicated carbonate productions and IRMS analysis are relatively small.

- Using the NBS19CO$_2$ prepared by EnCan as the primary anchor (with Craig/Allison O^{17} correction), the mean values of NBS18CO$_2$ in δ^{13}C and δ^{18}O from the 13 labs are **-5.059**±0.**037‰** and **-23.018±0.197‰**, respectively, on the VPDBCO$_2$ scale. These values are very close to the corresponding results (-5.06±0.03‰ and -23.01±0.22‰) reported by NIST in the Special Publication 260-149, 2004 Edition (using the same O^{17} correction as we do). The uncertainties (implied by the standard deviations) are mainly caused by individual instrumentation, including the differences in the type of the IRMSs (e.g. Finnigan vs. Isoprime) and in the degree of their cleanliness, which would cause scale contraction or expansion. This kind of uncertainties can be addressed by an approach of normalization using two anchor points at the primary scale.
- Using NBS19CO$_2$ prepared at individual labs as the primary anchors, the mean values of NBS18CO$_2$ in δ^{13}C and δ^{18}O from the 13 labs are **-5.070±0.038‰** and **-23.131±0.243‰**, respectively, indicating that the magnitudes in scattering and variations of these primary anchors are much larger than the targets (±0.01 ‰ in δ^{13}C and ±0.05‰ in δ^{18}O) set by WMO Expert meetings for data comparability.
- The differences in δ^{13}C and δ^{18}O between two individual labs (apparent differences) are mainly contributed by two factors: one is the difference in the primary scale (due to the variations of primary anchors); another is the difference caused by IRMS. Usually the sum of the two components is approximately equal to the apparent difference.
- The results from this exercise can be used to understand/explain the differences found in real flask samples (e.g. Sausage and flask ICP programs at Alert) and further to merge the datasets from different measurement networks, which are important for source and sink partitioning in carbon cycle study at different spatial and temporal scales.

HOW ACCURATE DO WE KNOW $^{13}C/^{12}C$, $^{18}O/^{16}O$ AND $^{17}O/^{16}O$ RATIOS IN CO_2 AND THEIR CORRESPONDING δ VALUES?

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Previous WMO/IAEA Experts' Meetings have endorsed recommendations on CO_2 isotope calibrations in order to eliminate ambiguities in calculating $\delta(^{13}C)$ (short: $^{13}\delta$) and $\delta(^{18}O)$ (short: $^{18}\delta$) values from mass-spectrometric measurements. This calculation is essentially a linear transformation of relative ion current ratio differences ($^{45}\delta$ and $^{46}\delta$) to $^{13}\delta$ and $^{18}\delta$ values that depends on two coefficients C and D, with $C = {}^{17}R/{}^{13}R$ and $D = {}^{13}R\,{}^{17}R/{}^{18}R$ (^{13}R, ^{17}R, ^{18}R are the isotope ratios $N(^{13}C)/N(^{12}C)$, $N(^{17}O)/N(^{16}O)$ and $N(^{18}O)/N(^{16}O)$ [*Kaiser*, 2008]). WMO/IAEA have suggested to adopt the 'ratio assumption set' of Assonov and Brenninkmeijer (2003). The transformation also assumes a certain mass-dependent relationship between $^{17}\delta$ and $^{18}\delta$, namely $^{17}\delta = (1+{}^{18}\delta)^{0.528} - 1$. While this recommendation does eliminate ambiguities in data processing between different laboratories, it fails to address the accuracy of the calculated $^{13}\delta$ and $^{18}\delta$ values and of the elemental isotope ratios derived from them.

Here, I identify several sources of inaccuracy: (I) the coefficients C and D, (II) the assumed mass-dependent relationship and (III) the value of the 'absolute' isotope ratios of the reference material NBS19-CO_2. (I) and (II) affect both δ values and derived sample isotope ratios, (III) affects just the isotope ratios. Two previous determinations of C and D agree with the result of Assonov and Brenninkmeijer (2003) to within 2σ, suggesting that these coefficients are unlikely to be a significant source of inaccuracy for atmospheric CO_2. In contrast, the validity of the assumed mass-dependent relationship remains to be verified. Experimental measurements and theoretical estimates indicate possible deviations ($^{17}\Delta$) of between –0.3 and +0.7 ‰ from the assumed relationship, which results in systematic errors between –0.05 and +0.02 ‰ in the computed $^{13}\delta$ value. More importantly, $^{17}\Delta$ values differ for CO_2 from combustion processes and from stratospheric return flux, so that tropospheric CO_2 is expected to show variations in its $^{17}\Delta$ value. Finally, a literature survey reveals significant uncertainty in the 'absolute' isotope ratio of the reference material NBS19-CO_2. Little sign of convergence on a single value emerges for ^{13}R. No direct measurements exist for ^{17}R. Only in case of ^{18}R, three independent measurements agree within their mutual range of errors.

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JRAS Isotope reference: A generalized VPDB scale anchor for CO_2 in air?

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The Jena Reference Air Standard, JRAS, is a direct result of the recommendations formulated and discussed during the CO_2 Experts Meeting in Toronto 2003. Based on a number of attempts to unify the CO_2 isotope scale for air samples using pure CO_2 [1, 2] it was decided at this meeting that a common scale anchor for CO_2 in air measurements was not established yet but urgently needed. This anchor/reference should address both the need for a direct link to the VPDB scale[3, 4] and allow for identical treatment of both standard and sample. Since then the IsoLab at MPI-BGC in Jena has taken on the task to develop the capability to produce a consistent reference gas containing artificial air mixed with CO_2 from precisely characterized (calcite) source closely tied to the VPDB scale.

Thanks to funding provided by the European Commission through the TACOS and IMECC projects, JRAS[5-7] sets have been evaluated during the last two years by eleven laboratories worldwide. This presentation will, apart from a short introduction to JRAS production and quality control, summarize the intermediate results of this effort and discuss some of the consequences for a unified scale anchor.

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Title: Calibrations, Corrections, and Challenges for isotopes of Methane and Carbon Dioxide

Authors: B.H. Vaughn, J.W.C. White, S.E. Michel, J. Winokur and V. Claymore

Isotopic analyses performed on large numbers of network samples present unique challenges, ranging from solving daily analytical problems that make turnkey-like operations illusive, to long-term scale and calibration issues. Significant advances have been made in all these areas for isotopes of carbon dioxide, while isotopes of methane remain in the formative stages for the global GHG measurement community. Data will be presented on the current scaling and corrections of 13C and 18O of CO2 from the NOAA/INSTAAR flask measurement program, as well as comparisons with other labs. Methods of 13C and D/H of methane measurements present real challenges both for calibration to a carbonate scale, as well as robustness of routine measurements. For example, small volume GC-IRMS methods are fundamentally different from large volume dual inlet methods that can make ties to a carbonate, or water scale. Several approaches the to problem are explored, in hopes of prompting broader discussion by the measurement community.

MERGING ATMOSPHERIC $\delta^{13}C$ DATA SETS

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This presentation will describe a preliminary attempt at merging two of the larger atmospheric $\delta^{13}C$ data sets; the CSIRO Marine and Atmospheric Research (CMAR) data set and the Institute for Arctic and Alpine Research (INSTAAR) data set.

AN FTIR ANALYSER FOR SIMULTANEOUS HIGH PRECISION MEASUREMENTS OF CO_2, CH_4, CO, N_2O AND $\delta^{13}C$-CO_2 IN AIR: INTERCOMPARISON MEASUREMENTS AT CAPE GRIM

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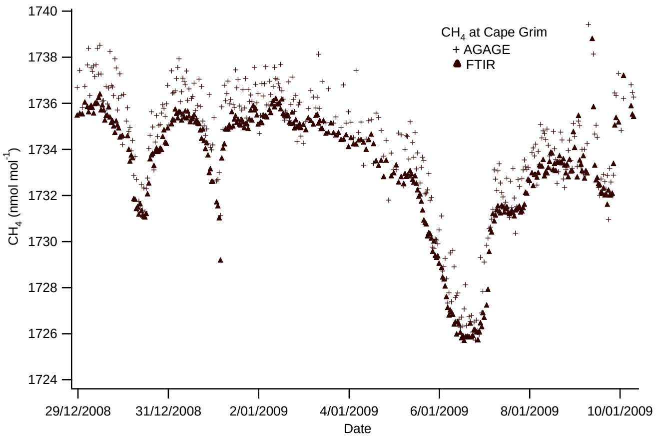
Over the past decade we have developed and refined a multi-species trace gas analyser based on Fourier Transform Infrared (FTIR) spectroscopy for atmospheric composition measurements. The analyser determines mixing ratios of CO_2, $\delta^{13}C$-CO_2, CH_4, CO and N_2O simultaneously in air with high precision and accuracy.

From October 2008 to February 2009 we operated a new analyser at Cape Grim, parallel to the CSIRO LoFlo CO_2 analyser and AGAGE automated GC system. The FTIR analyser operated autonomously, measuring 10-minute average mixing ratios continuously over the 110 day trial. In this paper we compare the FTIR measurements to coincident measurements from LoFlo and AGAGE instruments. The figure illustrates the results with a 12-day CH_4 record of FTIR and AGAGE measurements (absolute calibrations not finalised), and the table collects the demonstrated 10-minute precisions (1-σ repeatabilities): these precisions are significantly higher than those of the AGAGE measurements but somewhat lower than LoFlo for CO_2.



FTIR 1-σ precision

CO_2	0.05 μmol mol^{-1}
$\delta^{13}C$-CO_2	0.08 ‰
CH_4	0.2 nmol mol^{-1}
CO	0.2 nmol mol^{-1}
N_2O	0.06 nmol mol^{-1}

The FTIR analyser provides a cost-effective, low maintenance solution for the simultaneous high precision measurement of the five target species. The only consumables are mains power, a small flow of purge N_2, magnesium perchlorate drying agent and calibration gas (one calibration per day). The analyser can be managed remotely if the controlling PC is connected to the internet. Several analysers have been deployed in applications including continuous measurements at fixed locations (such as Cape Grim and Lauder, NZ), on mobile platforms (trains, ships), and in field campaigns, for example for micrometeorological flux measurements.

Field testing of cavity ring-down spectroscopy instruments measuring CO2

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Prevalent methods for making tower-based measurements of CO2 mixing ratio, notably non-dispersive infrared spectroscopy, require frequent system calibration and drying of the sample gas. Cavity ring-down spectroscopy (CRDS) is an emerging laser-based technique for detecting trace quantities of gases, eliminating or significantly reducing the frequency of calibration and the need to dry the sample gas. We present results from 24 months of field measurements from five CRDS systems in the midwestern U.S, deployed in support of the North American Carbon Program's Mid Continental Intensive. Analysis and results include an examination of long-term stability, discussion of overall uncertainty, and the effects of using the water vapor correction instead of drying the sample gas.

RECENT DEVELOPMENTS IN INSTRUMENTATION FOR GREENHOUSE GASES AND RELATED TRACER MEASUREMENTS

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Within the past few years, there have been significant advances in instrumentation available to the scientific community for high-precision greenhouse gas measurements and related tracer gases including stable isotopes. In particular, a new collection of analyzers based on Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) have, in the past two years, been deployed in over 33 countries and in mobile applications including airborne, ship-based and vehicle-based monitoring campaigns. In addition to the common greenhouse gases (CO_2, CH_4), new analyzers have been produced for measuring isotopes and tracers including $\delta^{13}C$ in CO_2, $\delta^{18}O$ and δD in water, CO, COS and acetylene. Work is currently underway to significantly broaden this list to include gases such as N_2O (including $\delta^{15}N$) and well as $\delta^{18}O$ in CO_2 and others. This presentation will highlight these instrumentation developments as well as the following specific applications:

Total methane emissions from extended sources

A promising method for determining total methane emissions from landfills and other extended sources which does not depend upon characterizing time-varying meteorological conditions is the tracer method in which another gas, such as acetylene (C_2H_2), is released at a known rate from the same location as the landfill. The idea behind the tracer method is to simultaneously measure the concentration of methane and the tracer gas as a function of position around the methane source and back calculate how much methane must have been emitted. Picarro, in collaboration with the US EPA executed on a study demonstrating the applicability of Picarro's technology to determine the total methane emissions from landfills using the tracer method. To carry out the tracer study, continuous measurements of C_2H_2 and CH_4 concentrations, ambient temperature, and analyzer location (GPS) were made by a newly designed analyzer while moving through the overlapping plumes. Results from the field campaign, including the effectiveness of the tracer technique to measure total methane emissions, will be shown.

Regional scale measurements

A regional-scale network (part of the NACP's Midcontinental Intensive) of five communications-tower-based atmospheric CO_2 observations ("Ring 2"), from April 2007 through October 2008, was added to the long-term atmospheric CO_2 observing network (tall towers, aircraft profiles, and well-calibrated CO_2 measurements on Ameriflux towers) in the mid-continent intensive region. The Ring 2 uses WS-CRDS instrumentation, and the locations are regional in scale (roughly a 500-km diameter ring). We present results concerning data quality, including water vapor correction and uncertainties, as well as small-scale temporal and spatial variations that can be seen with this unique network.

Eddy covariance flux measurements

The EC Flux method is commonly employed to study biogeochemical scalar fluxes of greenhouse gases between the land surface and the atmosphere. Its use has so far been limited mainly to flux measurements of CO_2, water vapor and ozone due to the lack of adequate instrumentation for other greenhouse gases. Picarro's new closed-path analyzer has been evaluated against conventional instrumentation for performing simultaneous CO_2 and CH_4 flux measurements. We present field data evaluating the performance of a high-frequency fast-response (10Hz) WS-CRDS gas analyzer. Data comparing the performance of this WS-CRDS analyzer with currently-used AmeriFlux instrumentation is presented.

Evaluation of the use of EnviroSense 3000i analysers (now called G1301) for continuous CO2/CH4 measurement in ambient air by CRDS

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The joint presentation between the French Institute LSCE, the Irish Environmental Protection Agency (EPA) and the British Department of Earth Sciences, Royal Holloway, University of London will show the results obtained with the use of the Picarro EnviroSense 3000i (now called G1301) for continuous CO_2, CH_4 and H_2O measurements. In total, five instruments, running in different experimental conditions, will be compared for stability in CO_2 and CH_4 concentrations. Moreover, we will focus on the work done by the two groups to evaluate the water correction of the CO_2 measurements and to establish a correction of the CH_4 measurements.

REFINEMENT OF ATMOSPHERIC Ar/N_2 TECHNIQUES: IMPLICATIONS FOR O_2/N_2 MEASUREMENT

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Atmospheric Ar/N_2 ratios serve as an integrated measure of ocean heat content changes, and a constraint over coupled atmosphere/ocean models. Here we summarize methodological advances made over five and a half years of semi-continuous Ar/N_2 measurement at La Jolla, CA. Thermal fractionation and mass dependent fractionation during gas flow affect Ar/N_2 ratios more strongly than O_2/N_2, making Ar/N_2 a useful diagnostic for improving O_2/N_2 precision. Measurements of air pumped from the Scripps pier directly to the inlet of a mass spectrometer show reduced variability over flask-collected samples, clear seasonal cycles, and unusual high Ar/N_2 events lasting for several days. Air is pumped from the pier through polyethylene-lined aluminum tubing (Dekabon / Synflex 1300). Tests in which the pressure of gas flowing through Dekabon tubing was suddenly increased show that the tubing lining preferentially absorbs Ar, but eventually returns to a steady state with no discernable deviation. Protecting the collection inlet from thermal fractionation by surrounding it with a high flow aspirator removed diurnal changes from the continuous Ar/N_2 record as well as improving summertime flask measurements. Standard gases showed signs of use-related drift in Ar/N_2, possibly due to temperature gradients even within our thermally-insulated, horizontally-orientated standard enclosure. Dip tubes within the gas cylinders, allowing gas to be removed from the exact center of the cylinder, removed the drift effect. Linearly averaging calibration results over the life of a working standard, additionally reduced week-to-week variability. Our record consists of two separate lines to the pier, switched each hour, with their own water traps, pumps, and flow controllers. This duplication has allowed identification of subtle offsets from small leaks arising in the system, which typically cause both CO_2 and Ar/N_2 offsets to be slightly elevated in one line compared with the other. We have additionally created a completely separate system that uses a low-flow inlet design, separate calibration gases, and its own mass spectrometer. Overlapping records from this second system show that days-long, high Ar/N_2 events detected by the original system are likely to be real atmospheric changes and not analytical biases. We are additionally using the alternate system to investigate pick-off tee design in order to flow air from the pier at a faster rate than gas from our standard cylinders. We have also developed a system to reproducibly increase the CO_2 content of gases as they flow into system during calibration to quantify the production of CO from CO_2 in the source, which interferes with the N_2 measurement and is sensitive to source tuning parameters.

Tracing local natural gas oxidation by means of oxygen to carbon dioxide ratio measurements

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Since 2004, we are monitoring CO_2 and O_2 concentrations at our laboratory site in Bern. We do calculate the carbon oxidation factor (COF, COF = O_2 [ppm]/CO_2 [ppm]) readily in order to improve our understanding of the local CO_2 source mixtures. Form time to time we experienced oxidation factors around two. This high COFs were only observed for short time periods of 10 minutes or less. We argue that these CO_2 concentration enrichments and associated oxygen depletions are due to natural gas (methane) oxidation. This is not unrealistic since the energy consumption for the City of Bern is to one third based on natural gas for heating and cooking purposes. A three-hour record is display in Fig. 1. Exemplarily, COFs were calculated for two specific periods of this record displayed in Fig.2 and Fig. 3, corresponding to normal fossil fuel mix and methane oxidation, respectively. Based on those methane oxidation signals moderately precise natural gas budget for the City of Bern can be given, which in turn can be compared to the local energy statistics.

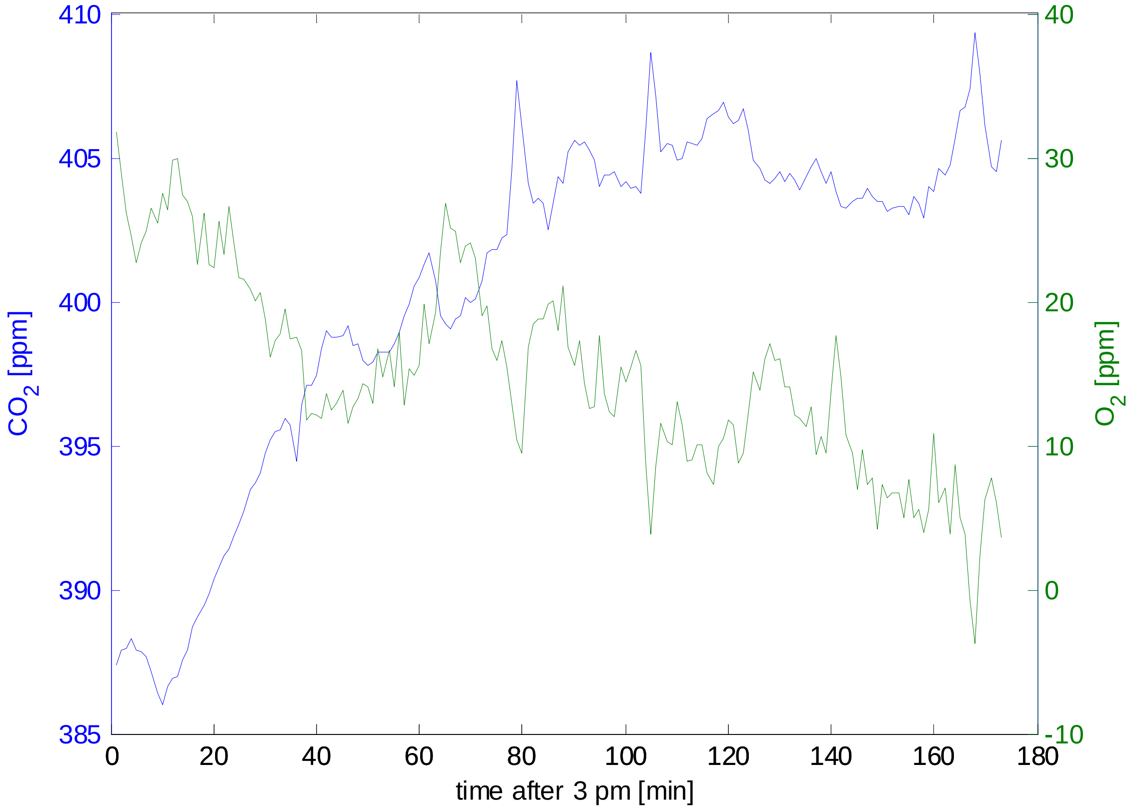

Fig. 1: CO_2 and O_2 time series for a 3 hour time period.

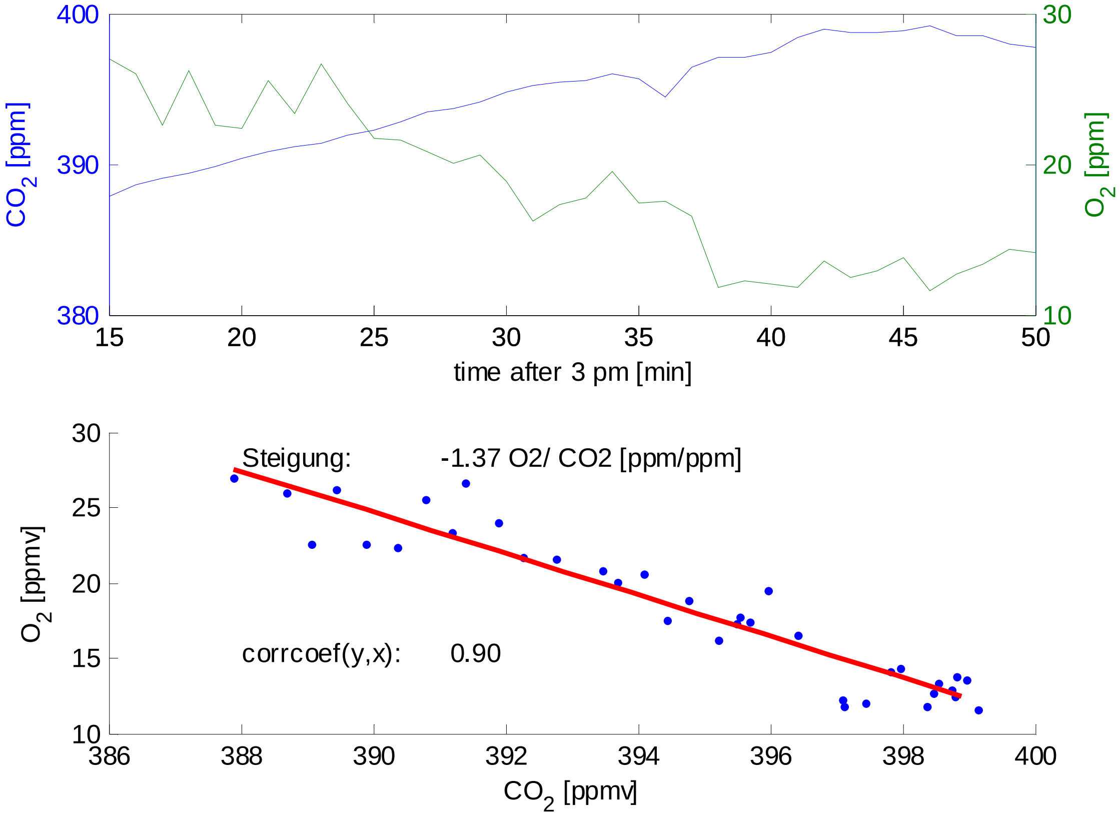

Fig. 2: Top, sectional display of the record given in Fig. 1. Bottom, correlation between O_2 and CO_2 with an apparent slope for normal fossil fuel mix oxidation.

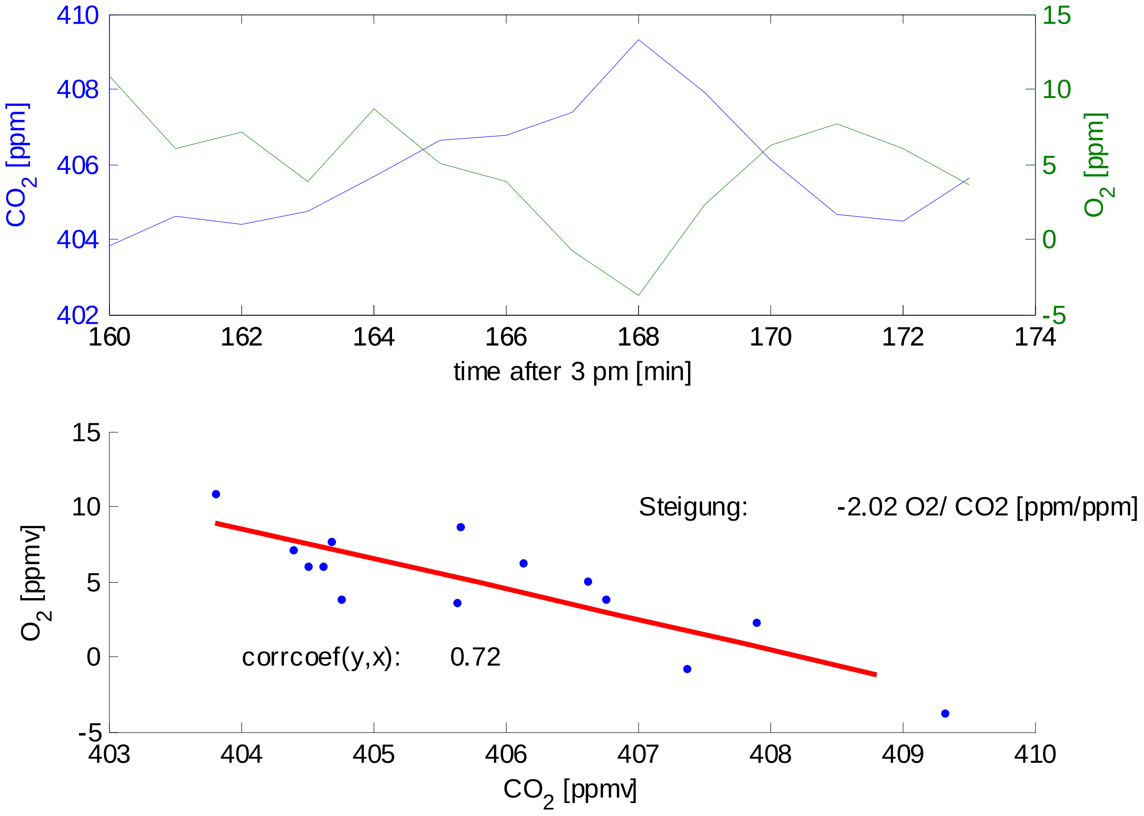

Fig. 3: Top, sectional display of the record given in Fig. 1. Bottom, correlation between O_2 and CO_2 with an apparent slope for methane oxidation.

CONTINUOUS MEASUREMENTS OF ATMOSPHERIC OXYGEN AND CARBON DIOXIDE ON A NORTH SEA GAS PLATFORM

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A new atmospheric measurement station has been established on the North Sea oil and gas production platform F3, 200 km north off the Dutch coast (54º51’ N, 4º44’ E). Atmospheric mixing ratios of O_2 and CO_2 are continuously measured using fuel cell technology and compact infrared absorption instruments, respectively. Furthermore, the station includes an automated air flask sampler for laboratory analysis of the atmospheric mixing ratios of CO_2, CH_4, CO and O_2 and isotope measurements of $\delta^{13}C$, $\delta^{18}O$ and $\Delta^{14}C$ from CO_2. This station is – to our knowledge – the first fixed sea based station with on-site continuous O_2 and CO_2 measurements and therefore yields valuable additional information about the CO_2 uptake in coastal marine regions, specifically the North Sea. We present the measurement station and the used methodologies in detail. Additionally, the first data is presented showing the seasonal cycle as expected during August 2008 through June 2009. In comparison to land-based stations, the data show low day-to-day variability, as they are practically free of nightly inversions. Therefore, the data set collected at this measurement station serves directly as background data for the coastal northwest European region. Additionally, some shortterm O_2 and CO_2 signals are presented, including very large (over 200 per meg) and fast negative atmospheric O_2 excursions.

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$^{14}CO_2$ MEASUREMENTS IN THE NOAA/ESRL COOPERATIVE AIR SAMPLING NETWORK: AN UPDATE ON MEASUREMENTS AND DATA QUALITY

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Measurements of the radiocarbon content of carbon dioxide ($\Delta^{14}CO_2$) are becoming an important component of carbon cycle studies. $\Delta^{14}CO_2$ measurements likely provide the best method for top-down constraints on fossil fuel CO_2 emissions, and can also be applied to understanding of other carbon exchange processes. $\Delta^{14}CO_2$ measurements on samples from the NOAA/ESRL Co-operative Air Sampling Network were started in 2003, and have since been expanded to include weekly measurements from several surface sites, vertical profile measurements taken from aircraft, and most recently, discrete samples from tall towers. Samples are prepared at the University of Colorado, INSTAAR, Laboratory for AMS Radiocarbon Preparation and Research, and AMS ^{14}C measurement has been performed at the University of California, Irvine.

We will discuss the methods used in sample preparation and AMS ^{14}C measurement for atmospheric samples, including a newly developed automated system for extraction of CO_2 from air for ^{14}C measurement, and high-count AMS measurement. Current repeatability is about 2‰, dominated by counting statistical uncertainty, but also including some additional uncertainty from day-to-day variability in AMS performance, and a smaller source of variability from graphite preparation. Details of current precision and repeatability and the sources of uncertainty will be presented. In addition, recent applications will be discussed.

Development and use of CF-GC-IRMS and small airbag sample techniques to investigate Arctic methane sources 2008-9: wetland, clathrates and gas leaks - the isotopic picture

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The Arctic has large methane stores vulnerable to warming, both as clathrate and in underlying pools of free gas. Wetland and thermokarst emissions are also very sensitive to temperature change. Arctic warming may sharply increase methane emissions, producing strong feedback as the warming feeds the warming. Methane sources can best be identified by combining isotopic analysis with trajectory tracking. Isotopically, the incremental methane inputs, above ambient background, can be characterised and linked to source type. Back—trajectory analysis can then identify and locate the source region.

Air sampling in tedlar bags is a fast, inexpensive method of collecting samples. Rapid analysis by CF-GC-IRMS allows large numbers of samples to be analysed at high precision (±0.05 ‰) (Fisher et al., 2006). Stable carbon isotopic analysis of atmospheric methane ($\delta^{13}C_{CH4}$) in air samples collected at high frequency (daily) on Spitsbergen during two 60 day periods in summer 2008 and spring 2009 has been used to obtain isotopic signatures of the major Arctic source regions. The signatures of the specific methane sources are calculated by comparison of each air mass with regional background, to determine both the incremental input to mixing ratio, and the change in $\delta^{13}C$ of CH_4, in air coming from specific sectors (selected using back trajectory analysis).

In addition to the ambient air measurements, $\delta^{13}C$ has been measured in methane from some key Arctic sources: wetland, gasfields, coal mines, and marine clathrate.

1. Keeling plot analysis of $\delta^{13}C_{CH4}$ in air samples collected throughout diurnal cycles at Lompolojänkkä wetland in Finland has been used to characterise the source signature of emitted methane. Depending on season, $\delta^{13}C_{CH4}$ is in the range -69 to -66 ‰. Similar results were obtained by from N.W. Siberia.

2. Plumes of gas bubbles were identified during a cruise along the West Spitsbergen continental slope in water depths shallower than 400 m in September 2008 (Westbrook et al., 2009). These plumes rose from the edge of the clathrate stability field. At the plume sites concentrations of methane dissolved in seawater were up to 20 times greater at the bottom of the water column than in surface water. However the plumes did not input into atmospheric methane, as atmospheric mixing ratios measured on board the ship tended to be slightly lower than measurements made at the Zeppelin station on the same days. The methane clathrates themselves were sampled: $\delta^{13}C_{CH4}$ was -51‰.

3. Siberian gasfield emissions vary, but $\delta^{13}C_{CH4}$ in emissions from the Ob River region is approximately -49‰.

Keeling-plot isotopic analysis of methane in air samples collected at various Arctic locations showed that the bulk Arctic methane increment in summer 2008 had a $\delta^{13}C_{CH4}$ signature of –65‰. This indicates the source of the Arctic methane increment in summer 2008 was dominantly from wetland sources. Emissions from methane clathrates ($\delta^{13}C_{CH4}$ around -51‰) are occurring but as yet these inputs to the air are not of atmospheric significance.

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Westbrook, G. K., et al. (2009), Escape of methane gas from the seabed along the West Spitsbergen continental margin, *Geophys. Res. Lett.*, 36, L15608, doi:10.1029/2009GL039191.

Methane and Nitrous Oxide Isotope Ratios measurements on NEEM firn air

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Methane (CH_4) and nitrous oxide (N_2O) are two important greenhouse gases. In order to predict their future concentrations, their present budgets (sources and sinks) and past variations need to be understood.

Nitrous oxide plays a significant role in the greenhouse effect and is also involved in the stratospheric chemistry, regulating the ozone layer. Despite great research effort, significant uncertainties in the quantification of sources and sinks remain. Therefore measuring its stable isotope ratios in the past will help to better understand its global budget.

Concerning methane, it is well known that its atmospheric concentration increased by about 150% since 1750, but many physical and chemical processes leading to methane emission are not well understood yet. Recent data have revealed surprising variations in the stable isotope signatures ($_{13}C(CH_4)$) over the past millennium. Therefore further research, notably $D(CH_4)$ measurements of firn air and air trapped in ice core over the last 1000 years are essential.

We will present new high precision stable isotope data (D, ^{13}C, ^{15}N and ^{18}O) for both CH_4 and N_2O obtained from analyses of air firn from the "North Greenland Eemian Ice Drilling" (NEEM). Firn air was sampled in 2008 on NEEM site and enables to obtain atmospheric concentrations and isotopes ratios data for the last decades. These data, together with existing records, allow reconstructing an isotope history for these two important trace gases.

Atmospheric molecular Hydrogen measurements in the RAMCES network

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Molecular Hydrogen (H_2) is one of the most abundant trace gases in the atmosphere with a mean ratio of 530 ppb. Its possible use in the future energy chain would increase its mixing ratio through leakage and influence the lifetime and mixing ratio of some greenhouse gases such as methane. However uncertainties on its budget are still large. A better understanding of the hydrogen cycle and of its budget is then essential to provide a better estimation of its impact on other trace gases.

RAMCES is running a global network of 20 sampling sites where H_2 is measured at 15 flask sampling sites, 2 flight sampling sites and 2 in-situ sampling sites.

In 2006, a new gas chromatograph with reduction gas detector (PP1, PeakLaboratories, LLC, California, USA) was optimized to measure H_2 and CO. It has been coupled with an Agilent gas chromatograph, which already measures CO_2, CH_4, N_2O and SF_6 in the frame of RAMCES greenhouse gases monitoring network at LSCE. Since June 2006, semi-continuous measurements (3 analyses per hour) of tropospheric molecular hydrogen have been performed at Gif-sur-Yvette, a suburban sampling site in France, 25 km south west of Paris. At the same time, H_2 analysis of flask samples from 18 stations has been started. Since October 2008, semi-continuous measurements at the tall tower of Trainou, a remote site 100 km south west from Paris, have been performed at three different heights (50m, 100m and 180m).

Here we will present measurement techniques, quality strategy and analysis of the data provided by the RAMCES network for H_2. 3 years of in-situ measurements at Gif-sur-Yvette, one year of in-situ measurements at the tall tower of Trainou and measurements from flasks are also presented. A first attempt of optimizing H_2 budget through a variational atmospheric inversion is finally shown.

Atmospheric observation-based global SF_6 emissions – comparison of top-down and bottom-up estimates

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Sulphur hexafluoride (SF_6) is one of the strongest greenhouse gases per molecule. SF_6 belongs to the gases whose emissions are targeted to be collectively reduced under the Kyoto Protocol. Because of its long atmospheric lifetime of around 3000 years, the accumulation of SF_6 in the atmosphere is a direct measure of its global emissions. Examination of our extended data set of globally distributed high-precision atmospheric SF_6 observations shows an increase in SF_6 abundance from near zero in the 1970s to a global mean of 6.7 ppt by the end of 2008. In-depth evaluation of our long-term data records shows that the global source of SF_6 decreased after 1995, most likely due to SF_6 emission reductions in industrialised countries, but increased again after 1998. Taking off emissions reported by Annex I countries to the United Nations Framework Convention of Climatic Change (UNFCCC) from our observation-inferred SF_6 source leaves a surprisingly large gap of more than 70-80% of (non-reported) SF_6 emissions in the last decade.

Validation of high altitude measurements of CO2 and CH4 using the AirCore

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Abstract:

The AirCore is a simple and innovative methodology for sampling the atmosphere using a long stainless steel tube (~150m) treated with Sulfinert®. For a vertical sample of the atmosphere the AirCore can be carried to altitude with one end open and the other closed. As the AirCore descends it relies on positive changes in pressure for passive sampling of ambient air. Measurements of known air standards stored in AirCore show repeatability and accuracy of better than 0.05 ppm for CO_2 and 0.4 ppb for CH_4 under a variety of conditions, including changes in pressure, storage times and flow-through speeds. Comparisons of AirCore data with in situ and flask data in aircraft field tests indicate average absolute differences of 0.6 ppm and 9 ppb for CO_2 and CH_4, respectively, with no apparent bias. Accounting for molecular diffusion and Taylor dispersion, the expected measurement resolution for CO_2 and CH_4 is 110m at sea level and 260m at 8000 masl after three hours of storage. After 9 hours of storage the resolution decreases to 170m and 400m respectively in a 150 m tube. These validation tests confirm that the AirCore is likely to be a robust sampling device for many species on a variety of platforms including balloon, UAVs, and aircraft.

In situ and ground-based remote sensing measurements of atmospheric CO_2 in New Zealand

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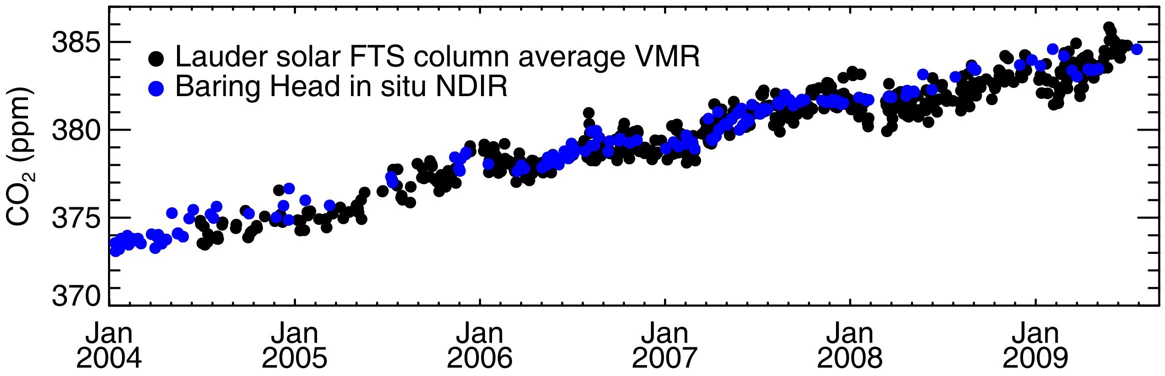
The mid and high latitudes of the southern hemisphere are dominated by the Southern Ocean, however it has been shown to be a key region of the globe for carbon cycle processes. We present data from the New Zealand regional CO_2 programme, from both *in situ* surface and column measurements at two sites.



FTS airmass-corrected column-average dry air VMR, preliminary calibration C=1.012

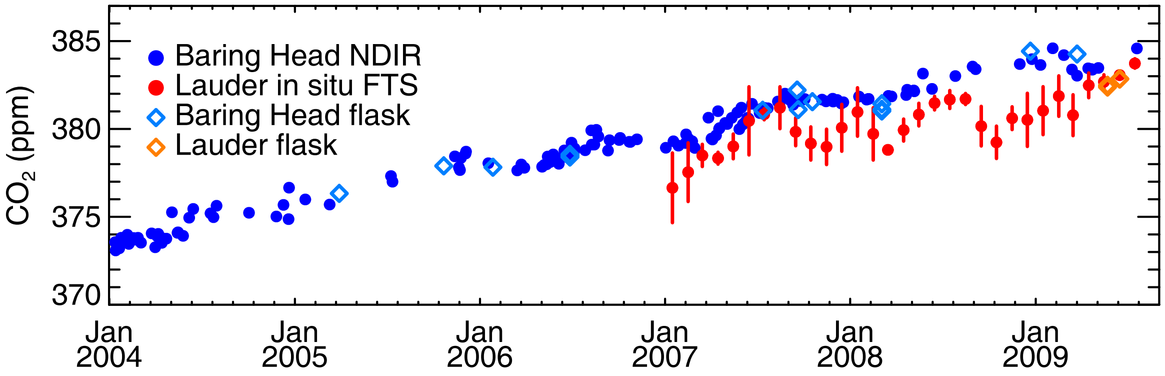


Fig.1. The Baring Head steady interval time series are plotted with the Lauder FTS column-average CO_2 volume mixing ratio (upper panel) and in situ FTS measurements from Lauder (lower panel). Flask comparisons with the in situ series for both sites are plotted in the lower panel.

Situated in the mid-latitudes of the Pacific Ocean, New Zealand provides an ideal location to study the trends and variability of atmospheric CO_2 that are representative of the wider Southern Ocean region. For this reason *in situ* measurements of atmospheric CO_2 have been made with non-dispersive infrared (NDIR) instruments at Baring Head (-41.41°, 174.87°) since 1971 providing the longest record of continuous data from the southern hemisphere. For 30% of the time, the site is exposed to air-masses that have not been in contact with land for 5 days, providing a high number of background level determinations that are representative of the high latitudes. To complement these long term *in situ* measurements, in 2004 we established a total column measurement programme using ground-based near infrared solar absorption Fourier Transform Spectroscopy (FTS) at Lauder (-45.04°, 169.68°) as part of the Total Carbon Column Observing Network. Routine *in situ* CO_2 measurements are also made at the Lauder site using traditional NDIR and closed path FTS (see ICDC8 presentation by Griffith *et al.*). All measurements in this programme are referenced to the WMO CO_2 mole fraction scale; reference gases obtained from NOAA GMD are utilised for the *in situ* measurements, while for the FTS this is achieved using calibrated *in situ* measurements acquired during instrumented aircraft over-passes of the Lauder site (see ICDC8 presentation on HIPPO by Wofsy *et al.*). Intercomparison between the sites is achieved by way of a flask measurement programme.

The *in situ* data from Baring Head site show a long term trend that is similar to those established elsewhere. The amplitude of the seasonal cycle is small (1-2 ppm) due to the oceanic dominance in the southern hemisphere. While the *in situ* and column measurements have very different averaging kernels, event selection criteria imply that Baring Head measurements are representative of larger spatial scales similar to those characterised by the FTS measurements. Baring Head and FTS time-series are compared in figure 1. As expected FTS and *in situ* data show very similar secular trends. The amplitude of the seasonal cycle observed by the two techniques is comparable, but there are differences in the phase.

This integrated and inter-calibrated approach will provide data in a sparsely measured region for interpretive tools for determining regional fluxes, including the imminent development of a Carbon-Tracker / TM5 model for the Australasian region.

GHG Inter-comparison NOAA/IPEN and Efforts in to start a GHG Network in Brazil

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In 2004 a replica of NOAA/ESRL greenhouse gases analysis system (MAGICC) started operation in the Atmospheric Chemistry Laboratory of IPEN, Brazil. The precision and stability of system in Brazil laboratory is shown in the table 1. The precision is similar to that of NOAA, but in some cases slightly worse by consequence of quality of available carrier gases, but it is inside the WMO recommendations.

Since October 2006, NOAA/GMD and IPEN started an inter-comparison program at Arembepe Station, Bahia, Brazil. This station is located 70km north of Salvador, and the wind is strong and from ocean the majority of the time. For sampling, we require the wind speed to be higher than 4m/s. The sample time is between 12-14 hours. One pair of flasks for each laboratory is sampled, and the time between pairs is around 17 min (14 - 43min). The average agreement from flasks samples collected at Arembepe is shown in Table 1. Considering that samples are in a different pair and collected in sequence, the results show very good agreement. The next step in the inter-comparison will be making the measurements in the same flask pair.

Table 1 - Comparison between MAGICC system on GMD/NOAA and IPEN/Brazil for Precision and stability and the difference showed in inter-comparison in Arembepe Station

Species	Repeatability of MAGICC/GMD NOAA	Repeatability of MAGICC/IPEN LQA	%	Reprodu-cibility*	Difference IPEN/NOAA Arembepe	Instrument Information
CO_2	0.05 ppm	0.04 ppm	0.01	0.03 ppm	0.07 ± 0.25 ppm	CO_2 Analyzer (LI-COR)
CH_4	< 1 ppb	2.6 ppb	0.14	0.99 ppb	3.10 ± 6.37 ppb	FID Chromatograph (HP)
CO	0.5 ppb	0.98 ppb	0.71	0.79 ppb	5.11 ± 5.97 ppb	CO Monitor (Peak Laboratories)
N_2O	0.2 ppb	0.33 ppb	0.10	0.13 ppb	0.39 ± 0.90 ppb	ECD Chromatograph (HP)
SF_6	0.03 ppt	0.04 ppt	0.69	0.02 ppt	0.04 ± 0.13 ppt	ECD Chromatograph (HP)

*Defined as the standard deviation found for the same high pressure cylinder measured for all gases an average of one time per month, since the system was installed.

In 2004 vertical profile measurements above Santarem (2S, 64W) and Manaus (2004-2007; 2S, 60W) began at IPEN, and in 2006 measurements were started at Arembepe station (12S, 38W) run by INMET station. In 2007 we started measurements at a forest station in Rondonia State (11S, 61W), and in this year, funded by NERC (UK), we will start more 3 profiles sites in Amazonia: Tabatinga (AM; 4S, 64W), Rio Branco (AC; 10S, 68W), Cuiaba (MT; 16S, 56W). More two background sites at Bragança (1S, 46W) and Kourou, French Guiana (5N, 52W) and an Andean site in Cuzco, Peru (13S, 72W). Until now all measures are supported by scientific projects.

Understanding Northeast Asian CO_2 emissions from continuous monitoring at Gosan station

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As international efforts to understand and regulate the anthropogenic emissions of CO_2 continue, there's much interest in quantifying the emissions from Northeast Asia, especially China and Korea, where large emissions are expected from the actively developing industries in those countries. High-precision, high-frequency measurements could be especially helpful for this purpose, with top-down estimation of anthropogenic emissions for validating various bottom-up emission estimations.

Gosan station(126°E, 33°N), situated on Jeju Island, south of the Korean peninsula, is optimal for monitoring pollution events from China and Korea, due to the dominantly north~northwesterly winds throughout winter as well as most of the spring and fall season. Ambient CO_2 measurements at Gosan first began in 1990 with weekly flask measurements that continue to contribute to GLOBALVIEW [Park et al., poster session P37], while continuous measurements were conducted with an automated NDIR measurement system during '04~'05 [Jin et al., TAO in press], superseded in Nov. '07 with the LOFLO continuous measurement system developed at CSIRO. Other notable studies at Gosan include the AGAGE network study for global monitoring emissions of anthropogenic halocarbons, and the ABC program for understanding the emissions and effects of aerosols.

Using 3D particle dispersion models to better analyze the wind patterns arriving at Gosan, we have found that the air mass trajectories can be distinctively separated between dominantly Chinese, dominantly Korean, and dominantly clean northern air mass transport into Gosan. From this, we can better distinguish the nature of pollution events from different source regions, as well as define a baseline within the measurement data.

Of note, statistical algorithms developed in AGAGE seem to capture the clean northern air events very well. However, we find rare occurrence of extremely stable baseline events within the baseline data, perhaps indicative of special transport events bringing in cleaner, more stable air close to regional baseline levels. Work is in progress to publish the different baseline/pollution events observed at Gosan.

While the LOFLO system has considerably reduced the difficulties of accurate continuous measurements, we are still working to improve the operational techniques for dealing with various problems. To deal with the high humidity brought in during the summer monsoons, we have designed and installed a glass water trap to remove "bulk" water before the instrument. We are also preparing a high pressure reference gas filling system utilizing a modified Rix compressor with Scott-Mariner aluminum cylinders.

Future work will focus on top-down calculations of the anthropogenically emitted portion of CO_2 fluxes, utilizing 3D particle dispersion modeling tools, as well as clues from multi-species analysis with other measurements at Gosan, including various halocarbons that can reveal influences of distinctive anthropogenic activities, and CO.

Jin, F., Kim, J., and Kim, K.-R., Estimation of Potential Source Region in Northeast Asia through Continuous In-situ Measurement of Atmospheric CO_2 at Gosan, Jeju Island, Korea, *Terrestrial, Atmospheric and Oceanic Sciences*, in press, 10.3319/TAO.2009.03.25.01(A)

NETWORK OBSERVATION OF GREENHOUSE GASES AND RELATED TRACERS IN CHINA

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China GAW stations Waliguan, Shangdianzi, Lin'an and Longfengshan

In the past decades, there were kinds of long-term or short period observation and research program at a few sites in China conducted by different agencies. However, none of these measurements could effectively document spatial and temporal distributions of greenhouse gases. Thus, it is essential to establish a long-term observational network at multiple sites in China and to carefully calibrate on internationally agreed reference scales, and quality controlled under the GAW framework. In this talk, preliminary results of weekly paired flask air samples and in-situ measurements for greenhouse gases from China GAW stations were presented. Recent WCC CH_4 Reference Gas Inter-comparison in Asia and CO, CH_4 and N_2O audit activities at Beijing Lab and Waliguan station were introduced. Historical data re-processing and preliminary co-located ICP results were discussed. Furthermore, near future intensive monitoring implementation and transfer of the NOAA 'Carbon Tracker' model technology and possible vertical profiling of greenhouse gases in background regions of China were initiated.

CO_2 and CH_4 are key greenhouse gases regulated by the Kyoto Protocol. Since 1990, long-term observation validated comparable atmospheric CO_2 and CH_4 concentrations at Waliguan GAW global station (WLG, 36.29ºN, 100.90ºE, 3816m asl) in western China to that of other background stations in the world and were widely referenced by the WMO Greenhouse Gases Bulletin and relevant scientific reports. Since July 2006, preliminary data from grab air sampling at the four GAW regional stations in China showed slightly higher atmospheric CO_2 and CH_4 concentrations at Shangdianzi (SDZ, 40.39ºN, 117.07ºE, 293.9m asl), Lin'an (LA, 30.3ºN, 119.73ºE, 138m asl) and Longfengshan (LFS, 44.73ºN, 127.6ºE, 310m asl) comparing to observed values at Waliguan. Since December 2008, in-situ measurements of atmospheric CO_2 and CH_4 mixing ratios by CRDS technique reflected diurnal and spatial variations result from nature and human activities at the different regions of China.

In order to establish a unified Chinese atmospheric greenhouse gases and related tracers observing system and well integrated into the global network, the CMA is keen to work with international and national institutions through further and intensive cooperation especially under the GAW framework. The observing system will be very well calibrated relative to the international standard scale, which is necessary for integrated database and for making proper use of the data. The aim of these long-term measurements are of the highest quality and accuracy possible to identify trends, seasonal variability, spatial and temporal distribution, source and sink strengths of greenhouse gases to permit climate and carbon cycle researchers to improve our understanding of the carbon cycle and predict how the atmosphere and climate will evolve in the future as a result of human's activities.

Continuous CO_2/CH_4 measurement at Zotino Tall Tower Observatory (ZOTTO) in Central Siberia

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As part of the tall tower network, the Zotino Tall Tower Observatory (ZOTTO, 60°N, 90°E), located in central Siberia next to the Yenissei River, was equipped with a $CO_2/CH_4/H_2O$ analyzer in April 2009.

The measurement principle is based on the cavity ring-down spectroscopy (CRDS). The analyzer setup within a measurement container allows for switching between the continuously flushed inlet lines from six different heights between 4 and 300 m. In each sampling line buffer volumes integrate the atmospheric signal over a typical time period of 40 minutes. Combined with a switching time of three minutes this setup allows for a quasi continuous measurement of the time series, nearly simultaneous for all six measurement heights, although only one analyzer is available. As a consequence of the averaging as well as the precision of the analyzer, the newly gathered data show a low noise level, and gradients between different levels can be determined to a very high accuracy.

The setup does not involve any drying of the sample air. Instead we make use of the simultaneous water vapor measurement to correct the dilution and pressure-broadening effects. Laboratory experiments with humidified air were carried out to characterize those water vapor corrections. Moreover, the sensitivity of the CRDS instrument to the isotopic composition of the calibration gases is considered.

RECENT RESULTS FROM MEASUREMENTS OF CO_2, CH_4, CO AND N_2O AT THE GAW STATION CAPE POINT

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The long-term records of CO_2, CH_4, CO and N_2O at the southern hemispheric coastal station Cape Point (CPT, 34 °S, 18 °E) are now spanning 16 complete years for CO_2, 26 years for CH_4, and 30 years in the case of CO. From the N_2O observations, the first seven years (1989 – 1995) have been excluded from current analyses because of lower data quality during this period. Although the predominant air advection at Cape Point is from the marine sector, clean air data filtering is a prerequite for estimating long-term trends representative of southern hemispheric background conditions. Data selection is done by way of a statistical filter which rejects locally elevated trace gas concentrations. Updated results for long-trerm trends and growth rates are presented. In particular, recent developments of the CH_4, CO, and N_2O records are discussed.

CO_2 levels have steadily increased from 355.6 ppm at the start of the measurements in 1993 to approximately 383 ppm in 2008. Growth rates were calculated as derivatives of the trend curve obtained via 5-year smoothing. These fluctuated between 1.5 and 2.2 ppm yr^{-1}. A straight line fitted to the rates has yielded an increase of the fit from 1.6 ppm yr^{-1} in early 1993 to 2.1 ppm yr^{-1} at the end of 2008.

In the case of CH_4, the high average growth rates during the 1980s decreased with marked fluctuation over the years. Methane levels stabilized from 2003 onwards, and during 2006 the growth rate even dropped to about -1 ppb yr^{-1}. A linear fit of the growth rates has yielded values of 13 ppb yr^{-1} for the beginning of 1983 and zero growth for mid-2005. However, starting around October 2007, an increase was observed again. This is in line with observations made at several other southern and northern hemispheric locations. Possible causes, such as an increase in emissions in both hemispheres or a reduction in hydroxyl radical concentration are being discussed in the literature (e.g., Rigby et al., GRL, 2008).

In addition, trends of non-background CO_2 and CH_4 have been examined for the past 14 years. Wind sector-dependent growth rates of the two gases (periods 1999 - 2005 and 2006 – 2008) reveal maxima for the northerly directions, where densely populated areas are located.

Over most of its 30-year measuring period, the CO time series has not displayed any significant long-term trend, whereas some inter-annual variability is evident. However, since 2003 an overall decline has been observed in the CO mole fractions with an abnormally low annual minimum during February 2006 followed by a lower than normal annual maximum in October 2006. Thereafter CO returned to previously observed levels again, but decreased to an unprecedented low annual maximum in 2008. Observations during the first half of 2009, however, indicate a rise of CO concentrations again. The causes of the decrease are still under investigation. In spite of thorough instrumental checks, the possibility of recent analytical artefacts cannot entirely be ruled out.

For N_2O a nearly linear increase at a rate of 0.72 ppb yr^{-1} was determined for the period 1996 till 2006. During mid-2007 a new gaschromatic system was installed. Despite the new analytical system, certain issues with regard to instrumental sensitivity and overall data uncertainty still persist and are discussed.

LONG TERM OBSERVATIONS OF CLIMATE ALTERING GASES AT THE "O. VITTORI" OBSERVATOTY AT MONTE CIMONE (ITALY)

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Mountains are marginal environments highly sensitive to global change. At the same time mountains provide unique opportunities to detect and analyse global change processes and phenomena, and at high mountain stations atmospheric background conditions and global change processes can profitably be studied by means of continuous monitoring activities. The ISAC-CNR “O. Vittori” Research Station is located on the top of Mt. Cimone, the highest peak of the Northern Apennines, which lies at the border of two climatic regions, the continental Europe to the North and the Mediterranean to the South. Due to its altitude and geographical position, the site is considered to be representative of European continental background conditions.

Here a number of long term observations on well mixed non-CO_2 greenhouse gases and other reactive climate altering species are carried out in a collaborative effort involving research groups from different institutions.

Among others, continuous measurements include surface ozone, methane, nitrous oxide, halocarbons, molecular hydrogen, carbon monoxide, and black carbon.

The availability of such a wide range of measurements is also used to study chemical processes affecting climate change and the impact of long range transport on changes in atmospheric composition. An overview of the above mentioned activities will be given together with example of relevant scientific results.

15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques

September 7-10, 2009
Max-Planck-Institute for Biogeochemistry (MPI-BGC)
Jena (Germany)

Posters

Current Activities of the Greenhouse Gas Scientific Advisory Group

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E. Brunke, J. Butler, M. Heimann, P. Krummel, E. Scheel, K. Suda, and D. Worthy

The role of the GHG SAG is to organize and co-ordinate GAW activities within our research community. This presentation will summarize current activities of the GHG SAG and allow members of the GHG monitoring community to offer feedback and comments to your SAG members.

SAG members have organized publication of the WMO Greenhouse Gas Bulletin since March, 2006. This document summarizes trends in CO_2, CH_4, N_2O, CFC-11 and -12, and ~10 minor radiative forcing agents. Bulletins are technically and scientifically rigorous, but they are written for a non-scientific audience. Each Bulletin highlights current climate issue on its cover; e.g., No. 4 highlighted the savings in GHG warming inadvertently brought about by the Montreal Protocol. Bulletin No. 5, which will be released before COP-15 in early-December, 2009, will highlight CO_2.

The SAG has worked on various documents including “Guidelines for the Measurement of Methane and Nitrous Oxide and Their Quality Assurance” and a glossary on ISO QA/QC terms. We are currently working on measurement guidelines for CO_2; this will be published as a review paper rather than a GAW report, and we hope it will include contributions from many GAW participants.

WMO intends to sign the Mutual Recognition Agreement (MRA) of the International Committee for Weights and Measures (CIPM), and the SAG is insuring that conditions of the agreement are acceptable to our community. As a result of signing the MRA, standards prepared by GAW Central Calibration Laboratories (CCL) will be equivalent to standards from national metrology institutes, once ISO requirements for quality systems are met by the CCLs. NOAA ESRL, which is CCL for CO_2, CH_4, N_2O, and CO, has agreed to develop the necessary quality system over the next couple years. This will give GAW participants credibility to withstand legal challenges to measurements used to verify emissions.

Finally the SAG is working on a new direction for reporting results from global GHG standards intercomparisons. The new approach will allow results to be more easily ingested into other intercomparison studies.

SUMMING UP 13 YEARS OF INTERCOMPARISON ACTIVITIES OF THE WORLD CALIBRATION CENTRE AT EMPA (WCC-EMPA): METHANE, CARBON MONOXIDE AND OZONE

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WCC-Empa has been conducting regular system and performance audits at global GAW stations according to the GAW strategic plan [*WMO*, 2007] since 1996. Here, we present audit results for surface ozone, carbon monoxide and methane with respect to the corresponding GAW data quality objectives (DQOs).

Since 1996, a significant improvement was observed for surface ozone inter-comparisons. Today most of the audited stations fulfill the DQOs for surface ozone [*Klausen, et al.*, 2003], but differences between instrument types can be seen.

For methane, the deviations to WCC-Empa were at most stations better than the recommended inter-laboratory (network) comparability of ± 2 nmole/mole [*WMO*, 2009]. However, the differences between individual GC/FID systems concerning repeatability were large. A first audit of a Picarro CRDS methane analyzer at Mt. Waliguan showed the capabilities of this analytical technique. Better repeatability in combination with higher temporal resolution compared to GC/FID systems can be achieved compared to GC/FID. Consequently, WCC-Empa will use such an instrument for the calibration of traveling standards to further minimize instrumental uncertainty in the propagation of the reference scale.

In contrast to the above parameters, carbon monoxide inter-comparison between WCC-Empa and GAW stations often resulted in a large bias. The recommended inter-laboratory (network) comparability for CO [*WMO*, 2009] of ± 2 nmole/mole was met in few cases only, and deviations of more than 10 nmole/mole were common. Significant differences could be seen between analytical techniques and calibration schemes. Despites these large deviations, it could be shown that sufficiently accurate and precise CO measurements are possible using different analytical techniques [*Zellweger, et al.*, 2009].

Beginning in 2010, WCC-Empa plans to host and operate the WCC-CO_2 (audits) with a mandate to conduct system and performance audits at Global GAW stations. For this purpose the Picarro G1301 CH_4/CO_2 analyzer will be used to propagate the WMO/GAW reference scales to traveling standards.

Klausen, J., et al. (2003), Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *J. Geophys. Res.-Atmos.*, *108*, 4622, doi:4610.1029/2003JD003710.

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PREPARATION OF STANDARD GAS MIXTURES FOR MEASUREMENT OF AMBIENT LEVEL OF GREENHOUSE GASES

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Greenhouse gases (GHG) have been known as causing materials of the greenhouse effect. Because it is very important to reduce their emission, they has been paid attention since Kyoto protocol to the United Nations Framework Convention on Climate Change. Accurate observation data of ambient GHG are vital for the study of the relationship between GHGs and global warming, but it is not easy to quantify their mixing ratios owing to their globally and temporally tiny variation. For example, mixing ratio of carbon dioxide in the atmosphere, is reported to be growing by +1.7 ppm (parts per million)/year for recen 10 years according to GAW report.

For the purpose of accurate measurement of GHGs, it is essential to have a accurate standard gas mixtures with global scale under well controlled quality system. We have prepared the standard gas mixtures by using a gravimetric method since 2002 and those of carbon dioxide, methane, nitrous oxide, sulphur hexafluoride, and 3 chlorofluorocarbons are now available. Their specifications including good intercomparison results are presented.

Keywords: greenhouse gas monitoring, standard gas mixtures, scale harmonization, KGAW station

Review of NOAA/GMD CO measurements: methods and reference gases

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Since 1988 the NOAA CMDL/GMD carbon cycle group has measured carbon monoxide (CO) in air samples. Our reference gases are related to four sets of standards prepared between 1989 and 2000 using a gravimetric method. These are the basis of the NOAA/CMDL scale, reported in nmol mol^{-1} or ppb by mole fraction. Samples from the Cooperative Air Sampling Network have provided near-weekly, globally-distributed measurements of CO in the remote troposphere. Over the course of the past two decades these measurements have been made using two different techniques and numerous reference gases. One method, gas chromatography with mercuric oxide reduction detection (GC), has a non-linear response and requires a multi-point calibration covering atmospheric levels. The other, resonance fluorescence of CO in the VUV (VURF), is linear over a broad range. Here we examine the consistency of the NOAA reference gases. Calibrations made using GC and VURF show significant differences at the low end of the atmospheric range (<100 ppb). The sensitivity of measurement results to different reference gases and calibration methods suggest the GC results are low. A correction applied in 2005 to calibrations made between 2001 and 2004 provides a 15 year scale consistent to within ~2 ppb. We also find that air samples collected in the Southern Hemisphere as part of the cooperative sampling network and measured using GC are also lower than samples measured by VURF. Sensitivity of the GC multi-point calibration to its lowest level standards and to its zero assignments may explain a good part of the difference.

Re-evaluation of NIES CO Scale using High Concentration Gravimetric CO Standard Gases

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The National Institute for Environmental Studies (NIES) employs the carbon monoxide scale (NIES 96 CO scale) established in 1996 based on four CO-in-air gravimetric standards in 10L aluminum cylinders (96Primary). CO mole fractions of these cylinders are 50.04, 150.01, 250.05 and 350.10 ppb, respectively. Secondary standards have been prepared in 48L aluminum cylinders and calibrated against 96Primary standards using GC-RGD (Agilent, HP5890/ Traceanalytical, RGD2). It is known that CO-in-air standards in high-pressure cylinders drift upward over time, with rates being greatest in the standards with lower mole fraction [*Novelli et al.*, 2003]. In 1998, additional four gravimetric CO-in-air standards (98Primary) were prepared, and we evaluated 96Primary and Secondary standards. We found 96Primary standards had substantially drifted, and Secondary standards had been stable. After 1998, 98Primary standards and Secondary standards were analyzed regularly by GC-RGD. 98Primary standards drifted against Secondary standards. The residuals from the quadratic fit of Secondary CO value and the GC-RGD responses were within ±1 ppb during between 1998 and 2009. In 2008, four gravimetric CO-in-air standards were prepared in 10L aluminum cylinders (08Primary) at ppm levels. The ppm-level gas mixtures are expected to reduce the effect by relative drift for a long period. Standards with CO mole fraction in atmospheric levels (70 – 350 ppb) were calibrated against 08Primary by a vacuum-ultraviolet resonance fluorescence (VURF) CO analyzer (AERO-LASER, AL5002-AIR), whose linearity was confirmed by comparing dynamic dilution method [*Katsumata et al.*, 2009]. CO free air was prepared by removing CO by using Sofnocat 514 from purified air. The VURF response is defined as signals of sample air minus CO free air. Residuals from the liner fit of CO mole fractions of 08Primary and VURF responses were within ±3 ppb, with intercept of a least linear fit being -27.55 ppb. This value was regarded as an amount of impurities in these cylinders. CO mole fraction of 08Primary standards ware then corrected to account for this 27.55 ppb, resulting in the corrected concentrations of 2029.7, 3028.1, 4026.5 and 5032.0 ppb as NIES 09 CO scale. Difference between NIES 09 CO scale and NIES 96 CO scale are shown in Figure 1.

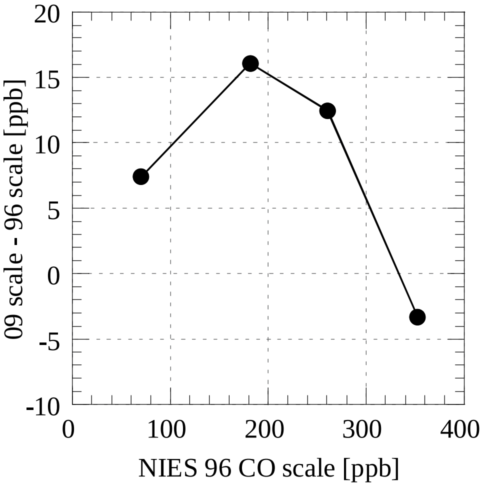

Figure 1. Difference between new CO mole fraction scale (NIES 09 scale) and current scale (NIES 96 scale)

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NOAA SF_6 Measurements from 1986-2009

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Tropospheric mixing ratios of sulfur hexafluoride (SF_6), a very long-lived greenhouse gas, have been increasing steadily over the last few decades. The NOAA Earth System Research Laboratory has maintained programs to monitor SF_6 in the background atmosphere. As part of one such program, air samples have been collected at eight sites throughout the world since 1994 and three additional sites added later. These samples are compared to compressed gas standards prepared gravimetrically at NOAA. The SF_6 calibration scale has recently been updated, resulting in small changes to the NOAA SF_6 scale. All SF_6 data have been updated to reflect these changes. Here we present a comparison of SF_6 data collected and analyzed on different instruments. Slightly different SF_6 emission trends are calculated from the different NOAA measurement networks. A long-term growth rate of 0.215 ppt yr^{-1} was determined based on archive samples collected in Colorado since 1986. The combined data show that the SF_6 growth rate started to increase above the long-term average in about 2006. They show a smaller rate of increase from 2000 to 2006.

High precision isotopic analysis of CO_2 in air using a non-cryogenic GC-IRMS approach

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In this preliminary report we describe our attempts to use a Finnigan Delta V Plus and a modified Gas-Bench for measuring the isotopic composition of CO_2 in air without the need for liquid nitrogen or a dual inlet system. The goal is to create a highly precise and accurate method with the results comparable to the classical dual inlet techniques and capable of a moderate to high throughput.

The continuous flow preparation method is build around a 10 port Valco valve with two loops, fed from two sources and sent to the same column, thus enabling identical treatment of both standard and sample air. The 1-mL loops are made from 1/16” stainless steel, one continuously flushed with standard air and the other with sample air. As the valve turns, 1 ml aliquots of standard or sample air are injected onto a Poraplot Q column (0.53 um, 30 m) . The CO_2 contained in the air is here separated from the main constituents (nitrogen, oxygen, and argon) as well as N_2O, and is introduced into the mass spectrometer by using the open split to perform a heart cut. With the alternating injection of standard and sample gas, the CO_2 peak from each sample gas injection is flanked by two standard peaks analogous to a Dual Inlet analysis. The normalization of the sample ratios can therefore be done in the similar manner as with the Dual Inlet minimizing the time between assigned and measured ratios and, to some extent, also account for instrument drift. High precision is obtained from repeating the injections, a total of 15 injections providing 7 sample peaks seem to be optimal.

Although we have been using the least challenging of all samples - a pressurized air tank with a continuous small bleed, the preliminary results from this setup are very promising; For $\delta^{13}C$, the run to run precision is ~ 0.01 ‰ while the results for $\delta^{18}O$ have a precision ~ 0.05 ‰. The precision of the repeatability of the daily averages is better than 0.01 ‰ for $\delta^{13}C$ and ~ 0.02 ‰ for $\delta^{18}O$.

The consistency of this setup has allowed us to explore several basic properties which can interfere with the accuracy and robustness of the system. Inter alia we tried to assess the “Chemical State” of the ion source on the measurement precision. The surfaces of the ion source and, in particular the presence of the hot tungsten wire (~2300°C) interact with the sample gas entering and can leave residues from chemical reactions that interfere with the next sample peak. By introducing a small background of CO_2, O_2 or a combination of the two we have been able to compare the results over a few days of repeated analysis. While conclusions cannot be drawn rigorously we see effects that need to be taken care of in a systematic fashion for making this technique as robust as required for the targeted precision level.

REEVALUATION OF ISOTOPIC SCALE FOR CO_2 IN NIES AND ITS RELATION WITH INTER-COMPARISON WORKS

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To establish isotope scale for CO_2, we need to study many analytical steps, such as working standard, calculation scheme, N_2O correction and extraction process. Overall comparability with other laboratories is related to summation of the shifts, caused at each analytical step. Through some inter-comparison works for CO_2 isotope analysis for several years, we found key points which we can include in revised isotope scale (NIES2009iso).

NBS19 and NARCIS scale in NIES; Because NARCIS-II has a similar isotope ratio to NBS-19-CO_2, we can check an anchor point for isotope analysis, comparing with other laboratories. However, due to cross contamination effect in mass spectrometer, determination of isotope values for working standards (such as NARCIS-I) may include small uncertainty. In NIES, air sample is analyzed against working standards, which have similar isotope values to air CO_2 such as NARCIS-I. Therefore, NIES isotope scale for air analysis is almost based on the same scale as NARCIS-I rather than NARCIS-II.

Sample extraction effect and sample preserving property; We found that the extraction by NIES glass vacuum line have little effect on isotope values. On the other hand oxygen isotope ratio in the sample was found to be modified by contact with water in a glass bottle during preservation. We tried several chemical treatments and heating of the glass bottles, but they did not affect strongly to it. Although this modification effect in $\delta^{18}O$ is about -0.3 per mil/month, it is difficult to include the effect into the scale, because it must differ according to the bottle properties.

N_2O correction; Although NIES has two kinds of N_2O correction factors, which were experimentally determined and estimated from ionization efficiency, these factors were found to be too low and too high respectively. Using mass 30 method and dilution experiment with N_2O containing zero air, we determined revised N_2O correction factors. These change of factors had a large effect (above 0.02 per mil) to the final values of isotope ratios.

Inter-comparison; Some results such as Sausage, JRAS and Melon will be re-assessed from the viewpoint of the scale re-evaluation of NIES.

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Measurement of $\delta^{13}C$ of Atmospheric CO_2 on a Routine Basis

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The $^{13}C/^{12}C$ signature of CO_2 in canopy air provides valuable information about physiological processes underlying biosphere-atmosphere net CO_2 exchange. Since CO_2 from tropospheric (“background air”) and respired CO_2 from terrestrial ecosystems have very different $\delta^{13}C$ values, these CO_2 sources can be distinguished, and the coupling of terrestrial and atmospheric carbon fluxes can be addressed. For this differentiation, a ‘Keeling Plot’ approach can be applied, in which the carbon isotopic ratio of CO_2 in canopy air is regressed to its inverse CO_2 mixing ratio in order to determine the carbon isotopic signature of ecosystem-respired CO_2 with the possibility to partition net CO_2 exchange into assimilation and respiration. This implies the precise determination of $\delta^{13}C$ in CO_2 in large numbers of air samples in order to assess temporal and spatial variability within an ecosystem.

To attain an optimal precision we further developed a sampling device suitable for field sampling and laboratory analysis as described by Theis et al. (2004). Our modifications improved the overall performance, in particular the measurement reliability and shortened the analysis time. The approach described by Theis et al. coupling automated air samplers (ASA) to the IRMS yields a good measurement precision for $\delta^{13}C$ values of repeats (σ = 0.06 to 0.08 ‰, n = 11) but offers only limited possibilities for referencing using the “Identical Treatment” principle (i.e., diverting laboratory standards through the same flow path as the samples). The introduction of two 4-port 2-position valves and a 6-position dead-end path valve (all Vici/Valco) in the measuring line and in front of the ASA allows the inclusion of up to four independently switchable reference air gas bottles (laboratory air gas cylinder with CO_2 of different origin and δ-values) using the same path as the gas sampled with the ASA. The sample preparation line was modified by replacing the sampling loop of the 8-port valve inside the Gasbench with a home-built cold trap (filled with Ni-wire). To improve precision and accuracy of our measurement system, we adapted the peak amplitude of the sample CO_2 peak to the signal of the reference standards by introducing a dynamic trapping algorithm using predetermined empirical relationships between amplitude and CO_2 mixing ratio.

The above described measurement system with all its modifications was highly reliable and improved the precision of the $\delta^{13}C$ measurements to 0.03 to 0.05 ‰ n = 11, and ascertained an accuracy of ±0.1 ‰.

ISOBARIC CORRECTION OF MASS-SPECTROMETRIC ISOTOPE RATIO MEASUREMENTS OF O_2, CO, CO_2 AND N_2O

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Gas isotope ratio mass spectrometers usually measure ion current ratios of molecules, not atoms. Often several isotopologues (i.e., isotopically substituted molecules) contribute to an ion current at a particular mass-to-charge ratio (m/z). Therefore, for data reduction purposes, corrections have to be applied to derive the desired atomic isotope ratios. The mathematical formulation of these corrections is usually made in terms of isotope ratios (R), but this does not reflect the practice of measuring the ion current ratios of the sample relative to those of a reference material. Correspondingly, the relative ion current ratio differences (expressed as δ values) are usually first converted to isotopologue ratios, then to isotope ratios and finally back to elemental δ values.

Here, we present a reformulation of this data reduction procedure entirely in terms of δ values and the 'absolute' isotope ratios of the reference material [*Kaiser and Röckmann*, 2008]. This also shows that not the 'absolute' isotope ratios of the reference material themselves, but only product and ratio combinations of them are required for the data reduction. These combinations can be and, for CO_2, have been measured by conventional isotope ratio mass spectrometers. The frequently implied use of 'absolute' isotope ratios measured by specially calibrated instruments is actually unnecessary.

We will present the reformulated data reduction equations for the species O_2, CO, CO_2 and N_2O. We also suggest experiments to measure the required 'absolute' ratio combinations for O_2, CO_2 and N_2O.

Kaiser J. and Röckmann, T. (2008) Correction of mass-spectrometric isotope ratio measurements for isobaric isotopologues of O_2, CO, CO_2, N_2O and SO_2, *Rapid Commun. Mass Spectrom.* 22, 3997-4008.

Use of CO2 dynamic mixing for mass-spectrometric isotope analyses of air CO2.

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Until now isotope measurements on air CO2 are performed by using mass-spectrometric analyses on CO2 cryogenic extracts from air samples. Calibrating reference CO2-air mixtures and/or reference air tanks vs. the primary scale carrier NBS-19-CO2 (plain CO2) is a long lasting problem and seems to be the main reason for inter-laboratory biases. Recently W.Brand and co-workers have started preparation of CO2+N2O-air mixtures, initially based on NBS-19-CO2 and later on other carbonate-CO2 linked to NBS-19-CO2. The approach aims to reach inter-laboratory scale consistency. As the number of flasks distributed and the amount of mixtures is limited, these mixtures cannot be used for regular tests and/or optimizing a CO2 extraction. For testing and optimizing a new CO2 extraction system at JRC-IRMM [1] we used a dynamic mixing set-up. A flow of "known " CO2 from a low pressure tank via a crimped capillary was diluted with CO2-free synthetic air. This plain CO2 was linked to NBS-19-CO2. Given that synthetic air is CO2-free and corrections applied are satisfactory, the values obtained on the extracts should agree with the values of "mother" CO2 used for dilution. Several tests with variable CO2 flow rates and/or variable extraction time were performed. These tests helped to understand specific effects related to the CO2 extraction system (dependence of isotope signals on CO2 amount and systematic increase of d18O(CO2)) as well as to prove our quantification of the corrections applied. CO2-air mixtures used as laboratory reference were prepared based on isotopically characterized CO2 with and without N2O doping. Finally we were able to close the circle and demonstrate that isotope signals obtained on cryogenic extracts agree with signals of the "mother" CO2 used for dilution and for reference mixtures.

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1. Assonov S., Taylor P., Brenninkmeijer C.A.M. (2009) *Rapid Communications in Mass Spectrometry*; **23**: 1347-1363.

Δ^{14}C of Atmospheric CO_2 at Point Barrow, Alaska

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We report here a continuous, high precision and high temporal resolution $\Delta^{14}CO_2$ record obtained at the Point Barrow Observatory, Alaska (71°N, 157°W) since July 2003. Sample collection was through the NOAA/ESRL flask sampling network program, which enables us to compare radiocarbon data with other trace gases and isotopes, including CO, CO_2 mixing ratios and δ^{13}C and δ^{18}O of CO_2. Before 2008, two duplicate samples were collected biweekly. Because of good reproducibility between flasks, after that one sample was collected weekly. Air samples were collected into pre-evacuated 6-liter canisters, which were then pressurized to 2 atmospheres by an oil free pump. Upon returning to the laboratory, CO_2 was extracted cryogenically on a vacuum line and converted to graphite using the sealed tube Zn reduction method, and measured for ^{14}C at the Keck AMS Facility at the University of California, Irvine. The precision of our measurement is ~2‰ at the current atmospheric Δ^{14}C level, based on duplicated samples and secondary standards. During the collection period, Δ^{14}C of CO_2 decreased by ~5‰/year, to ~40‰ in Mar-2009. We find distinct seasonal cycles for $\Delta^{14}CO_2$, with a minimum around March and a maximum around September with an amplitude of ~10‰. These seasonal cycles generally lag those of CO and CO_2 mixing ratios by ~ one month and half month respectively, and their pattern is highly variable from year to year. Increasing ^{14}C values may reflect injection of stratospheric air in April and May, and higher soil respiration with enriched $^{14}CO_2$ between May to August; rapid declines may be due to reduction in soil respiration and changes in the poleward advection of fossil fuel burned in the winter months. Our record adds to the a few available records worldwide to provide observational constraints for the roles of ^{14}C isotope disequilibirum among different reservoirs, and hopefully can enhance our understanding of the patterns of atmospheric $^{14}CO_2$ distribution and its seasonal variation.

Evaluation of a new setup for long-term monitoring of fossil fuel CO_2 and other trace gases

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In the last years many regions in Germany and Europe started to make an effort becoming independent from energy supply based on fossil fuels. Besides the use of wind and solar energy, these activities are often also accompanied with expanded bio-fuel production (e.g. biogas and ethanol from dedicated plantations) and/or increasing domestic use of wood fires. Reductions in fossil fuel CO_2 emissions may, therefore be accompanied by increases of other trace and greenhouse gas emissions such as nitrous oxide, methane or carbon monoxide. The community of Isny started such a project with the ambitious goal to reduce fossil fuel CO_2 emissions by 75% in the next 30 years. Their effort shall be documented by accompanying atmospheric long-term monitoring of the regional fossil fuel CO_2 offset, determined using $^{14}CO_2$ measurements. Analysis of weekly integrated air-samples are further used to investigate and quantify trends of other important trace and greenhouse gases such as CH_4, N_2O, SF_6, H_2 and CO.

Our robust low-maintenance and low-cost sampling setup consists of a 300 litre aluminium-coated bag sampling device which allows collecting over a few days or a week integrated whole-air samples. After transfer into standard glass flasks these are analysed for CO_2, CH_4, N_2O, SF_6, H_2 and CO mixing ratios. A conventional radiocarbon sampling system is deployed to obtain $^{14}CO_2$ analyses, but these can also be realised by AMS analysis of the whole-air samples collected in the bag. Accompanying half-hourly radon daughter measurements help to characterise atmospheric mixing intensity and can further be used to estimate trace gas fluxes with the radon-tracer method. The system presented here has been extensively tested in the Heidelberg laboratory and compared to quasi-continuous GC measurements. The measurements of the trace gas mixing ratios from the bag show some small systematic differences to the continuous GC data, hence each sampling bag has to be characterised and tested on a regular basis. While the sample analysis effort is comparable to a flask sampling program, a lot of additional and more representative information can be gained from the integrated samples.

A prototype of the sampling device has been deployed in autumn 2008 on a 30m high tower in the centre of Isny (ca. 14500 inhabitants) located in a rural forested area in southern Germany. Here we present first results from winter 2008/2009. Our aim is to accompany this endeavour and monitor changes of greenhouse and other traces gases in the course of the coming years.

Performance test of a mobile fossil fuel CO_2 monitoring station developed in ATOMKI

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Fossil fuel CO_2 emissions are a major component of the European carbon budget. Separation of the fossil fuel signal from the natural biogenic one in the atmosphere is, therefore, a crucial task for quantifying exchange flux of the continental biosphere through atmospheric observations and inverse modelling. An independent method to estimate trace gas emissions is the top-down approach, using atmospheric CO_2 concentration measurements combined with simultaneous radiocarbon (^{14}C) observations. As adding fossil fuel CO_2 to the atmosphere, therefore, leads not only to an increase in the CO_2 content of the atmosphere but also to a decrease in the $^{14}C/^{12}C$ ratio in atmospheric CO_2.

The ATOMKI has more than two decades long experience in atmospheric $^{14}CO_2$ monitoring. As a part of an ongoing research project being carried out in Hungary to investigate the amount and temporal and spatial variations of fossil fuel CO_2 in the near surface atmosphere we developed a mobile and high-precision atmospheric CO_2 monitoring station. We describe the layout (Figure 1.) and the operation of the measuring system which is designed for the continuous, unattended monitoring of CO_2 mixing ratio in the near surface atmosphere based on an Ultramat 6F (Siemens) infrared gas analyser. In the station one atmospheric $^{14}CO_2$ sampling unit is also installed which is developed and widely used since more than one decade by ATOMKI.

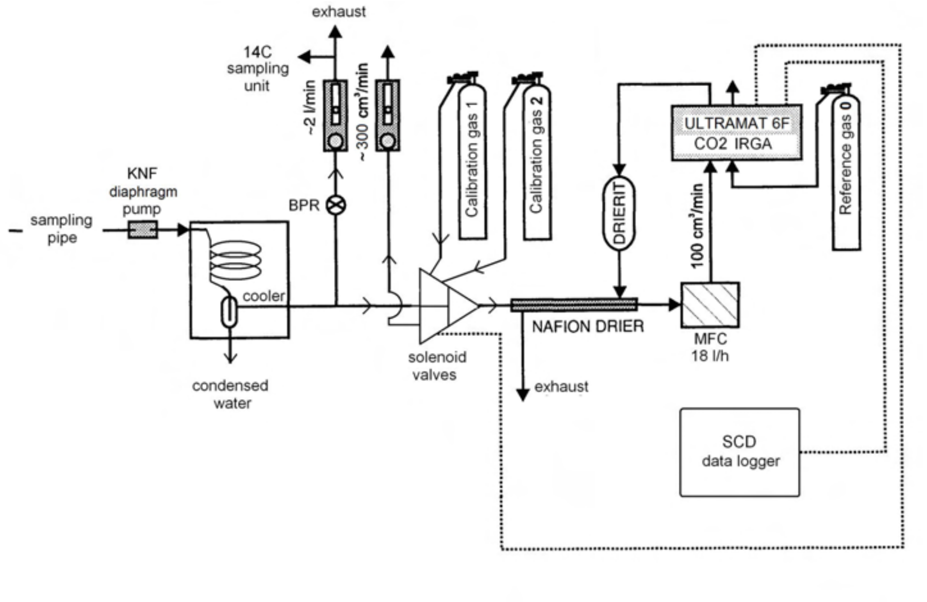

Figure 1. Layout of the setup of gas handling line used in the field CO_2 monitoring system.

Mixing ratio of CO_2 is measured at 3 m above the ground by the monitoring station. Air is pumped through a 9.5-mm-diameter plastic tube (PFA, Swagelok) to a CO_2 analyser located in a container box. Container box (Containex) is 1.5 m wide, 1.2 m deep and 2.2 m high, designed as a mobile measuring room which is field deployable, only electric power is required. A 15 micron pore size stainless steel Tee-Type (Swagelok) particle filter is located at the inlet of the sampler tube. Diaphragm pump (KNF) is used to draw air continuously through the sampling tube from monitoring level at flow rate of ~ 3 L/min.

The air at 5 psig overpressure enters a glass trap for liquid water that is cooled in a regular household refrigerator (BPR), to dry the air to a dew point of 3°-4°C. Liquid water is forced out through an orifice at the bottom of the trap. The air sample inlet tube and the standard gases (Linde Hungary) are connected to miniature solenoid valves in a manifold which are normally closed and controlled by the CO_2 analyser, which selects which gas is sampled. The air leaving the manifold through its common outlet is further dried to a dew point of about -25°C by passage through a 360-cm long Nafion drier (Permapure), so that the water vapour interference and dilution effect are <0.1 ppm equivalent CO_2.

Analysis is carried out using a non-dispersive infrared gas analyser (IRGA) Ultramat 6F which is a specialised model for field applications by Siemens. A constant sample flow rate of 300 cm^3/min is maintained by a mass flow controller (MFC, Aalborg). The reference cell of the CO_2 analyzer is continuously flushed with a compressed reference gas of 350 ppm CO_2 in synthetic air (Messer Hungarogáz). The typically used calibration cycle is 2 hours, consisting of a zero-point calibration and a span calibration. Each calibration is consisting of 2 min flushing and 20 sec signal integration. The usual change of the response function is below 0.2 ppm after 2 hours following a previous calibration.

The analyser measures the CO_2 mixing ratio in the sample gas in every 3 seconds. Output data are registered by a data logger developed for this application (SCD data logger, Special Control Devices). The overall uncertainty of our atmospheric CO_2 mixing ratio measurements is < 1 ppm (< 0.3 % of measured level). This level of error is acceptable for our fossil fuel CO_2 calculations as the uncertainty of the other required parameter, (?) radiocarbon content of atmospheric CO_2 is usually 0.3-0.5%. Figure 2. shows the developed field deployable fossil fuel CO_2 monitoring station in the backyard of ATOMKI.

Figure 2. Photo of the developed field deployable fossil fuel CO_2 monitoring station.

PERFORMANCE TEST, CALIBRATION AND VALIDATION OF A NOVEL OPTICAL ANALYZER FOR CONTINUOUS AND HIGH PRECISION CO_2 ISOTOPE RATIO MEASUREMENTS

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Isotope ratios of carbon dioxide are highly valuable to investigate CO_2 sources, sinks and fate at local and global scales. This is possible because the physical and biochemical processes that are involved lead to characteristic isotopic fractionation. However, such studies often require extensive and long term measurements under field conditions, which may not be feasible with standard isotope ratio mass spectrometers (IRMS).

Here we present the successful development of an alternative analytical tool based on direct absorption spectroscopy employing quantum cascade lasers (QCL). The instrument is designed for continuous and high precision CO_2 isotope ratio measurements at ambient air concentration without any sample treatment [1, 2]. Being a compact and entirely cryogen-free instrument greatly facilitates field applications that require long-term, fast and *in situ* monitoring. The concentration of the three main stable isotopologues ($^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$ and $^{18}O^{12}C^{16}O$) is simultaneously measured and both the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios are obtained with a precision of 0.05 ‰. This instrumental performance alone, however, does not suffice for accurate data retrieval. Therefore, a unit providing calibration gases with mixing ratios and isotope ratio values of CO_2 in the range of measured concentrations is required. An automated calibration system capable of dynamic dilution and manifold switching was developed and will be presented. The calibration function for the QCL system allows for δ^{13}-value determination with an accuracy of 0.1 ‰.

Some field measurements will be presented illustrating that the derived isotopic ratios are in excellent agreement with laboratory based IRMS measurements made on field-collected flask samples, while the CO_2 concentration values are consistent with standardized IRGA instrumentation.

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VERTICAL PROFILES OF GREENHOUSE GAS CONCENTRATIONS VIA AIRBORNE MEASUREMENTS

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Picarro in collaboration with scientists at the National Oceanographic and Atmospheric Administration in Boulder, Colorado executed on a performance assessment of a new greenhouse gas analyzer capable of recording CO_2, CH_4, and H_2O mixing ratio of outside ambient air by conducting two flights of the analyzer aboard a NOAA Cessna 210 aircraft over Briggsdale, Colorado. In addition, Picarro in collaboration scientists at Lawrence Berkley Laboratory executed on nine flights aboard a Cessna 210 taking CO_2 and CH_4 profiles over northern California. All flights included CO_2, CH_4, and H_2O profiles taken during take-off, landings, and level flight. Flasks were taken at random intervals to help quantify analyzer drift over ambient pressure, temperature, and time. The aircraft reached altitudes in excess of 25,000 ft with the analyzer located in an unpressurized cabin where temperature changed by 10C.

This presentation will show results from these various flights and will discuss the completed and ongoing engineering efforts enabling analysis of additional gas species in new, airborne applications.

FAST PORTABLE OPEN-PATH GAS ANALYZER FOR METHANE FLUX MEASUREMENTS

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Open-path configuration of gas analyzers offer a number of advantages for measuring methane fluxes, including undisturbed in-situ flux measurements, spatial integration using the Eddy Covariance approach, zero frequency response errors due to tube attenuation, confident water and thermal density terms from co-located fast measurements of water and sonic temperature, and remote deployment due to lower power demands in the absence of need for a pump.

The LI-7700 is an open-path methane analyzer, a VCSEL (vertical-cavity surface-emitting laser)-based instrument. It employs an open Herriott cell and measures levels of methane with RMS noise below 6 ppb at 10 Hz sampling in controlled laboratory environment. Field maintenance is minimized by a self-cleaning mechanism to keep the lower mirror free of contamination. The power consumption of the stand-alone LI-7700 in steady-state is about 10W so it can be deployed in any methane-generating location of interest on a portable or mobile solar-powered tower, and it does not have to have grid power or permanent industrial generator.

Eddy Covariance measurements of methane flux using the LI-7700 open-path methane analyzer are presented for the period between 2006 and 2008 in four ecosystems with contrasting weather and moisture conditions, and with drastically different infrastructure:

- Fluxes over a short-hydroperiod sawgrass wetland inside Florida Everglades were measured in a warm and humid environment with temperatures often exceeding 25oC, variable winds, and frequent heavy dew at night. Portable solar powered setup was used.

- Fluxes over pacific mangroves in Mexico were measured in an environment with moderate air temperatures high winds, and sea spray. Small portable generator was used to power the permanent Eddy Covariance station.

- Fluxes over coastal wetlands in an Arctic tundra were measured in an environment with frequent sub-zero temperatures, moderate winds, and ocean mist. Large generator was used to power the broader ecosystem manipulation experiment there.

- Fluxes over bare agricultural field were measured in Nebraska in winter to verify "zero-flux" computations. The site had a history of chamber measurements of methane fluxes, and had a grid power available.

NEW COMPACT GAS ANALYZER FOR EDDY COVARIANCE MEASUREMENTS OF CARBON DIOXIDE AND WATER VAPOUR FLUXES

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Open-path gas CO2/H2O gas analyzers have excellent frequency response, long-term stability, and low sensitivity to window contamination. They are pump-free and require infrequent calibrations. However, they are susceptible to data loss during precipitation and icing-over, and may need instrument surface heat flux correction when used in cold conditions.

Closed-path CO2/H2O gas analyzers can collect data during precipitation, can be climate-controlled, and are not susceptible to surface heating issues. However, they usually experience significant frequency loss in long intake tubes, especially when computing water vapor flux. They may require frequent calibrations and need powerful pump.

Here we present an alternative design: a compact closed-path analyzer enabled for operations with very short intake tubes, intended to maximize strengths and to minimize weaknesses of both traditional open-path and closed-path designs.

This new gas analyzer has number of advantages over open-path analyzers. Similar to the closed-path analyzers, it has minimal data loss during precipitation events and icing, it does not have surface heating issues, and it has improved water specs due absence of solar filter.

The new gas analyzer also has a number of advantages over traditional closed-path analyzers. It has good frequency response (close to that of open-path analyzers) due to small and easily correctable flux attenuation loss in short intake tube. Similar to open-path analyzers, the new analyzer does not need frequent calibration, has minimal maintenance requirements, and can be used in low power configuration with short intake tube. It is also small, light-weight and weather-proof.

Field experimental data from the new CO2/H2O gas analyzer collected over three contrasting ecosystems for the period from 2006 to 2009 are presented. The design and specifications of the instrument, frequency response, concentration and fluxes are examined within the framework of Eddy Covariance measurements.

Long-term Performance of Picarro Instruments Prior to South Atlantic remote Deployment

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Understanding ocean uptake of atmospheric CO_2 by the Southern Ocean is important for modelling of future global warming scenarios. A current UK-funded project aims to help our understanding of this problem by flask sampling air from 5 South Atlantic sites with continuous monitoring at the 2 most accessible of these: Ascension Island and the Falklands. Flask sample measurements of CO_2 and CH_4 mixing ratios and the $\delta^{13}C$ measurement of both of these gases using the rapid continuous flow trace gas analysis system at Royal Holloway, University of London (RHUL) has already started.

To meet the continuous monitoring requirements of the new project, three Picarro G1301 CO_2 / CH_4 / H_2O Cavity Ring Down Spectrometers (CRDS) were installed at RHUL in October 2008 for testing, calibration and the development of an automated air inlet system suitable for analysis of calibration gases at the remote sites. Testing has included calibration with NOAA calibrated and target gases, validation of the Picarro-defined H_2O-correction of CO_2, and derivation of an H_2O-correction for CH_4. Continuing checks on the H_2O correction are made by having 2 instruments side-by-side taking air from the same inlet, but one having a combined Nafion / Mg-perchlorate drying system that utilizes the analysis system exhaust gas for the reverse flow through the Nafion and maintains water-levels at better than 0.08% for 2 weeks.

Flow rates vary between the internal pumps of the CRDS instruments, but within the range 260-300 cc/min when inlet valves are fully opened. Controlling flows below 200 cc/min significantly increases stabilisation time for cylinder gases. Setting outlet pressures for NOAA and target gases at 4 psi and allowing the instrument pumps to control flow has speeded up stabilization time. Currently the instruments are measuring CO_2, CH_4 and H_2O at 10-second intervals, and as 1-minute averages in the user-defined file. Precisions (1 SD) of NOAA tanks, based on the final 10 minutes of a 30-minute analysis period are better than ±0.035 ppm for CO_2 and ±0.25 ppb for CH_4. Over the period of November 2008 to August 2009 the CO_2 of our NOAA 5 standard shows no apparent drift within analytical error. CH_4 in the same calibration gas does drift by 0.5 ppb / month when the ambient air entering the instrument is not dried, but shows no drift within analytical error when the water in the ambient air flow is maintained at below 0.1 %.

NOAA standards supplied in 2008 and 2009 contain CO_2 depleted in ^{13}C by 28 ‰ and ^{18}O by 30 ‰ relative to ambient background, and CH_4 enriched in ^{13}C by 8 ‰. As the instruments measure only $^{12}CO_2$ and 12CH_4, the data calibrated using these gases has to be corrected for the isotopic effect. These standards underestimate ambient air CO_2 by 0.11 ppm and overestimate CH_4 by 0.16 ppb. This offset has been proven by using an older calibration gas with $\delta^{13}C_{CO2}$ of -12 ‰ as an unknown. Residuals relative to NOAA assigned values are reduced to better than ±0.15 ppm for CO_2 and better than ±0.16 ppb for CH_4 following isotopic correction.

The instruments will begin tests with an automated inlet system in September 2009 prior to South Atlantic deployment.

A high accuracy analyzer for airborne measurements of greenhouse gases (CO_2 and CH_4)

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High accuracy continuous airborne measurements of CO_2 and CH_4 have been made with an analyzer using cavity ring-down spectroscopy (CRDS) technique. Unlike any previously deployed instrument for high accuracy airborne measurements of tropospheric CO_2, the analyzer (Picarro Inc., CA, USA, model G1301-m) was flown without a drying system and without any in-flight calibration gases. Dry mole fractions of CO_2 and CH_4 were obtained after correcting water vapor dilution and pressure-broadening effects, using simultaneous measurements of H_2O made in the same spectral region. The water vapor correction functions were derived from a series of laboratory experiments and were described by quadratic equations, resulting in residual errors below 0.05 ppm for CO_2 and below 0.8 ppb for CH_4 for a range of water mixing ratios up to 6%. Further, calibrations of the CRDS analyzer using synthetic air and ambient air standards were investigated. Given the measurement of a single absorption line of $^{12}C^{16}O_2$, calibration of the CRDS analyzer with synthetic air CO_2 standards requires corrections for pressure broadening effect due to variations of the main components N_2, O_2 and Ar and for isotopic effects due to differing isotopic signatures in synthetic vs. ambient air. We show that the pressure-broadening effect for CO_2 can be corrected by using the linewidth of the fit of the spectral profile in addition to the peak height of the absorption line, while the isotopic effect for CO_2 can be corrected by accounting for the change in the abundance of $^{13}C^{16}O_2$ and $^{12}C^{16}O^{18}O$. A comparison of CO_2 measurements between the CRDS analyzer and a nondispersive infrared (NDIR) analyzer operated on board the same aircraft during the airborne campaign BARCA showed a mean difference of 0.22 ± 0.08 ppm for all flights over the Amazon rain forest. Measurements of synthetic calibration gases of the NDIR analyzer made by the CRDS analyzer at the end of the campaign were derived after correcting for the isotope and the pressure-broadening effects. These measurements provided $-0.16 \sim 0.27 \pm 0.16$ ppm differences for the calibration gases used by the NDIR analyzer. Application of these measurements reduced the mean of the difference between the CRDS and the NDIR during BARCA to -0.02 ± 0.17 ppm. The results clearly show that the water vapor correction is fully adequate for high accuracy airborne measurements of CO_2 and CH_4, and that the CRDS analyzer experienced no detectable drift during the flight period covering a full month.

ICON – A NEW IN-SITU CAPABILITY FOR O2/N2 MEASUREMENTS FROM AIRBORNE PLATFORMS

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Atmospheric oxygen is a useful tracer for partitioning the global oceanic and terrestrial sink of anthropogenic carbon. In addition, the combination O_2 and CO_2 measurements can help to identify local source-sink-patterns since different combustion processes have different oxidative ratios. In this context, airborne measurements are an important complement to the global network of surface stations because they provide access to different spatial and temporal scales. Data from aircraft campaigns can be used for testing or evaluating atmospheric transport models as well as for getting detailed information on regional budgets. However, detecting the relevant (ppm-level) variations in atmospheric oxygen relative to the large background concentration of ~ 21% makes these measurements very challenging. Only a few methods provide the necessary precision, most of them requiring heavy instruments not suitable for measuring on board small research aircrafts.

Here we present a newly developed instrument which is able to perform airborne in-situ measurements of O_2/N_2 with a precision of a few per meg (4.8 per meg ~ 1 ppm). This device is based on the ROXAN instrument developed by Britt Stephens [*Stephens et al, Tellus 2003*], but has a completely different design adapted for the requirements of airborne use. The measurement principle is UV absorption: Radiation from the 147nm line of a Xenon lamp is absorbed by the oxygen in a low-pressure gas stream. A two-cell design allows for simultaneous measurement of sample and reference gas. Directly connected cell outlets and a pressure regulation based on matching the two cell pressures instead of stabilizing the absolute pressure make it possible to avoid a complicated gas handling. With a weight of less than 15 kg and dimensions of 44 cm x 36 cm x 23 cm (i.e. fitting into a 19”/ 6 HE rack), the ICON can be also used onboard small research aircrafts. Additionally, due to low sample flows (~10 sccm/min) only small tanks are required for external reference gases; that saves additional space and weight in the aircraft. Another advantage for airborne use is the supply voltage of 28V and the low power consumption of the device.

Here we show first measurements with this new instrument, indicating its achievable precision and accuracy, temporal stability, reproducibility as well as the necessary calibration sequences.

A new system for isotope measurements of CO_2 from ice cores at the Centre for Ice and Climate developed in view of obtaining the first CO_2 ice core record from Greenland.

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The Centre for Ice and Climate has a strong interest in the Holocene and the previous Interglacial, the Eemian period. During that period, global temperatures were about 5°C warmer than present with slightly lower greenhouse gas concentrations. The two periods are thus ideal to find the natural baseline of a climate system as warm as predicted for our mid-term future. Sources and sinks of CO_2 differ between hemispheres and inter-hemispheric gradients exist in the concentration and also the isotope ratios. Records both from Antarctica and Greenland are therefore important for a profound understanding of the carbon cycle. The currently drilled ice core at NEEM (Greenland) is expected to cover the necessary time-span for the Northern Hemisphere.

The compared to Antarctica high accumulation rate in Central Greenland during warm periods (~0.2 m ice per year) allows obtaining a CO_2 record with a higher temporal resolution. Further the age offset between the enclosed gas and the surrounding ice can be constrained more accurately. However, CO_2 measurements in ice cores from Greenland have not been fully exploited yet due to the occurrence of CO_2 in-situ formation (i.e. disturbance of the records) most likely caused by the relatively high content of chemical impurities in this ice. Suggested processes leading to CO_2 production in the ice cores are acid based reaction of carbonates, or oxidation of organic material. Each of these reactions will have an imprint on the isotopic composition of the trapped CO_2 since the isotopic composition of the possible contaminants and the atmospheric CO_2 are significantly different (around 0‰, -25‰ and -7‰ for carbonates, organic matter and atmosphere, respectively). We are thus not only interested in the isotopic signal of CO_2 ($\delta^{13}C$) due to its importance for a better insight in the climatic processes but also because it is a promising tool to separate clean from altered CO_2 data.

In a first step we designed and built a new dry extraction systems allowing for isotope measurements of CO_2 on small ice samples (~ 13 cm^3). Compared to existing systems (known as 'needle crushers'), we are able to reach lower temperatures during extraction (~ -55°C) which we think is crucial especially for the analysis of ice containing high concentrations of potential 'CO_2 contaminants'. We also used a new approach to allow for a fast exchange of samples, thus increasing the number of daily measurements. The extraction system is connected on-line to the analytical section consisting of a coupled GC-IRMS. Different from other approaches using cryogenic pumping, we actively use Helium as a carrier gas to flush the sample out of the extraction chamber before subsequent continuous flow measurements of both CO_2 concentrations and $\delta^{13}C$. Here, we will present details of the extraction system, the analytical set-up together with first results of the analytical performance (i.e. precision of pCO_2 and $\delta^{13}C$ measurements) and calibration of working standards (pure CO_2 and full air). Also we will give an outlook for the basic concepts of the studies/measurements planned for the near future.

Evaluation of the Picarro G1301 analysers for continuous CO_2/CH_4 measurements and deployment at three Irish stations.

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Appeared in the late 1980’s, the cavity ring-down spectroscopy (CRDS) is now a well established technique which is more and more used for the high precision trace gas measurements. Several characteristics of CRDS make it attractive for a deployment of such instrument in the greenhouse gas monitoring network: combined measurements of several trace gases, high sensitivity and good linearity, field deployable, low maintenance, etc… During the last year the LSCE RAMCES group had the possibility to evaluate the EnviroSense CRDS analyzer (now called G1301), marketed by Picarro Inc. and designed for continuous measurement of CO_2, CH_4 and H_2O. Regarding to its future participation in the ICOS measuring network, the Irish Environment Protection Agency intends to install in 2009 three of these new instruments in Mace Head (West coast), Carnsore Point (South-East coast) and in Malin Head (North coast).

The poster will present the results of the laboratory tests performed at LSCE. Results of precision, repeatability, sensitivity to ambient temperature and to water vapour content will be discussed. In a second part, we will present the first results obtained at the Mace Head atmospheric station with the Picarro G1301, in comparison with the existing instrumentation for CO_2 and CH_4 measurements.

PERFORMANCE TEST OF A CRDS INSTRUMENT FOR CONTINUOUS CO_2/CH_4 MEASUREMENT AND ITS SUITABILITY FOR THE ICOS ATMOSPHERIC STATIONS NETWORK

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ICOS (Integrated Carbon Observation System; http://www.icos-infrastructure.eu/) is a new European research infrastructure for quantifying and understanding the greenhouse balance of the European continent and adjacent regions. During its preparatory phase, the project will be developed to a fully operational level, but with a reduced number of observational sites. For this purpose, a prototype atmospheric station is under construction.

A WS-CRDS instrument for continuous CO_2/CH_4 measurement, two of ICOS atmospheric stations core parameters, is being tested at LSCE and in the field (Lamto station, Ivory Coast) to evaluate its suitability for the atmospheric station prototype. We present a part of the performance tests, focusing on calibration routines, water vapour correction, and on preliminary results of a very low-maintenance drying system, which would help to reduce measurement uncertainties for this and other instruments on remote, low-maintenance atmospheric measurement sites.

Methodology and calibration for continuous atmospheric measurements of oxygen and biogeochemical trace gases at field stations

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We present an integrated system for measuring atmospheric concentrations of CO_2, O_2, CH_4, CO, N_2O and SF_6 which was deployed in central Siberia (60.80°N, 89.35°E) and more recently in Cape Verde (16.86°N, 24.87°W). Our work aims to demonstrate the feasibility of establishing long-term, continuous, high precision atmospheric measurements to elucidate greenhouse gas processes from very remote environments. Common features to all species' measurements include air intakes (potentially from several heights), an air drying system, flushing procedures, and data processing methods. Calibration standards are shared among all six measured species as a result of extending and optimising a proven methodology [*Keeling et al.*, 2007] for long-term O_2 calibration. Our system achieves the precision and accuracy requirements specified by the European Union's *CarboEurope* and *ICOS (Integrated Carbon Observing System)* programmes in the case of CO_2, O_2, CH_4, CO and SF_6, whilst N_2O requires some further improvements. We found that it is not possible to achieve these high precision measurements without either skilled technical assistance on-site or real-time data accessibility. We also present results on the stability of reference standards in high-pressure cylinders and discuss the methods we used to mitigate fractionation of O_2 in a sample airstream. The results discussed in this presentation are partly published in [*Kozlova and Manning*, 2009].

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Kozlova, E. A., and A. C. Manning, Methodology and calibration for continuous measurements of biogeochemical trace gas and O_2 concentrations from a 300-m tall tower in central Siberia, *Atmospheric Measurement Techniques*, *2 (1)*, 205-220, 2009.

DEVELOPMENT OF CO_2 MEASUREMENT SYSTEM IN REMOTE AREAS UNDER HARSH OBSERVATION ENVIRONMENT –A CASE OF Mt, FUJI

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Now that over 150 atmospheric observation sties around the world are registered to measure carbon dioxide and other Green House Gasses (GHGs) (WDCGG, 2008), constant global warming has been observed, and its mechanism and future effect are under discussion. The next step and demand is burying existing gap area of data (e.g. in South America, Africa, Siberia, and Oceanic areas especially around equator) to explain the world scale carbon cycle in details and improve inverse model results. In general, widely used measurement system needs big stable power supply, constant check-ups, and properly maintained surrounding conditions. Then it is highly likely that in those gap areas of GHGs observation, lack of facility and hard environmental conditions prevent establishments of measurement systems.

We have been developing a CO_2 measurement system with the purpose of expanding CO_2 observation in those gap areas. The main features of the instrument are self-sustain power securement, little electric power consumption, satellite date communication, and portability in addition to accurate date acquirement. The first instrument was designed for lowered temperature areas.

The summit of Mt, Fuji (35ºN 138ºE, alt. 3776m) was chosen as an experimental site and trial observation was conducted for two months in summer, 2008 while Mt, Fuji Weather Station was open (NPO Valid Utilization of Mt, Fuji Weather Station).

This presentation will describe the developed CO_2 measurement system and the result of the experiment that lead to a full-year observation started in July, 2009. The result also suggested that the summit of Mt, Fuji is a good observation site for representative CO_2 concentration of mid-latitude Asian atmosphere.

Greenhouse gas measurement capability at the new Carbon Related Atmospheric Measurement (CRAM) Laboratory at the University of East Anglia, United Kingdom

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We report on the establishment of high precision greenhouse and carbon-related gas measurements at the Carbon Related Atmospheric Measurement (CRAM) Laboratory, School of Environmental Sciences, University of East Anglia (UEA), United Kingdom. The CRAM Laboratory is equipped to make highly precise and accurate O_2, CO_2, CH_4, CO, N_2O, SF_6, and Ar/N_2 measurements. The Laboratory houses a custom-built vacuum ultraviolet O_2 analyser, a *Siemens Ultramat 6F* CO_2 analyser, a *Perkin Elmer Clarus 500* gas chromatograph equipped with a flame ionisation detector (FID), methaniser, and electron capture detector (ECD) for measuring CH_4, CO, N_2O and SF_6, and an *Isoprime* 10-collector isotope ratio mass spectrometer for Ar/N_2 ratios. The mass spectrometer will be installed and integrated into the exisiting measurement system in early 2010. The full measurement system operates as a single contiguous unit, with sample air passing through all analysers in series. The measurement system is designed to accommodate analyses of air from high pressure cylinders or glass flasks, as well as direct *in situ* monitoring of outside air. Up to 16 flasks can be analysed in automated fashion via a custom-built inlet system employing 32 computer-controlled DC motors to open the flask stopcocks. All analysers are routinely calibrated with a suite of 14 primary calibration gases purchased from NOAA/ESRL (the UN/WMO Central Calibration Laboratory (CCL) for CO_2, CH_4, and CO) and Scripps Institution of Oceanography (for O_2/N_2 and Ar/N_2).

To support the CRAM Laboratory and our field station operations, we have built a high pressure cylinder filling facility (CFF) for preparing calibration and working standards. The cylinders are filled with dry air (<1 ppm H_2O content) at up to 300 bar. In addition, the CFF has the capability to produce below or above ambient concentrations for all measured species within a cylinder.

The CRAM Laboratory and CFF also support our field stations, notably Weybourne Atmospheric Observatory (WAO) on the north Norfolk coast (52.95°N, 1.12°E) where, together with the Atmospheric Chemistry Group at UEA, we make continuous measurements of O_2, CO_2, CH_4, N_2O, SF_6, CO, and H_2.

THE ROCKY MOUNTAIN REGIONAL ATMOSPHERIC CONTINUOUS CO_2 NETWORK

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The Rocky Mountain Regional Atmospheric Continuous CO_2 Network (Rocky RACCOON, http://raccoon.ucar.edu) includes four high-alpine sites and two valley sites instrumented for CO_2 measurements beginning in August of 2005. Among these are Niwot Ridge (NWR) at 3523 m elevation near tree-line on Niwot Ridge, just west of Ward, Colorado; Storm Peak Laboratory (SPL) at 3200 m on Mt. Werner near Steamboat Springs, Colorado; Hidden Peak (HDP) at 3351 feet elevation on Hidden Peak near Snowbird, Utah; and Fraser Experimental Forest (FEF) at 2743 m in the Fraser Experimental Forest at the bottom of the St. Louis Creek Valley near Fraser, Colorado. We are utilizing these measurements to provide information on regional carbon exchange in the U.S. Central Rocky Mountains and Southwest, as well as to monitor the impact of disturbance on local valley-scales, with a goal of resolving key drivers of variability and trends in carbon fluxes of mountain and semi-arid ecosystems, including drought, fire, and insect outbreak.

A number of recent studies (e.g. [1]) have demonstrated that continuous observations of CO_2 concentration over the continents contain quantitative information about fluxes on regional scales, and that these fluxes can be estimated with simple boundary-layer (BL) budgeting techniques. We are making use of these techniques, comparing our mid-afternoon CO_2 observations to marine background and free-troposphere measurements, in order to infer regional-scale monthly-mean fluxes upwind of our sites. Figure 1 shows monthly-mean afternoon CO_2 concentrations derived at a subset of the RACCOON sites after filtering the data for strong local influences, and a proxy for free-troposphere concentrations constructed by interpolating NOAA GMD measurements from Mauna Loa, Hawaii and Cold Bay, Alaska. The differences between the continental and marine BL sites reveal clear signals of regional carbon exchange with maximum uptake signals in spring as expected for this region, and the agreement among the continental records lends confidence to their ability to capture spatially integrated fluxes. We are using models to estimate atmospheric mixing depths in order to convert these concentration differences to monthly flux estimates, and to estimate upwind influence regions for comparison to independent flux estimates and driver maps.

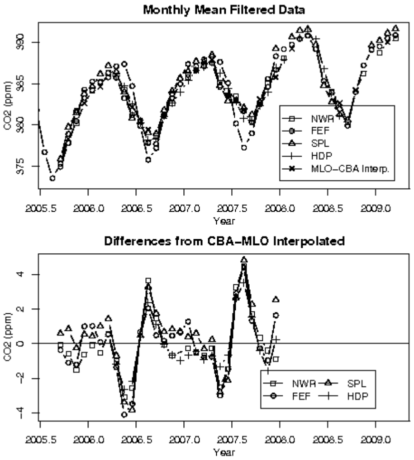

Fig. 1. Monthly mean filtered CO_2 concentrations at 4 sites and differences from interpolated marine boundary layer concentrations.

Other promising approaches to obtain regional CO_2 fluxes focus on adapting atmospheric data-assimilation techniques to make use of continuous atmospheric CO_2

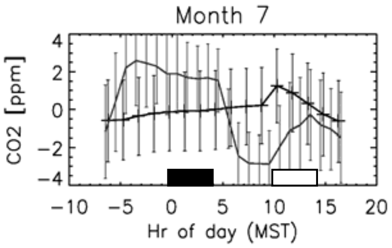

Fig. 2. Observed (dark gray line) and modeled (black crosses) diurnal cycles at NWR, and assimilation time (black box). Courtesy John Miller.

measurements made on the continents [2]. NOAA's CarbonTracker (CT, http://www.esrl.noaa.gov/gmd/ccgg/carbontracker) product uses global CO_2 observations to optimize fluxes predicted by various submodels, including a remote-sensing driven land-flux product. Significant uncertainties in the retrieved flux estimates are associated with gaps in the observing network and with limitations in the ability of atmospheric models to ingest continental CO_2 data, in particular in complex terrain. Data from our NWR and SPL sites have been included in the 2007 and 2008 CT runs. CT is presently ingesting nighttime RACCOON data at the corresponding above-sea-level model altitude. However, because of smoothed model topography, this leads to a mismatch of around a thousand meters between observation and model height above ground. Figure 2 illustrates that this can result in important features of the diurnal cycle being misrepresented and possible bias in the retrieved fluxes. We are analyzing our data using hourly CO_2 variability, wind speed and direction, and local vertical CO_2 gradients to assess their regional representativeness and we are comparing the observed diurnal cycles to CT predictions, with a focus on hour-to-hour variability and trends to assess model representativeness and to ensure that CT is ingesting our data at the optimal time and model height.

Mountain pine bark beetles are a re-occurring pest in lodgepole pines in western North America [3]. The current infestation in the Rocky Mountains has been exceptionally virulent and a warming climate has been at least partially implicated as the cause. Our RACCOON observations at FEF have occurred while the trees in the St. Louis creek drainage have experienced widespread mortality. Our CO_2 measurements at the base of this valley show large increases in CO_2 at night as the valley drainage flow pools respiration from a large area. Figure 3 shows that this nocturnal build-up has decreased over the past three years, suggesting a decrease in ecosystem respiration in response to the insect outbreak. This decrease indicates that the reduction in autotrophic respiration is greater than any short-term increase in litter fall, and will be a valuable test of models predicting the impact of the recent outbreaks on regional scale carbon fluxes.

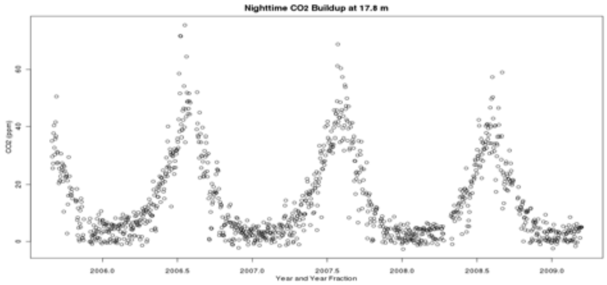

Fig. 3. Nighttime CO_2 buildup measured at the FEF site, plotted as the difference between CO_2 averaged from 23-05 and from 11-16 MST.

We will also report on efforts to ensure that our measurements are tied to the WMO CO_2 scale, through laboratory transfer calibrations, field surveillance cylinders, in situ – flask intercomparisons, and round-robin cylinder intercomparisons.

References

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TTORCH: an ESF Research Networking Program on the (Tall Tower) high precision observations of greenhouse gases in Europe

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Observations of the long lived non-CO2 greenhouse gases and related tracers are an essential part of the Earth System Observation system. The combination of atmospheric observations and inverse atmospheric transport models will enable us to detect trends in concentrations and emissions, take up the challenge to validate the emission estimates of these gases of natural and antropogenic sources for large areas of Europe (independently checking the Kyoto protocol and beyond) and to test process based emission models.

In TTORCH we will strengthen the further integration of the network of observatories of these gases and related tracers in Europe to an observational system of high consistency, quality and precision, while taking care of coordinating carefully with the developments in the ICOS project. Extension to the more Eastern part of Europe is needed. TTORCH will contribute by preparing and helping in building of the necessary infrastructure and will aid in the capacity building of (young) scientists in that part of Europe.

TTORCH will provide the framework to continue the development and improvement of the network and prepare the extension to other parts of Europe. The TTORCH network will work as a basis for defining and building new projects, all in close contact with the ICOS infrastructure initiative.

In TTORCH we will bring together the observed concentration data in a uniform database. We will organise 1-2 joint international workshops per year to bring together the participants including the observation and modelling communities from within and outside Europe. Exchange of young scientists and students between observation sites and modelling groups will be an important tool for capacity building. Another important task of TTORCH is the setup and implementation of joint papers with measurement and modelling work as well as communication with the general public on the need for and benefits of a ground based European greenhouse gas observing and emission verification system.

Every two years the TTORCH network will organise a summer school on measurements techniques, the interpretation of data series, data selection and the use of data in mesoscale and long range transport modelling.

REGIONAL GHG OBSERVATION STRATEGY OF KOREA METEOROLOGICAL ADMINISTRATION

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Korea Meteorological Administration (KMA) has contributed the WMO Global Atmosphere Watch (GAW) program since December 1996. There are two regional GAW stations on the operational basis. One is Anmyeon-do (#47132) which is an integrated observation site, the other is Pohang (#332) which is a stratospheric ozone observation station. A variety of atmospheric species are monitored at the Anmyeon-do station such as greenhouse gases (GHG), reactive gases, aerosols, atmospheric radiation, stratospheric ozone and UV-radiation and precipitation chemistry. In the Anmyeon-do station, 5 species of greenhouse gases (CO_2, CH_4, N_2O, CFC-11 and CFC-12) have been measured since 1998 and recently chlorofluorocarbon-113 (CFC-113) and sulfur hexafluoride (SF_6) have been monitored since 2007. In addition, the operational measurement of PFC-14 (CF_4) is planned to start from JAN 2010. For the past 10 years, the growth rate of CO_2 of the Anmyeon-do station was 2.3 ppm yr^{-1}. The annual mean CO_2 concentration of 2008 reached 391.4 ppm that is 5.8 ppm larger than 385.6 ppm measured at Mauna Loa of 2008. All GHG measurements were calibrated using the standard gases provided by the Korea Research Institute Standard and Sciences.

Since East Asia is one of the rapidly developing regions in the world, the representativeness as a background atmosphere monitoring site is very important. In the circumstances, KMA made a plan to expand the GHG observation network and a new station was established at Gosan in Jeju-do in the late of 2008. Gosan is well known as an international super site as a background region which is located at the southern part of Korea. The domestic in-situ GHG measurement network of KMA will be complete by 2011 as establishing the Ulleung-do station which is located at the eastern part of Korea. It is, therefore, expected that the triangle-shaped GHG network after 2011 plays an instrumental role to measure GHG which are originated from the East Asia and are transported to the Pacific.

A Web-based Application to Manage Carbon Cycle Network Operations

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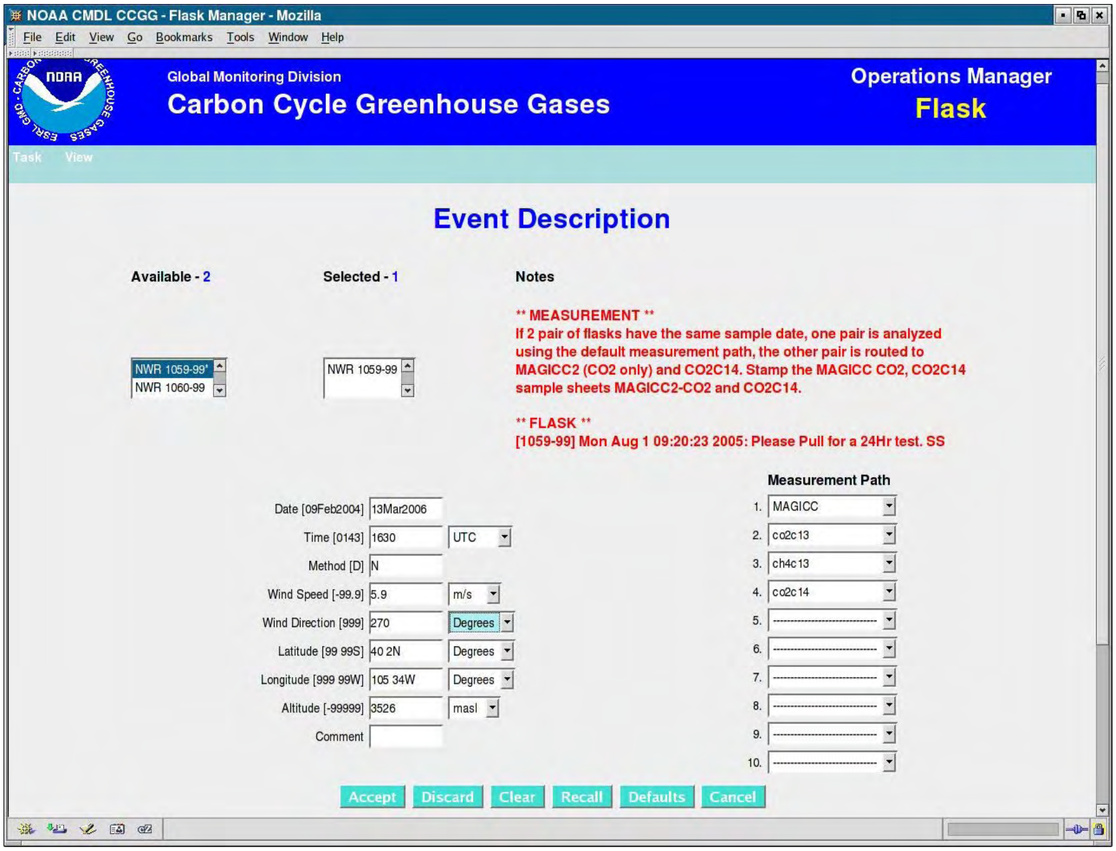
The ESRL Carbon Cycle program has expanded considerably in the past few years. Since 2004, the surface network has added 17 fixed sites and 1 ocean crossing. The aircraft network has doubled in size with the addition of 15 sampling locations in North America. In 2008, more than 16,800 discrete samples were collected and analyzed for CO_2, CH_4, CO, H_2, N_2O, SF_6, and the stable isotopes of CO_2 and CH_4. Approximately 8500 aircraft samples were also analyzed for as many as 41 compounds by the ESRL HATS group. VOCs were measured by INSTAAR, University of Colorado (CU) in nearly 4000 surface samples.

Operating a discrete measurement program that includes 72 surface sites, 20 aircraft sites, 5200 network flasks, 100 surface samplers, and 160 aircraft samplers is increasingly difficult. Logistics are further complicated as the number of laboratories measuring the air samples and the number of compounds measured increases. A high degree of organization and automation is essential to ensure that field sites have a steady supply of flasks and reliable equipment; and in Boulder, that samples are routed to the appropriate analytical systems and critical operational information is readily accessible to researchers.

To help manage the logistical and operational tasks of the carbon cycle observing network, we developed a web-based "Operations Manager". From any location, ESRL and CU researchers have web-based access to the carbon cycle measurement and meta-database. We will demonstrate several key features with emphasis on tasks which are likely relevant to other measurement programs.



Event Description

Available - 2

NWR 1059-99*
NWR 1060-99

Selected - 1

NWR 1059-99

Notes

** MEASUREMENT **
If 2 pair of flasks have the same sample date, one pair is analyzed using the default measurement path, the other pair is routed to MAGICC2 (CO2 only) and CO2C14. Stamp the MAGICC CO2, CO2C14 sample sheets MAGICC2-CO2 and CO2C14.

** FLASK **
[1059-99] Mon Aug 1 09:20:23 2005: Please Pull for a 24Hr test. SS

Date [09Feb2004]	13Mar2006	
Time [0143]	1630	UTC
Method [D]	N	
Wind Speed [-99.9]	5.9	m/s
Wind Direction [999]	270	Degrees
Latitude [99 99S]	40 2N	Degrees
Longitude [999 99W]	105 34W	Degrees
Altitude [-99999]	3526	masl
Comment		

Measurement Path

1. MAGICC
2. co2c13
3. ch4c13
4. co2c14
5. ----------------------------
6. ----------------------------
7. ----------------------------
8. ----------------------------
9. ----------------------------
10. ----------------------------

Figure 1: Entering sample collection details and the analysis path in Operations Manager

UK Report: Greenhouse Gases in the London Urban Hotspot 1996-2009

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Records of CO_2, CH_4 and CO mixing ratios for the Egham (EGH) station are continuous and calibrated to the NOAA scale for more than 10 years. The introduction of an IUP-Heidelberg Radon monitor in 2003 allows independent calculation of emissions estimates for the Greater London region.

Long-term trends show that CO_2 has been increasing by on average 2.5 ppm / yr for the last decade with the exception of a small downturn in 2004. CH_4 declined rapidly from 1996-2000, was stable for the next 6 years, but reached decadal highs in late 2007 and record lows in summer 2009. CO has decreased exponentially since 1996, but the reduction influences of the introduction of catalytic converters and lead-free petrol came to an end in 2005 since when the cycle has been stable. Over the last 3 years the dominant influence on the long-term trends is now the global cycle and not seasonal synoptic influence on local emissions.

The ratios of excess over background between different carbon gases highlight striking changes over the last decade. Selection of week long events of easterly sector air (London emissions) from Octobers in 1999, 2003 and 2007 show for example an increase in the ratio of excess CO_2 over CO from 42 to 149, and an increase in CO_2 over CH_4 from 85 to 125. If, as UK and London inventories suggest, CO_2 emissions have remained constant ±5% over the last decade, then this implies that there have been reductions in CO and CH_4 of 72 and 31%, respectively. This is in line with national inventories that suggest reductions of 72.4% in CO from transport emissions (London had 98% CO from transport in 1995), and 34% CH_4 reduction. Our Greater London proportion of the national average for these gases are much higher than the latest (2004) inventory, at 11.2 compared to 3.2% for CO and 12.6 compared to 1.2% for CH_4. Considering that 13% of the UK population live within the Greater London area we suggest that our figures are more in line with a wider London source emission. The 2004 London inventory has a zero entry for landfill emissions, although many within the region are recently closed and known to be still emitting. In addition, more recent landfills for the region are frequently located directly outside the London orbital motorway and so with the motorway itself will influence our atmospheric measurements.

As a test of the robustness of these figures the radon tracer method was also used in emissions calculations. For the week of easterlies in October 2007 the CH_4 emissions estimate was 191.3 ± 34.5 ktonnes, compared to 282 ktonnes ± 26 % calculated using the excess CO_2 against CH_4 ratio method.

Graphs of the variation of excess ratios by time of day clearly show that the two daily rush hour peaks of CO relative to CO_2 and CH_4 had mostly disappeared from the cycle by 2007, with evidence of a small but delayed morning peak and slightly more pronounced evening peak. This can be linked to local evidence of better morning traffic movement on the M25 London orbital and the positive effects of congestion charging on inner London boroughs. The dominant influence by 2007 on the diurnal ratio trends was the local biological CO_2 cycle, with low CO/CO_2, producing a sinusoidal trend of excess during overnight respiration and higher ratios during daytime photosynthesis.

Overall our data suggest that UK inventories for CH_4 and CO reduction are in line with atmospheric observation, but that the atmosphere of greenbelt London is now showing no further signs of improvement.

A Study on the atmospheric CO_2 and its carbon isotopes at Gosan, Korea

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Flask sampling started summer 1990 at Gosan, Jeju Island (33°17.4 N, 126°9.9 E, 72m above sea level) as an effort to establish a background monitoring station for CO_2 in Korea. The analysis has been carried out in cooperation with Prof. Keeling at Scripps Institution of Oceanography since the beginning of the monitoring.

Since 1994 the $^{13}C/^{12}C$ isotopic ratio of atmospheric CO_2 has been determined from the same flask samples of CO_2 that have been measured for CO_2 concentration and C-14 value recently measured.

The CO_2 concentrations vary widely from about 345ppm to 391ppm, and the amplitude of these seasonal variations is about 16 ppmv and it is larger in high altitude among marine stations. Besides seasonal variability, the increasing trend of atmospheric CO_2 in the air is clearly seen with an average rate of 1.8 ppm per year.

The $\delta^{13}C$ value shows seasonal variation ranging from -8.4 to -7.2, and the $\Delta^{14}C$ values vary from 60‰ to 100‰. The $\delta^{13}C$ values are lighter than the similar latitude. And C-14 isotopes in atmospheric CO_2 observed at the Gosan station are lower than the global average, which is a result of the fossil fuel effect.

Rayleigh equation was used to explain the cause of decreasing CO_2. The isotope discrimination (ε) of C-13 of the CO_2 decreasing periods in every year, with ε showing range from -17 to -16.5‰, the linear line of ε correspond to our data. These results suggest that the seasonal cycle of the CO_2 is produced mainly by CO_2 exchange between the atmosphere and the biosphere. The trend of isotopic composition reflects the addition of carbon dioxide with lighter isotopic compositions compared to atmospheric CO_2. The results for the addition of carbon dioxide, δ_{add} decreased by -25‰, which is generally explained as a combination of fossil fuel combustion ($\delta^{13}C$ around -27‰) or biomass burning ($\delta^{13}C$ around -27‰).

The observed increase in atmospheric CO_2 equals the known amount of carbon released by fossil fuel burning minus the carbon that has been taken up by the ocean and the land biosphere. If the arrow labeled fossil fuel burning were the only process inducing changes, then atmospheric CO_2, C-13 isotope and C-14 isotope would have changed by +24 ppm, and 1.6‰ and 59‰, respectively. Also the atmospheric CO_2 had been removed by 5.3ppm from terrestrial biota and 3.3ppm from ocean over the eight-year period.

Estimates of Gosan station budget show carbon uptake by the terrestrial biota strongly affected, while the ocean as a whole were not a strong sink. That is, our data with a budget for the 1993-2001 period, the terrestrial biota and ocean removed about 22%, 14%, respectively, while the global terrestrial biota and ocean each removed approximately 30% of fossil fuel CO_2 emissions. Thus, the amplitude reflecting continental influence at the Gosan is much higher than those of marine stations with similar latitude.

IMPROVEMENTS IN THE CARBON DIOXIDE AND METHANE CONTINUOUS MEASUREMENT PROGRAMS AT IZAÑA GLOBAL GAW STATION (SPAIN) DURING 2007-2009

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Continuous in-situ measurements of atmospheric CO_2 and CH_4 have been carried out at Izaña Global GAW station (Tenerife, Spain) since 1984. In the present report, we briefly summarize some improvements done in those programs during 2007-2009. Firstly, we deal with the CO_2 program. In January 2007, we installed a new NDIR analyzer (Li-7000), which became our main CO_2 analyzer. The instrumental system is briefly described, additionally to the acquisition/control software and raw data processing numerical code, which have been developed by us. Some details are provided about the processes used to transfer the WMO scale to the atmospheric CO_2 measurements, together with the instrumental response function used, its determination and uncertainty. We perform an uncertainty propagation analysis, *obtaining a standard uncertainty of 0.035 ppm for the consistency of our atmospheric* CO_2 *measurements with the WMO-X2005* CO_2 *scale*. Secondly, the CH_4 program is considered. The new numerical codes developed by us to integrate peak area and to process calibrations are very briefly described. Finally, our intercomparison activities are mentioned.

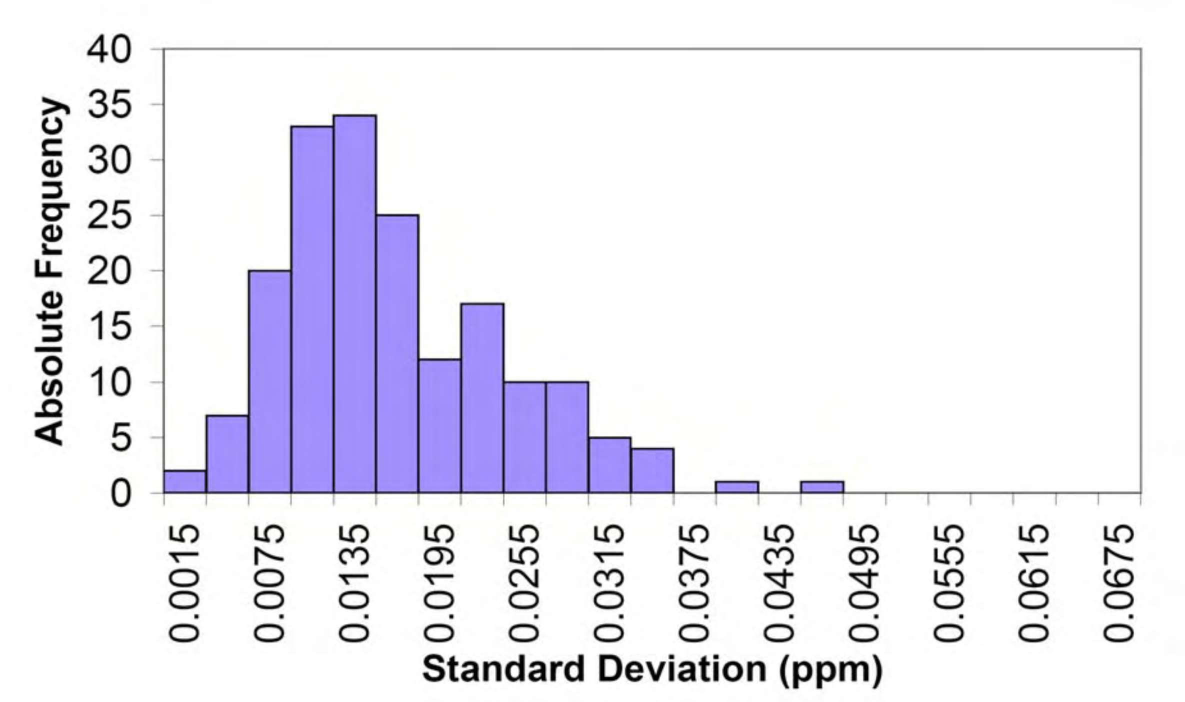

Figure 1. Histogram with the empirical standard deviations of the working standards, obtained during the calibrations of them against the laboratory standards, for the period February 2007 – April 2009 (median: 0.015 ppm; 68th percentile: 0.019 ppm).

A NEW ATMOSPHERIC MONITORING STATION IN IVITTUUT, SOUTHERN GREENLAND

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In summer 2007 we have established a new atmospheric monitoring station in Ivittuut (61.21°N, 48.17°W), on the western coast of South Greenland. The motivation for choosing this location was to study the role of the North Atlantic Ocean in the global and regional carbon cycle and to add a continuous measurement site in a still uncovered area. This work is part of the EU CarboOcean IP project, and was endorsed by the International Polar Year through the Polarcat project.

High precision CO_2 and O_2 analyzers have been developed at LSCE and installed on site together with meteorological sensors. Regular flask samples are done and independently analyzed at LSCE and MPI-BGC for quality control, and to provide complementary trace gases and isotopic measurements. Since September 2007, continuous measurements of CO_2 and O_2 have been recorded.

We will present the Ivittuut continuous CO_2 and O_2 data as well as the flask measurements, and compare both data sets to illustrate their reliability and precision. A preliminary data filtering attempt based on meteorological criteria (wind speed and direction) used to identify the origin of air masses (and corresponding CO_2 and O_2 concentration levels) will be compared to back trajectories from the Hysplit4 model. Concurrent measurements of atmospheric CO_2 and O_2 allow to calculate the Atmospheric Potential Oxygen (APO), a tracer of air-sea gas exchange of O_2, and from which, given certain assumptions, the strength of marine biological activity can be elucidated. A comparison of the data-derived APO and the one obtained with the OPA-PISCES coupled ocean circulation/biogeochemical model will be presented. Based on our APO results, we will suggest an estimate of oceanic and land biotic carbon fluxes.

Techniques for measuring greenhouse gases in ENEA Station on the Island of Lampedusa

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ENEA CLIM/OSS

The measures of greenhouse gases at Lampedusa (35.5 ° N, 12.6 ° E), Italy, started in 1992 with the determination of the molar mixing ratio of CO_2 in weekly sampling flasks shipped to ENEA laboratories in Rome. Over time, the measure line moved from Rome to Lampedusa and started to measure the molar mixing ratio of CO_2 continuously.

To date, the measure line has undergone significant changes and a major breakthrough was the creation of Ultrastation, a software created by ENEA to control and manage the entire line of measurement of CO_2. With this new software you can control each step of the measure, both for the determination of the flask, continuous data, or for any other measure of CO_2 you want to run.

The measures of greenhouse gases in Lampedusa also involve the CH_4, N_2O, CFC-12 and CFC-11. These species are determined by gas chromatographic technique and also the data processing method was developed to measure the molar mixing ratio values in the flask, continuously, etc..

All data generated are then corrected and submitted to international networks of data such WDCGG, RAMCES, Carboeurope-IP and are compared with data of other international stations.

In recent years, NOAA has launched, in collaboration with ENEA activities in Lampedusa, the sampling air in flasks (ESRL Carbon Cycle); the samples are sent to Boulder for the subsequent determination of values of CO, CO_2, CH_4 and other species.

Since 2005, ENEA has also started sampling for the measurement of greenhouse gases on Madonie in Sicily (37°52'N, 14°01'E, 1630 m a.s.l.) with the intent to put this site in Italian national network for background CO_2 measurement together with Monte Cimone and Plateau Rosa stations. The values that have come out show the consistency of the data produced in Lampedusa with those of Madonie sampling and with those of NOAA sampling.

From background to urban stations: A comparison of H_2 and other trace- and greenhouse gases within central Europe

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One of the major challenges when interpreting continental greenhouse gases (GHGs) records is to disentangle the variabilities caused by changes in source and sink strength from those arising from atmospheric transport and mixing. Especially if a mixture of various sources and sinks is present, as is the case e.g. for H_2, it is crucial to differentiate between these different processes, e.g. using information from other tracers. Moreover, this requires an accurate knowledge of background conditions. In autumn 2008 a gas chromatographic system for atmospheric hydrogen (H_2) measurements was set up at the GAW stations Schauinsland and Zugspitze. A previously optimized Peak Performer 1 (for H_2 and CO) was coupled with an existing HP6890 GC system (for CO_2, CH_4, N_2O, SF_6). Measurement precision for H_2 and CO was better than 0.25% which satisfies the WMO accuracy goals for background observations. Together with measurements at the urban station in Heidelberg an observation triangle measuring all major GHGs and the related tracers CO and H_2 is now operational in the southern part of Germany (Figure). At each station the measurements are supplemented by continuous ^{222}Radon daughter observations used to parameterise atmospheric mixing and transport at each station.

The global GAW station Zugspitze is located in the northern Alps 2660m a.s.l., i.e. above the limit of vegetation and is considered as continental background. The regional GAW site Schauinsland is situated in the Black Forest 1205m a.s.l., it is surrounded by forest and grassland but often also samples air from the polluted Rhine valley. The urban Heidelberg measurements are locally influenced by various anthropogenic activities. The combined interpretation of the continuous data sets within this triangle is challenging but provides a unique opportunity to investigate the local and regional European GHG sources and sinks as well as their correlations.

We apply an extended version of the Radon–Tracer-Method which allows separating transport- from source-driven variations of the respective trace gases and jointly interpret the data from all three sites in terms of common continental sources and sinks.

Measurements of H_2 vertical profiles at Cabauw tall tower station, in Netherlands

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Molecular hydrogen is an important atmospheric constituent, yet its sources, sinks and global distribution are at the moment relatively poorly known. The need to expand the knowledge regarding atmospheric hydrogen grew since the hydrogen started to be considered one of the main energy sources of the future.

The tall tower Cabauw (Netherlands) is a long term in-situ monitoring station for atmospheric greenhouse gases and related tracers. In 2007, an RGA-3 instrument (Trace Analytical Inc.) for H_2 and CO analysis was added to the already existing measurement system for CO_2, CH_4, CO, N_2O and SF_6. The system measures successively air sampled from four heights of the tower, between 20 and 200 m above ground, every 30 minutes.

The observed H_2 short term signals and vertical gradients are in many cases well correlated to other species, especially to CO. On the other hand, H_2 has at times a behaviour which differentiates it from all the other species measured. For example, there are periods when large vertical gradients are evident for the other species, while there is no detectable H_2 vertical gradient. Likewise, some large signals in H_2 have no correspondent in the other measured species.

Measuring air sampled at different heights helps in principle to distinguish signals from different influence areas, and it is particularly useful for H_2 which has sources and sinks both near ground and at higher altitudes. The short term signals and vertical gradients of H_2, compared to other species, can be interesting for better understanding and constraining processes affecting atmospheric H_2.

Urban and rural site regional fossil fuel CO_2 observations from Hungary using multi elevation sampling

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Fossil fuel CO_2 content in the air of a major Hungarian city (Debrecen) was determined using together measurement of CO_2 mixing ratio and radiocarbon (^{14}C) content of air. Location selected for urban atmospheric CO_2 observations is a city in East Hungary (47°32'N, 21°38'E). Its climate is characterized by dry summers and rather cold winters compared to other parts of the country. The area of the city covers 462 km^2 and it is only 85 m above sea level, which means that it is situated in a small basin. Debrecen with its almost 205 thousand inhabitants is the second largest town and industrial centre in Hungary. There is, among others, one natural gas based power plant in the city (95MW). Institute of ATOMKI where the observation station is installed is located close to the centre of the city. In this project we developed a high precision atmospheric CO_2 monitoring station in Debrecen. An integrating sampling system (developed by ATOMKI) was applied for radiocarbon measurements. One sampler was installed in Debrecen station and two independent $^{14}CO_2$ sampling line were installed ~ 300 km far from Debrecen at Hegyhátsál station, where high precision atmospheric CO_2 mixing ratio measurement is also running since 1997.

Synchronised $^{14}CO_2$ sampling and measurements with urban observations started in a rural site at Hegyhátsál to have solid regional reference level for fossil fuel CO_2 calculations in the city air. The measurements are carried out on a 117 m tall, free-standing TV and radio transmitter tower owned by Antenna Hungária Corp. The lower 56 m is a 7.75 m diameter cylinder made of reinforced concrete, while the upper 61 m is a steel cylinder of 1.82 m diameter. The tower is located in a flat region of western Hungary (46°57'N, 16°39'E), at an altitude of 248 m above sea level. This observation station is surrounded by agricultural fields (mostly crops and fodder of annually changing types) and forest patches.

During the winter of 2008/09 we measured the mixing ratio and radiocarbon content of atmospheric CO_2 at Debrecen and the reference station simultaneously. It was concluded that trends in CO_2 mixing ratio variations in time are very similar at the three different sampling points (2 m above ground in Debrecen, 10 m and 115 m above ground in Hegyhátsál). Air quality in Debrecen during September of 2008 seemed to be relatively clear from the point of view of its CO_2 content at least. When winter came closer in October, with lover outside temperature and less sunshine hours the CO_2 content of air was increased in general at all the three sampling points, but this effect was more intensive closer to the ground level.

Using Hungarian reference $^{14}CO_2$ observations from the two elevations (10 m and 115 m) in the rural site at Hegyhátsál (HHS) we could report atmospheric fossil fuel CO_2 component in the city of Debrecen in regional scale. On the other hand, if we apply the Jungfraujoch (Swiss Alps) data from Levin et al. (Levin et al. 2008 and Levin 2009) as reference we could report the Debrecen fossil fuel CO_2 in a continental scale. There were no significant differences between the two scales as Hegyhátsál observation in Hungary provided quite similar background results to the dedicated continental background observation station at Jungfraujoch in the Swiss Alps located more than 3000m above the sea level.

Similarity of the monthly average of the $^{14}CO_2$ results at 10 m and 115 m in Hegyhátsál also suggests that this station could not be strongly affected by local ground level anthropogenic fossil fuel sources. Small but significant difference between 10 m and 115 m observations only appeared in the spring (April) of 2009, but also this time the extrapolated Jungfrujoch results still remained very close to the 115 m $\Delta^{14}C$ data from HHS.

According to our radiocarbon observations it was clearly indicated that there was not significant amount of fossil fuel CO_2 in the air of Debrecen city during September in 2008. The observed urban fossil fuel CO_2 maximum in the middle of winter seems to be realistic as domestic heating is mainly based on fossil fuels in Hungary and outside temperature minimum was also in the middle of winter (first two weeks of January). The level of maximum in January was about 10-15 ppm fossil fuel CO_2 in the urban air, similar like in Heidelberg city in Germany (15-20ppm) reported by Levin et al. (Levin et al. 2008 and Levin 2009) and like in Krakow city (20 ppm) in Poland reported by Rozanski (Rozanski 2009). Furthermore we observed also a significant maximum (~20 ppm) in fossil fuel CO_2 during October of 2008 in Debrecen. Its explanation and possible source identification needs more study as meteorological conditions, especially because the main wind directions remained very similar during the whole observation period (Sept 2008-April 2009) in Debrecen.

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GLASS FLASK AIR SAMPLE ANALYSIS THROUGH GAS CHROMATOGRAPHY IN INDIA: IMPLICATIONS FOR CONSTRAINING CO_2 SURFACE FLUXES

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In recent years, the thrust of Transcom and the research community has shifted to investigate the interannual variability of fluxes (Baker et al., 2006) rather than long-term means. Some researchers (Peter Rayner, personal communication) believe these estimates to be more robust than the mean estimates. While this may be true in general, the scarcity of tropical data is unforgiving and large uncertainties continue to plague the estimates. India is one of the largest growing economies in the world, supporting a population around 1.2 billon and experiencing a steep rise in energy demand. According to the Ministry of Power, Govt. of India, 54.2% of the electricity produced in India in 2007-2008 was generated by burning coal, which is the most carbon-intensive of all fossil fuels. For instance, the anthropogenic emissions of carbon dioxide in India have risen from 469.67 Tg-CO_2 in 2005-2006 to 520.19 Tg-CO_2 in 2007-2008. Some of these emissions are compensated by vegetation uptake. Quantifying the carbon balance between the emissions of industry and transport, and the ecosystem uptake in India is an important step toward the design of effective greenhouse gases mitigation strategies in this subcontinent. The only land station in the tropics, Cape Rama in India which operated for 10 years has been discontinued since 2002, although efforts are underway to revive this station. LSCE (France), Centre for Mathematical Modeling and Computer Simulation (CMMACS), Bangalore, India and Indian Institute of Astrophysics (IIA), Bangalore, India jointly established two new stations in 2005 (Hanle and Pondicherry). LSCE is doing routine analysis of the glass flasks sampled at these two Indian stations. The ability to analyze glass flask samples to the precision required for inversion has been limited to a few labs such as MPI-BGC Jena, NOAA, LSCE, CSIRO etc. With several new stations being planned for the future in India, it is imperative that India also contribute to the analysis. Recently we have established a Gas Chromatograph (GC) lab, equipped with two detectors ECD (Electron Capture Detector) and FID (Flame Ionization Detector), at the Indian Institute of Tropical Meteorology (IITM), Pune, India which uses Calibration Standards imported from NOAA/ESRL Carbon Cycle Greenhouse Gasses Group (Duane Kitzis). In future it is proposed to conduct intercalibration exercises with International labs (e.g. MPI-BGC Jena, LSCE etc.) to reach the level of precision required for use in inversions. Air samples in two separate glass flasks are collected once every week at the selected sites. Flasks are analyzed for CO_2 and other greenhouse gases at GC laboratory at the IITM Pune, India. Results will be used to obtain better constrained global and regional carbon fluxes.

Baker, D. F., et al.,(2006), Transcom 3 inversion intercomparison: Impact of transport model errors on interannual variability of regional CO2 fluxes, 1998-2003, Global Biogeochem. Cycles, 20, GB1002, doi:10.1029/2004GB002439.

An *in situ* examination CO_2 and other greenhouse gas fluxes in the estuarine environment at high temporal resolution and their relationship to aqueous and sedimentary nutrient composition.

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Estuarine systems are highly active biological communities, and are known to produce and consume key greenhouse enhancing gases including CO_2. The importance of these systems as producers or consumers of CO_2 and other greenhouse gases, and their links to changes in the nitrogenous nutrient composition of the system is an area of current environmental investigation and concern. However, *in situ* studies with high temporal frequency are rare, especially of the Australian environment.

This study aimed to examine the balance between the production and consumption of these gases, quantify diurnal and seasonal changes in CO_2, CH_4 and N_2O fluxes *in situ* and relate changes in these fluxes to the sedimentary and aqueous nutrient composition of the estuary. Hourly gas flux measurements made in the nearshore zone of Lake Illawarra, NSW, Australia, an estuarine lagoon, during summer and winter 2006-2007. These fluxes ranged from - 4.0 to 42.4 mmol $CO_2/m^2/h$, -1.7 to 3.1 µmol $N_2O/m^2/h$ and -0.007 to 1.6 mmol $CH_4/m^2/h$. Coincident measurements of key aqueous and sedimentary nitrogenous nutrients and environmental parameters (pH, dissolved O_2, temperature, photosynthetically active radiation and salinity) were also made. Overall, the estuarine system studied was found to act as a net CO_2 source. The magnitude of this source varied seasonally, increasing in the warmer months.

Due to the carbonate buffering system, water-to-air CO_2 fluxes do not equate to sedimentary CO_2 production. In order to determine the inorganic carbon processing of the benthic (sediment dwelling biological) community these CO_2 flux measurements were combined with the temperature, salinity and pH in a simple carbonate equilibrium model to determine the true change in the inorganic carbon concentration of the water. Nearshore inorganic carbon processing was also examined using the change in the dissolved O_2 concentration as a proxy for carbon processing. A comparison of the two techniques highlighted the importance of anaerobic (non-O_2) based processing in these nearshore environments; higher than that noted in other laboratory based and *in situ* studies of deeper water environments. The rate of inorganic carbon processing was found to increase with increasing availability of organic carbon substrate and nitrogenous nutrients, but, this did not necessarily equate to higher atmospheric CO_2 fluxes.

These nearshore zones were found to play a unique role in the carbon processing within estuarine systems, quite different to that of deeper water areas. As such, they should be carefully accounted for when studying estuarine systems as a whole. Although links between nitrogenous nutrient availability and carbon processing were evident, they do not correlate with changes in the atmospheric CO_2 flux.

Four years of atmospheric research at LMU station (Tall Tower, La Muela, Spain).

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Continuous in-situ atmospheric CO_2 measurements at La Muela Tall Tower (LMU 41º36'N, 1º6'W, in the middle of the Ebre watershed) are carried out since May 2006 at three different altitudes (79, 57 and 41 m above ground level; ground level 570 m above sea level). Modifications and improvements have been applied in the analyzing system in order to exclude gaps and increase accuracy. A big effort has been made to reach a very high precision (<0,05 ppmv) although the big thermal oscillation on winter and summer of this arid site. 3 target gases are used to check drifts each 10 minutes, 3 hours and 21 hours in order to control daily and long-term drifts.
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Four-days-backwards GFS-NOAA-NCEP/FLEXPART Lagrangian Dispersion Model simulations have been used to calculate back trajectories of air and the residence time on the Footprint Layer (0-300 magl) for air masses arriving at LMU at 0 and 12 a.m. each day. Four-days-back trajectories allow identifying the possible main influence areas for the air masses arriving at LMU.

Releases and uptakes rates dominance areas at the different time scales for the different main upcoming wind trajectories arriving in La Muela have been evaluated.