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T1 AIRBORNE MEASUREMENTS OF OXYGEN CONCENTRATION FROM THE SURFACE TO THE LOWER STRATOSPHERE

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We have developed in situ and flask sampling systems for airborne measurements of variations in the O₂/N₂ ratio at the ppm relative level. We have deployed these instruments on the National Science Foundation / National Center for Atmospheric Research Gulfstream V aircraft during the START08 and HIPPO global (2009-2011) campaigns and have measured the distribution of atmospheric oxygen from 0-14 km and 87° N to 67° S throughout the seasonal cycle. The NCAR airborne oxygen analyzer (AO₂) is a vacuum ultraviolet absorption instrument with a d(O₂/N₂) precision in 5 seconds of +/- 2 per meg (1 s) and includes an infrared CO₂ sensor. The NCAR/Scripps Medusa flask sampler collects 32 cryogenically dried air samples per flight in 1.5 l glass flasks under actively controlled flow and pressure conditions. The collected flasks were analyzed at Scripps Institution of Oceanography for d(O₂/N₂), CO₂, d(Ar/N₂), and the ¹³C and ¹⁸O isotopologues of CO₂. After correcting for thermal fractionation during sampling with the use of concurrent d(Ar/N₂) measurements, Medusa flask d(O₂/N₂) measurements differ from interpolated Scripps O₂ Network station observations by only -1.6 ± 3.5 per meg (mean and SD of 9 global transect-mean offsets). The in situ AO₂ measurements showed significant differences from the flasks, that varied systematically during a flight, from flight to flight within a campaign, and from campaign to campaign. We attribute these differences to humidity effects on tubing surfaces and the introduction of a small amount of fractionated cabin air near the inlet, and we use flask data to derive empirical corrections to the in situ measurements. We will describe our sampling and measurement techniques and present a selection of observational results highlighting the individual and combined instrument performance. These include vertical profiles reflecting the distinct influences of terrestrial photosynthesis, ocean O₂ outgassing, fossil-fuel burning, and the tropopause.

T2 ASSESSING CO₂ EMISSIONS FROM PARIS MEGACITY: FIRST LESSONS FROM OUR ATMOSPHERIC CO₂ NETWORK, CO-EMITTED SPECIES AND CARBON ISOTOPES; OBSERVATION STRATEGY FOR FUTURE URBAN CO₂ NETWORKS.

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Today, more than 70% of global fossil-fuel CO₂ emissions come from less than 3% of the Earth surface. Megacities and their power plants are in the first line. Currently, most of the estimates of urban CO₂ emissions are given by bottom-up CO₂ emissions inventories, which rely on activity proxies and benchmarked emission factors. The associated uncertainties can be as high as several tenths of percents. Therefore, there is an urgent need for developing new methods to better Monitoring, Reporting and Verifying (MRV) CO₂ emissions from megacities.

Paris is the third megacity in Europe and emits about 15% of the French emissions. The CO₂-Megaparis project aimed to quantify CO₂ emissions from Paris using atmospheric top-down approaches. For the first time, a network of 5 in-situ CO₂ monitoring stations was developed by LSCE in Paris area in collaboration with the regional air quality monitoring agency (AIRPARIF) and the ICOS European GHG monitoring network. One of our stations was located on top of the Eiffel tower. From our observations, we will show the impact of Paris megacity on atmospheric CO₂ mixing ratio and report the urban atmospheric CO₂ variability at the diurnal to the seasonal scales.

Furthermore, during combustion processes, CO₂ is co-emitted with other species, and its carbon isotopic content changes with the emission sources. In the framework of the Multi-CO₂ and Primequal-Zapa projects, we carried out multi-species/carbon isotope campaigns, from which we inferred the emission ratios of CO₂ to co-emitted species, the partition between the fossil-fuel and biospheric fluxes, and the relative role of the emission sectors. These results will be presented, and compared to the regional inventory.

We will take our lesson from these projects, and a strategy of observation for future urban CO₂ network will be proposed.

INDIANAPOLIS FLUX (INFLUX) IN-SITU NETWORK: QUANTIFICATION OF URBAN ATMOSPHERIC BOUNDARY LAYER GREENHOUSE GAS DRY MOLE FRACTION ENHANCEMENTS

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We assess the detectability of city emissions via a tower-based greenhouse gas (GHG) network, and quantify the spatial and temporal patterns in atmospheric GHG dry mole fractions. Towards that end, we present afternoon-averaged results from a network of carbon dioxide (CO₂), methane (CH₄), and carbon monoxide (CO) mole fraction measurements in Indianapolis, Indiana, for 2011–2013, as part of the Indianapolis Flux (INFLUX) study. Twelve communications towers, ranging in height from 39 to 136 m above ground level, are instrumented with cavity ring-down spectrometers. Flask comparisons and round-robin calibration tank testing indicated accuracies to within 0.13–0.25 ppm CO₂, 0.8 ppb CH₄, and 3.4 ppb CO. A background site on the predominantly upwind side of the city is utilized. Averaging over several months during the dormant season, the urban enhancement ranges from 0.5 ppm CO₂ at the site 24 km downwind of the edge of the city to 3.2 ppm at the downtown site. The CH₄ urban enhancement ranges from 5 ppb at the site 10 km east of the city to 21 ppb at the site near the landfill, and for CO ranges from 6 ppb at the site 24 km downwind of the edge of the city to 29 ppb at the downtown site. While we present results at the highest sampling height available for each tower, we also used profile measurements to develop values adjusted to 40 m AGL. The unadjusted spatial differences (up to 3.2 ppm) are four times larger than the estimated difference between the measured CO₂ and the 40 m AGL estimated CO₂ (up to 0.7 ppm). These observations show that a dense network of urban GHG measurements yield a detectable urban signal, with spatial information that appears to be compatible with atmospheric inversion of urban-scale spatially- and temporally-varying emissions.

**T4 EARLY RESULTS FROM THE LOS ANGELES MEGACITY CARBON PROJECT:
EXPLORING SPATIAL AND TEMPORAL VARIABILITY IN URBAN GREENHOUSE GAS
OBSERVATIONS**

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The Megacities Carbon Project (megacities.jpl.nasa.gov) is a multi-national, multi-institution project aimed at measuring carbon emissions from large urban areas. We report initial results from the first extensive network of in situ greenhouse gas observations in the Los Angeles (LA) Megacity. The LA network includes thirteen surface in-situ sites designed to measure spatial and temporal variability in carbon emissions across the South Coast Air Basin. The surface sites include a combination of towers and rooftops equipped with laser absorption spectrometers measuring CO₂ and CH₄, with CO measurement capability at a subset of the sites.

We report CO₂, CO, and CH₄ observations during Jan-April 2015 from 4 tower sites: two urban sites and two “clean air” sites, which predominantly reflect local background concentrations. The LA sites exhibit significant CO₂, CO, and CH₄ enhancements, with the more urban sites reflecting systematically larger enhancements compared to “clean air” sites. These results are consistent with prior studies that utilized ground-based and space-based remote sensing data to demonstrate that the “urban CO₂ dome” hypothesis applies to Los Angeles. In addition, the tower measurements exhibit significant spatial and temporal heterogeneity, with evidence of diurnal, day of week, and monthly variability. Overall, the LA sites exhibit large urban signals, with hourly average levels ranging from roughly 395–650 ppm CO₂, 0.08–2.1 ppm CO, and 1.8–7 ppm CH₄. We will discuss the spatial and temporal variability of the greenhouse gas observations at midday as well as some of the unique challenges associated with measuring greenhouse gases in a complex urban environment.

T5 OBSERVATIONS OF ATMOSPHERIC CO₂, CO AND CO₂ ISOTOPES ACROSS AN EXPERIMENTAL TOWER NETWORK IN CALIFORNIA

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The US state of California has a progressive climate change mitigation policy and a relatively dense network of atmospheric greenhouse gas observations run by several universities, government laboratories and Earth Networks. Using this collaborative network, we conducted three field campaigns in 2014-15 to sample flasks at 10 sites across the state. Our primary objective was to perform high resolution observations of radiocarbon in CO₂ to distinguish patterns of biospheric and fossil fuel-derived CO₂. Flasks were analyzed for atmospheric CO₂ and CO concentrations and for stable isotopes and radiocarbon in CO₂. We will report initial results from these observations, which capture gradients between urban and rural sites and fluctuations associated with changing weather patterns. Further analysis will integrate the data into an inversion framework for fossil fuel and biospheric CO₂ fluxes over California, also incorporating satellite measurements of CO₂.

T6 HISTORY OF WMO CO₂ X2007 SCALE: LONG-TERM REPRODUCIBILITY

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Fifteen large cylinders were filled with clean air at Niwot Ridge in 1990, with CO₂ mole fractions adjusted to cover the range 250-520 ppm. They eventually became the WMO Primary cylinders on which the WMO scale is based. The cylinders received their first calibrations at Scripps from mid-1991 to early 1993, and from late 1995 to mid 1996 by infrared analyzer. The first NOAA manometric primary measurements took place during the second half of 1996, followed by repeat manometric measurements approximately every two years, and interspersed with two more infrared calibrations by Scripps during the 1990s. Before 2001 the assignment of values to the Primaries was based on both Scripps and NOAA measurements. Starting in 2001 the assignments have been based on NOAA manometric measurements alone. There is no evidence of drift of the CO₂ mole fractions in the Primaries, except perhaps in one case, but there has been a slow change in the assignments in the early years related to the change in how the assignments were determined in 2001, and some changes in manometric procedures at NOAA. We have compared most of the Primaries to each other with an infrared analyzer after each manometric episode. We then fitted a cubic polynomial to the responses as a function of assigned values. Strictly for the purpose of calibration transfer to secondary standards we “corrected” the assigned values by removing the residuals of the fit, so that each Primary represented the smooth fit. In 2007 we started naming the scale X2007 because the assignments used for transferring the ambient range (350-450 ppm) of the scale to secondaries did not change by more than 0.01 ppm since 2003. Confirmation of the stability of the scale is provided by long-term surveillance cylinders, for each of which we have at least 10 calibrations over a period of at least ten years. Based on those cylinders, the long-term reproducibility of “tertiary” standard calibrations, which are distributed to WMO GAW participants, is 0.03 ppm (1 σ). We also estimate statistics of the long-term drift rates of cylinders in use.

PRELIMINARY OUTCOME OF THE 6TH WMO/IAEA ROUND ROBIN COMPARISON EXPERIMENT

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The primary goal of the WMO/IAEA Round Robin Comparison Experiment is to assess the level to which participating laboratories maintain their link to the WMO scales using normal operating procedures. Maintaining a direct link to the WMO scales and successfully propagating the scales to working laboratory scales are fundamental to the measurement process and to achieving the desired levels of compatibility between laboratories as specified by the GGMT meetings.

A dedicated website (<http://www.esrl.noaa.gov/gmd/ccgg/wmorr>) was developed and works well which covers General Information (Documentation & Guidelines), Products (Archived Results & WMO Reports), Current Round Robin (Instructions, Participants, Calibration Scales, Cylinders, Time-Table, Status, and Reporting function such as Account Information, Cylinder Arrival, Cylinder Shipping and Measurement Results) as well as Contact & Feedback. Participants will no longer report results directly to the WMO/IAEA RR referee.

The 6th Round Robin started in January 2014 and will officially close on 7 September 2015.

Laboratories in each of the 5 circuits (Circuit 1: 13 labs, Circuit 2: 8 labs, Circuit 3: 10 labs, Circuit 4: 11 labs, Circuit 5: 6 labs) received a set of two RR cylinders. As in previous RR, air in each cylinder is near ambient range of CO₂, CH₄, CO, H₂, N₂O, SF₆, O₂/N₂, and δ¹³C and δ¹⁸O of CO₂. The preliminary results reported by the participants will be posted to the dedicated RR website on 8 September (the week before the GGMT-2015).

40 Participating labs reported for CO₂, 36 for CH₄, 28 for N₂O, 18 for SF₆, 27 for CO, 10 for H₂, 15 for CO₂ stable isotopes, and 6 for O₂/N₂. For reference, the 5th RR had 39 labs for CO₂, 26 for CH₄, 21 for N₂O, 17 for SF₆, 23 for CO, 10 for H₂, and 10 for CO₂ stable isotopes. The 4th RR had 26 labs for CO₂, 12 for CH₄, 6 for N₂O and SF₆, 8 for CO, 2 for H₂, and 7 for CO₂ stable isotopes. Stability of cylinders in the period of 6th RR for CO₂, CH₄, CO, H₂, N₂O and SF₆ will be discussed. Because most participants reported uncertainty as one standard deviation about the mean of N measurements, the reference labs (e.g., NOAA, INSTAAR, NCAR) will report the one standard deviation estimate of the reproducibility. This is an easy way to ensure that uncertainties are reported in a consistent and meaningful way across all parameters.

T8 COMPARISON OF CO₂ IN AIR STANDARDS FOR BACKGROUND AND URBAN GHG MEASUREMENTS

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Increased attention on urban areas as major sources of CO₂ emissions and efforts to verify these through measurement networks as global focus moves to mitigation efforts, is leading to increased demand for GHG calibration standards not only at background levels but also higher concentrations which are encountered in urban surroundings. In addition, the introduction of spectroscopic instruments into monitoring networks that measure specific isotopologues of CO₂ is leading to the development of calibration standards that require stringent characterization of both air matrix and isotopic composition to ensure the commutability of calibration standards with network monitoring instrumentation. In order to demonstrate that the gas standards are fit for their intended purpose, and the degree of equivalence between different standards, the BIPM and the NIST are coordinating an international comparison of CO₂ in air standards (CCQM-K120) starting in 2016. The comparison is organized under the auspices of the CCQM Gas Analysis Working Group (GAWG), with over twenty member institutes of the Working Group expected to participate, and following on from the successful comparison of methane in air standards performed in 2012 (CCQM-K82). For background CO₂ concentrations, participants are asked to produce standard mixtures of CO₂ in air at nominal mole fractions of 380 μmol mol⁻¹ and 480 μmol mol⁻¹ in an air matrix with the major matrix components (N₂, O₂ and Ar) maintained to within 0.5 mmol/mol of atmospheric values, so as to avoid biases in spectroscopic measurement techniques. For urban CO₂ concentrations, participants are asked to produce standard mixtures of CO₂ in air at nominal mole fractions of 480 μmol mol⁻¹ and 800 μmol mol⁻¹ in an air matrix. All standards submitted will be compared at the BIPM using GC-FID, Fourier Transformed Infrared spectroscopy and Isotope Ratio Infrared Spectroscopy (IRIS), with plans to provide confirmatory absolute CO₂ mole fraction measurements with a CO₂ manometric facility being developed at the BIPM. The comparison and measurement methods at the BIPM are currently being validated with a set of twenty standard mixtures prepared and/or certified by NIST and NPL for CO₂ concentration. The mixtures have been prepared with a range of CO₂ isotopic compositions, from highly depleted in ¹³C (-40 ‰ on VPBD scale) to less depleted than air (-1 ‰), as measured by MPI-JENA on a subset of mixtures. Three additional standards are being prepared by NOAA-ESRL and will be added to the validation set. Progress on the validation of the measurement methods and achievable uncertainties will be presented, including calibration strategies that are being developed both for isotope ratio measurements with IRIS and FTIR, so as to obtain measurement uncertainties smaller than 1 ‰, required to correct for biases in concentration measurements performed by spectroscopic techniques. The comparison capabilities demonstrated in the validation studies will also be compared to the current status of global equivalence other GHG calibration standards and notably for methane in air.

T9 UPDATE AND EXPANSION OF THE WMO X2004 METHANE MOLE FRACTION SCALE

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We have completed an update and expansion of the the WMO X2004 CH₄ mole fraction scale that will be designated X2004A. The updated scale addresses two issues: 1. As measurements at continental sites increase, so does the need for standards outside the typical background ambient range. 2. We identified non-linearity in our CH₄ calibration system that affects calibrations outside the ambient range (nominally 1600 to 2000 ppb). The magnitude of this non-linearity has changed over time, becoming especially large after October, 2013, and requires a new calibration strategy. To address these issues: 1. New primary standards from 2200 to 8100 ppb were prepared and added to the original set described in Dlugokencky et al. (JGR, vol. 110, doi:10.1029/2005JD006035, 2005). 2. We switched from a linear, single-point calibration extrapolated through zero to a non-linear response function based on 14 secondary standards (nominal range 390 to 5000 ppb) that were intensively calibrated against our primary standards over the past 2 years. These changes have had several impacts. 1. Assigned values to every secondary standard used by NOAA for standard calibrations from 1983 to present changed by an average of -0.3 ppb (s.d. = 0.3 ppb). These changes, when propagated to tertiary standards, result in average changes of -0.3 ppb (s.d. = 0.7 ppb) in the range 1600 to 2500 ppb. 2. Standards calibrated since 17 July 2013 will be corrected for non-linearity of our calibration system. The magnitude of the non-linearity correction is significantly greater for cylinders calibrated since October, 2013. 3. Standards calibrated before 17 July 2013 are only corrected for re-assignments to the secondary standards they were calibrated against.

T10 WMO/GAW GREENHOUSE GAS CALIBRATION SCALES: DEFINITIONS, UNCERTAINTIES, AND FUTURE DIRECTIONS

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WMO/GAW recommends that programs involved in greenhouse gas measurement reference their data to calibration scales maintained by the Central Calibration Laboratory (CCL). The NOAA Global Monitoring Division serves as the CCL for CO₂, CH₄, N₂O, CO, and SF₆. In addition to maintaining scales and preparing reference materials for WMO/GAW partners, it is a CCL function to establish traceability to the International System of Units, or SI. This is partially accomplished through comparison with National Metrology Institutes. The CCL has participated in recent Key Comparisons, such as K82 (CH₄), K68 (N₂O), and K84 (CO), and will participate in K120 (CO₂) planned for 2016. An understanding of total uncertainties is necessary for reporting Key Comparison results, and is also a requirement for SI traceability. Therefore, we have recently reviewed uncertainties associated with WMO/GAW calibration scales, and revised our calibration certificate accordingly. Total uncertainties for scales developed by the CCL are comparable to those developed by NMIs. Some of the main contributors to total uncertainty include: a) quantifying the amount of a trace gas of interest in the dilution air used to prepare gravimetric standards, b) repeatability of mass determinations, and c) quantifying the volume ratio of the manometer (CO₂). Scale transfer uncertainty is a relatively small component of total uncertainty for CH₄ (~25%) and CO₂ (~15%). We now report total uncertainty and the reproducibility of scale transfer on certificates. The new calibration certificate will be explained, along with scale definitions, uncertainties, results from some recent Key Comparisons, and future plans.

T11 REFERENCE STANDARDS FOR CARBON DIOXIDE AND OTHER HIGH IMPACT GREENHOUSE GASES

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Understanding the chemistry of the atmosphere and the mechanisms that control the levels of the gases involved in radiative forcing are of major global concern. Consequently, there is substantial demand from policy makers to improve our understanding, control the increasing influence of human activity on it and address the effects of climate change. There is a requirement for long-term observations based on accurate and stable standards of the highest impact greenhouse gases to ensure that the data meets the requirements of WMO DQOs compatibility goals, environmental policy makers as well as academic and regulatory users. We have made significant advances in preparing high accuracy, SI traceable and fully- synthetic gaseous reference standards of CO₂ and CH₄ in a synthetic air matrix to support UK and European monitoring networks. Current research aims to improve the uncertainty and stability of these reference materials by optimising passivation chemistry used in cylinder treatment, making high-accuracy quantification of target impurities in the matrix gas, characterising the isotopic composition of the target component and understanding its influence on measurements made in the field.

T12 UPDATE ON THE WMO H₂ X2009 SCALE

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The recommended procedure to achieve compatibility of long-term atmospheric trace gas observations is that laboratories calibrate and report measurements relative to a single carefully maintained scale. The general approach is the provision of high pressure standards by a Central Calibration Laboratory that maintains the respective calibration scale which is embodied in a set of standard gases that are linked to fundamental quantities (SI). A precondition for this concept to ensure data compatibility is the stability of the composition of these primary standard gases.

Limited long-term experience had been available for various high pressure cylinders with respect to their properties to maintain stable molecular hydrogen mole fractions in dry air standards when the H₂ X2009 scale was set up. Different cylinder types that were considered appropriate at that time have been used for the 13 primary standards to minimize the risk of an unnoticed homogeneous small drift of the entire scale. In recent years, however, trends in the calibration residuals of the primary standards suggest that three of the standards do not maintain a stable hydrogen mole fraction and therefore should be excluded from the set of primary standards. In this contribution we provide an update on this evaluation and present the available evidence for the stability of the H₂ X2009 scale.

T13 TRACKING DRIFT IN WMO PRIMARY CO STANDARDS

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1. NOAA

2. NOAA

3. NOAA

4. NOAA

The lack of CO stability in cylinders has forced the WMO CO scale to be defined by repeated sets of gravimetric standards produced every 4-6 years (in contrast to having a single set comprise the scale over time). Each set is used to calibrate secondary standards before significant drift can occur. All sets of gravimetric standard are considered equivalent and changes in the secondary standards calibrated against the various gravimetric sets are attributed to drift in the secondary standards. It is difficult to distinguish biases and drift in the gravimetric sets from real drift in the secondary standards. We are developing a traceable method to track drift in primary CO standards and to understand how future sets of gravimetric standards compare. Percent level gravimetric mixtures of CO and CH₄ in air are used as a stable reference point. CO growth in these cylinders is insignificant in relation to their mole fractions. The CO to CH₄ ratio is considered stable. Static dilutions of these "parent" mixtures are made by diluting a small aliquot of parent with zero air. The CH₄ in the dilution standard is measured and used with the gravimetrically known CO:CH₄ ratio of the parent tank to assigned a CO value to the dilution standards. The primary standards are calibrated against suites of dilution standards (covering the WMO range). Drift in the primary standards can be quantified by repeated calibrations of the primary standards against new suites of dilution standards made from the same stable parents. The primary CO standards have been calibrated 8 times against suites of dilution standards since May 2014 using both Off-Axis ICOS and VURF analyzers. Results using the Off-Axis ICOS analyzer are inconsistent due to N₂O interference but the VURF results show good agreement with suspected drift rates in the primary standards.

T14 A NEW SCALE FOR MEASUREMENTS OF ATMOSPHERIC CARBON MONOXIDE

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1. NOAA
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3. NOAA
4. NOAA/NIST
5. NOAA

The WMO central calibration laboratory (CCL) for carbon monoxide (CO) is located at the Global Monitoring Division, Earth Systems Research laboratory, NOAA, and as such is responsible for the WMO CO reference scale. Here we discuss a new scale, cited as WMO CO X2014, based on five sets of primary standards prepared by a gravimetric method between 1996 and 2011. First developed at NOAA in the early 1990s the scale was intended for measurements in the remote marine boundary layer (nominally 50 to 200 nmol mol⁻¹ CO); recently the range was expanded to 1000 nmol mol⁻¹ for measurements in regionally polluted environments. Because CO is often unstable in cylinders the scale was evaluated over time by repeated calibrations of several secondary standards against new sets of primary standards. The X2014 improves upon previous scales in its re-evaluation of the primary standard mole fractions and their transfer to secondary standards. The histories of secondary standards calibrated versus multiple sets of primaries between 1996 and 2011 are used to evaluate the internal consistency of the new scale. Provisional results suggest a mean internal agreement of X2014 is 1.0 nmol mol⁻¹ (k=2, over ~50-300 ppb). Their calibration results versus other secondary and tertiary standards suggest mean reproducibility of ±2.4 ppb and ±1.1 ppb between 1993-2012 and 2000-2012, respectively.

T15 STABLE ISOTOPES OF ATMOSPHERIC GASES MEASURED BY THE NOAA-CU INSTAAR COOPERATIVE PROGRAM

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1. CU INSTAAR
2. CU INSTAAR
3. CU INSTAAR
4. NOAA GMD
5. NIST
6. CU INSTAAR
7. CU INSTAAR
8. CU INSTAAR
9. CU INSTAAR
10. NOAA GMD
11. NOAA GMD
12. NOAA GMD

In 2015 we marked the 25th anniversary of stable isotope measurements in the NOAA Global Greenhouse Gases Reference Network. Measurements of stable isotopes of CO₂ began in 1990, isotopes of CH₄ were added in 1998 and isotopomers of N₂O began on a trial basis in 2013. This talk will focus on three issues related to stable isotopes of atmospheric gases: scales and calibration, technological developments - past, present and future - and the application and uses of stable isotopes in an era of global change. It is critical to maintain calibration scales and ties to primary standards, and we will explain the successes and challenges that we have had with stable isotopes of CO₂, CH₄ and N₂O. We will then discuss the potential impact, and also the limitations, of new measurement systems that use spectral properties of gases and absorption of light as opposed to traditional IRMS. Finally, we will discuss our recent scientific findings, with an emphasis on recent changes in atmospheric methane. Unlike previous increases in CH₄ concentration when there was little change in $\delta^{13}\text{C}$ of CH₄, the recent concentration increase has been concurrent with a decrease in $\delta^{13}\text{C}$ of CH₄. Our data and simple models suggest an increase in tropical, biogenic sources of methane with only a small contribution from extraction of natural gas and oil or from thawing Arctic permafrost. For $\delta^{13}\text{C}$ of CO₂, our long record of atmospheric measurements continues to show the remarkable anti-correlation with CO₂ concentrations at both seasonal and inter-annual timescales, demonstrating the strong role of the terrestrial biosphere in modulating atmospheric CO₂. These analyses underscore the value in measuring stable isotopes of greenhouse gases across a wide global network.

T16 JENA ISO-CCL AND THE JRAS-06 SCALE FOR ATMOSPHERIC CO₂

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The JRAS-06 ('Jena Reference Air Set') continues to be used as a common stable isotope anchor of air-CO₂ with a well-documented relation to the primary stable isotope scales¹. Although the scale defining stable isotope materials, NBS 19 and LSVEC, will have to be replaced in the near future for several reasons, this will not affect the JRAS scale in any way. The calcite materials used for JRAS (Mar-J1 and OMC-J1) have already been thoroughly calibrated and will continue their role in JRAS gas production. This is independent of any direct comparison with the new, yet to be defined replacement materials carrying the scales forward. The addition of a natural air sample to the JRAS set will also not change, although this material is second in line to reference air in the set directly generated using the calcites.

A major effort still ongoing is the new ICOS laboratory in Jena. Results from this laboratory will need to be exactly on the JRAS-06 scale; we strive for a situation where both labs can share the burden to disseminate calibrated air and also to further document the scale development with new reference materials.

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T17 IAEA STABLE ISOTOPE REFERENCE MATERIALS: ADDRESSING THE NEEDS OF THE ATMOSPHERIC MONITORING

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Isotope analyses of atmospheric CO₂ and methane are widely used in order to understand the global carbon cycle. To get reliable interpretation, all data of monitoring have to be comparable (be on the same scale) and be compatible within established limits. Presently compatibility goals for $\delta^{13}\text{C}$ of air CO₂ and air methane have been set at 0.01 permil and 0.02 permil respectively. These challenging limits can only be achieved through the use of reference materials (RMs) with low uncertainty. Traditional isotope ratio mass-spectrometry requires calibrations; recently optical laser analysers become available, thus increasing the demand for suitable RMs.

All isotope measurements are performed on relative scales defined by arbitrary chosen artefact (similar to meter and kg). The VPDB C-13 scale, defined by PDB (historical artefact), is realized via two highest-level RMs (NBS19 and LSVEC), the first defining the scale and the second used to normalize lab-to-lab calibrations. The two RMs are maintained and distributed by IAEA. The priority task is to maintain these RMs at the required uncertainty level, thus ensuring the long-term scale consistency. The second task is to introduce replacement RMs when needed (currently for exhausted NBS19). The next is to produce a family of lower level RMs (secondary, tertiary) addressing needs of various applications, e.g. gas mixtures ; these RMs should be traceable to the highest level. The uncertainty of measurements should be based on the RMs in use. This scheme allows addressing the comparability and long-term compatibility of measurement results.

T18 COMPATIBILITY OF LOW LEVEL COUNTING (LLC) AND ACCELERATOR MASS SPECTROMETRY (AMS) TECHNIQUES FOR ATMOSPHERIC RADIOCARBON MEASUREMENTS: A STATUS REPORT OF THE BUILDUP OF THE ICOS CENTRAL RADIOCARBON LABORATORY (CRL)

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The carbon cycle is subject to natural and anthropogenic forcing leading to changing distributions in the atmospheric $^{14}\text{C}/\text{C}$ ratio. Particularly at regional or global background sites, these signals are very small, of a few per mil only (Graven 2012). Thus, not only high precision but also excellent inter-laboratory compatibility is a fundamental requirement for global atmospheric radiocarbon research and was therefore demanded by the experts of the 17th WMO/IAEA GGMT conference (Tans and Zellweger 2014).

Existing long-term atmospheric radiocarbon records are often based on traditional counting techniques (e.g. Levin et al., 2010) while more recent monitoring uses AMS technique (e.g. Turnbull et al., 2007). This highlights the importance to achieve the radiocarbon compatibility goal (0.5 per mil inter-lab compatibility) among different measurement techniques. The ICOS central radiocarbon laboratory (CRL), which is currently set up at Heidelberg University, has undertaken the task of thoroughly investigating the inter-technique compatibility of the low level counting technique (LLC), which was operated in Heidelberg for more than 50 years, and AMS-based radiocarbon analysis.

Here we report on the status of the buildup of the ICOS CRL focusing on the internal quality control and ongoing LLC-AMS compatibility results. As part of an international comparison exercise, the ICOS CRL has prepared aliquots of five pure CO_2 samples, analyzed by LLC at the Heidelberg Radiocarbon Laboratory beforehand, and distributed to eleven AMS laboratories. The preliminary results of this international inter-technique comparison indicate that LLC agrees with the averaged AMS measurements within 0.1 ± 1.5 per mil. Details of this study will be presented.

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T19 A PROPOSAL FOR A SUITE OF ISOTOPE REFERENCE GASES FOR CH₄ IN SYNTHETIC AIR

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Meaningful measurements can only be made if they are related to a unifying and traceable reference. However, reference materials that fulfil these requirements are unavailable for measurements of isotope ratios in atmospheric methane. We developed a method to produce a suite of standard gases that can be used to unify methane isotope ratio measurements of laboratories in the atmospheric monitoring community. We calibrated eight pure methane gases of different methanogenic origin against international referencing materials that define the VSMOW and VPDB isotope scales. The isotope ratios of our pure methane gases range between -360 and 40 ‰ for $\delta^2\text{H}-\text{CH}_4$ and between -60 and -40 ‰ for $\delta^{13}\text{C}-\text{CH}_4$. They include the isotope ratios of atmospheric methane ($\delta^2\text{H}-\text{CH}_4$ about -90 ‰, $\delta^{13}\text{C}-\text{CH}_4$ about -47 ‰). We estimate a total uncertainty of <1.5 ‰ and <0.2 ‰ for our $\delta^2\text{H}$ and $\delta^{13}\text{C}$ calibrations, respectively. Aliquots of calibrated methane are diluted with methane-free air to atmospheric methane levels and filled into 5 L glass flasks. These synthetic gas mixtures comprise atmospheric oxygen/nitrogen ratios and krypton mole fractions to prevent gas-specific measurement artefacts to our best knowledge. We make the resulting synthetic atmospheric reference gases available to the atmospheric monitoring community in an analogous fashion as has previously been done with the “JRAS air set” that is used as reference material for the stable isotope ratios in atmospheric carbon dioxide. This will provide a unifying isotope scale anchor for isotope ratio measurements of atmospheric methane. A homogenous isotope scale will allow to merge methane isotope ratio data sets into one global data set with high spatio-temporal resolution. This will enable more rigorously constrained interpretative techniques of such data in future.

T20 TRACEABILITY OF MEASUREMENTS WITHIN THE GLOBAL ATMOSPHERE WATCH PROGRAMME: RESULTS FROM THE WORLD CALIBRATION CENTRE WCC-EMPA

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Empa operates the World Calibration Centre for Carbon Monoxide, Methane, Carbon Dioxide and Surface Ozone (WCC-Empa) since 1996 as a Swiss contribution to the Global Atmosphere Watch (GAW) programme. WCC-Empa has conducted over 70 system- and performance audits over the past 20 years. This activity significantly contributes to sustain and improve the data quality required for climate and environmental research. The concept of the performance audits was recently expanded by the addition of parallel measurements with a travelling instrument using an entirely independent inlet system and calibration scheme.

The presentation will highlight results of CO, CH₄ and CO₂ audits with relation to the measurement technique. In particular, the result of the CO comparisons will be discussed in detail. Audit results for CO showed that the WMO/GAW compatibility goals are often not met, and clear need for action is required to solve this issue. Further, the advantages of the new performance audit approach will be shown. Results from various stations using different analytical techniques will be analyzed, and aspects such as water vapour interference, calibration frequency, data coverage, and aggregation times will be addressed.

T21 AN UPDATE OF COMPARISONS OF NON CO₂ TRACE GAS MEASUREMENTS BETWEEN AGAGE AND NOAA AT COMMON SITES

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Three dimensional atmospheric model studies that estimate global and regional emissions often require data from more than one 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 and different measurement techniques. 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 15 years up to 300 comparisons of non CO₂ 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 (primarily using SIO calibration scales) 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.

This presentation will give an update of the comparisons presented at GGMT 2011 (Wellington, NZ) summarising the methodology and resultant output, with detailed results from selected comparisons. A summary of the overall level of agreement, the so called 'scale conversion factors', between AGAGE and NOAA data/scales based on the comparisons from the field sites for a range of species will be given.

T22 COMPATIBILITY OF ATMOSPHERIC GREENHOUSE GAS MEASUREMENTS IN EUROPE AS ASSESSED BY THE ‘CUCUMBERS’ INTERCOMPARISON PROGRAMME

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Combining datasets of atmospheric gas species measurements collected by different laboratories is essential in order to advance our knowledge and understanding of climate change and Earth system science. Doing so, however, is fraught with difficulties. How can we be confident that 380.0 ppm CO₂ mole fraction measured by one laboratory or field station in one part of the world is equivalent to 380.0 ppm CO₂ mole fraction measured by another laboratory or field station in another part of the world? Biases between measurements made at different field stations or in different laboratories can arise from numerous complications, for example, differences in analytical techniques (e.g. some techniques are ‘blind’ to $\delta^{13}\text{C}$ in an air sample, biasing CO₂ measurements), or possible changes over time in the calibration scales defined at a laboratory or field station.

To confidently address these issues, laboratories and field stations must analyse exactly the same air sample in what are known as intercomparison studies. The ‘Cucumbers’ intercomparison programme is an atmospheric greenhouse gas measurement programme that was established as part of the European Commission’s (EC) ‘CarboEurope’ project in 2005, continuing under succeeding EC projects. The programme involves 11 laboratories, 23 field stations, 34 organisations, and spans 16 countries. Here, we present 10 years of results from the programme, covering 9 atmospheric gas species, providing compatibility results referenced to the WMO/GAW compatibility goals.

T23 REGULAR AIRBORNE GHG OBSERVATIONS WITHIN IAGOS: QA/QC APPROACH

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Within the framework of IAGOS-ERI (In-service aircraft for a global observing system – European research Infrastructure) a cavity ring-down spectroscopy (CRDS) based measurement system for autonomous measurement of the greenhouse gases (GHG) CO₂ and CH₄, as well as CO and water vapor was designed, tested, and qualified for deployment on commercial airliners. The design meets requirements regarding physical dimensions (size, weight), performance (long term stability, low maintenance, robustness, full automation) and safety (fire prevention regulations). The system uses components of a commercially available CRDS instrument (G2401-m, Picarro Inc.) mounted into a frame suitable for integration in the avionics bay of the Airbus A-340 and A-330. To allow for trace gas measurements to be fully traceable to WMO scales, a two-standard calibration system has been designed and tested that periodically provides calibration gas to the instrument during flight and on ground for each six-month deployment period. The QA/QC concept was harmonized in the framework of IGAS (IAGOS for the GMES Atmospheric Service), an EU project which serves as a bridge between the data collected on board civil aircraft through IAGOS and the Copernicus Atmosphere Monitoring Service (CAMS) as well as the general user community. A concept for ongoing documentation of the data quality has been developed that allows users to trace each observation. Initial test flights have been successfully completed onboard the research aircraft HALO, and the first of the IAGOS-core GHG packages is scheduled for integration in 2015. The aim is to have five systems operational within four years, providing for regular, long-term GHG observations covering major parts of the globe. We present the QA/QC concept and results from recent test flights and laboratory tests that document the performance for GHG, CO, and water vapor measurements.

T24 PERSEUS: A SAMPLE PRECONCENTRATION AND GC/MS DETECTOR SYSTEM FOR ANALYSIS OF FLASK AIR SAMPLES FOR ATMOSPHERIC TRACE HALOCARBONS, HYDROCARBONS AND SULFUR-CONTAINING COMPOUNDS

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The development of PERSEUS represents a significant advancement, relative to existing in-kind instrumentation, in the analysis of atmospheric samples for a wide range of halocarbons, hydrocarbons and sulfur-containing compounds at ppq (1:1015) to ppb (1:109) dry gas mole fractions. The greater reproducibility, decreased artifacts and broader analyte suite of PERSEUS substantially enhances the research capabilities of the GMD global and North American sampling programs.

Major analytical improvements include a factor of 30 improvement in the precision of the extracted sample volume measurement, which can represent a major component in the overall analytical uncertainty, through use of high precision temperature and pressure instrumentation. Increasing the signal to noise ratio in this manner made possible other improvements. First, the amount of sample required is reduced by a factor of four, relative to that of Medusa (Miller et al., 2008), without compromise in overall reproducibility. This leads to a comparable reduction in the CO₂ and H₂O load on the pre-concentration, chromatographic and detector systems, thus reducing their potential for interference with their variability in the sample gas. Smaller sample sizes require less adsorbent mass, thus reducing the potential for interfering ‘bleed’ from these materials and at the same time reducing the time required to process sequential trapping steps. This smaller adsorbent mass additionally leads to improved chromatographic peak shape (i.e., closer to Gaussian) for better peak resolution.

Combining these benefits from the sample volume measurement with a change to a bi-modal thermal conductivity in the cryogenic pre-concentration leads to an over reduction in analysis cycle time of a factor 2.6 over that of Medusa. These changes, combined with improved data processing, particularly with regard to detector drift-correction, lead to an enhanced daily productivity by increasing ‘unknown’ sample throughput by a factor of four relative to that of Medusa.

**T25 AN OVERVIEW OF THE SCRIPPS PROGRAM TO PRODUCE AND DISTRIBUTE
REFERENCE MATERIALS FOR OCEANIC CO₂ MEASUREMENTS**

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Concern about the potential role of carbon dioxide as a “greenhouse gas”, and more recently its role in ocean acidification has led to a substantial interest in the global carbon cycle and hence in the geochemistry of the oceanic carbon system. The reliability of the measurements made is a key concern of researchers, and the research projects require that measurements made at different times, by different investigators from a number of laboratories around the world, be comparable and correct.

My laboratory at the Scripps Institution of Oceanography has developed sea water reference materials for measurements of oceanic CO₂. These reference materials are distributed widely all around the world and are used as the basis for calibration and quality control of oceanic CO₂ measurements. Presently, our reference materials are assigned values for total dissolved inorganic carbon, and for total alkalinity. We are presently examining whether we can assign values for pH in addition.

After a brief introduction to our reference materials, I shall describe the work we are doing to assess the uncertainty of the certified values we provide (total dissolved inorganic carbon, and for total alkalinity), and will indicate the potential role we can play in providing useful materials for *proficiency tests* of the international capacity to make seawater CO₂ measurements.

T26 RECOMMENDATIONS FOR OCEAN AND ATMOSPHERIC MEASUREMENTS OF CO₂ ON SHIPS OF OPPORTUNITY

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There are currently as many as 60 ships of opportunity (SOO) making measurements of the partial pressure of CO₂ (pCO₂) globally and contributing more than 1 million measurements to the Surface Ocean CO₂ Atlas (SOCAT) each year. With relatively minor changes to sampling, calibration and data quality control protocols these same ships could add significantly to the boundary layer CO₂ measurements in the Global Greenhouse Gas Reference Network.

To demonstrate the repeatability of atmospheric CO₂ measurements from a ship-based pCO₂ system, we will examine data collected on the Antarctic Research Supply Vessel (ARSV) Laurence M. Gould from 2002 – 2015 in the Drake Passage. These measurements will be compared to measurements made by the NOAA Greenhouse Gas Reference Network flasks and measurements made by an independently calibrated, NDIR CO₂ sensor which is part of a fuel-cell based atmospheric O₂ system.

The inclusion of atmospheric measurements on the Laurence M. Gould has not only provided a new set of constraints in the Greenhouse Gas Reference Network but also has provided a valuable metric for assessing the repeatability of the surface ocean pCO₂ measurements. We expect that as more ships contribute to the Global Greenhouse Gas Reference Network boundary layer CO₂ measurements subtle biases in surface water pCO₂ measurements are likely to be identified and removed.

T27 UK DECC & GAUGE TALL TOWER NETWORKS AND INTEGRATION WITH OTHER GREENHOUSE GAS DATA STREAMS

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Motivated by the UK 2008 Climate Change Act, which requires the UK to decrease its greenhouse gas (GHG) emissions by 80% of 1990 levels by 2050, the Greenhouse gAs Uk and Global Emissions (GAUGE) project aims to better quantify the UK CO₂, CH₄ and N₂O emissions. These new emission estimates will be used to assess the impact of new emission abatement and reduction strategies. GAUGE draws together new and existing GHG data streams from regional to global scales. These include high-density regional studies, tall tower sites, moving platforms (ferry and aircraft) and satellite observations. These observations will be combined with innovative modelling approaches to better quantify and characterise UK GHG emissions and place them in a global context.

This presentation will give an overview of stationary sites and moving platforms (including 6 near surface regional focused sites, 6 tall tower sites, ferry and aircraft measurements), detailing the analytical techniques used, calibration strategy and intercomparison program. Key to combining these data streams is an assessment of their intercomparability through a cylinder intercomparison program (ICP). Although still on going, the early results of the ICP are promising with all tall tower sites reaching the WMO intercomparison goal for both CO₂ and CH₄.

T28 TRENDS OF METHANE EMISSIONS IN SOUTHERN GERMANY DERIVED FROM 24 YEARS OF ATMOSPHERIC METHANE AND RADON MEASUREMENTS AT SCHAUINSLAND STATION

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Since 1991, the German Environment Agency (UBA) is measuring continuously the CH₄ mole fraction at Schauinsland station (47°55', 7°55'E, 1205 m a.s.l). The measurement station is a continental mountain station, located in the German black forest 1000m above the Rhine valley. During the measurement period two different gas chromatographs and calibration scales were used. For this study, all data have been carefully reevaluated, verified for consistencies and compared to the Heidelberg flask sampling at this station. Atmospheric Radon activity is measured by the Federal Office for Radiation Protection (BFS). In a second step we use the hourly CH₄ and 222Rn measurements to derive monthly CH₄ emissions in the catchment area of Schauinsland station. These CH₄ emission estimates show clearly a decrease of more than 30 % from the years 1990s to the more recent years 2007-2013. The major decrease of the CH₄ emissions is observed between 2000 and 2006. Regional and national emission inventories for the region Baden-Württemberg or from UNFCCC report for the same period a considerable larger CH₄ reduction of 55-60 %. They derived from statistical data a linear decrease of CH₄ emission over the whole period which is mostly related to the sector waste treatment.

T29 HIGH-PRECISION IN SITU ATMOSPHERIC MEASUREMENTS OF COS, CO₂, CO AND H₂O AT THE LUTJEWAD TOWER IN THE NETHERLANDS

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Carbonyl Sulfide (COS) may be a useful tracer for photosynthetic CO₂ uptake as it follows the same pathway into the plant through stomata as CO₂, but is not re-emitted by the plant. COS therefore provides a means to partition the Net Ecosystem Exchange into Gross Primary Production (GPP) and Respiration. Until now, most atmospheric COS measurements have been made on discrete samples from flasks, here we present high-precision in situ measurements of COS at the Lutjewad atmospheric monitoring station (60 m, 6°21'E, 53°24'N, 1 m a.s.l.) in the Netherlands. The COS measurements were made using a quantum cascade laser (QCL) spectrometer (Aerodyne Research Inc., MA, USA) since July 2014. The instrument is capable of simultaneously measuring COS, CO₂, CO, and H₂O after including a weak CO absorption line in the scanned wavelength range. The short-term precision of the analyser is 3.4 ppt for COS, 0.04 ppm for CO₂ and 0.4 ppb for CO (1 Hz). Calibrations were necessary on time scales of an hour to correct for instrument drift. Furthermore, we assessed the correction for water vapor interference applied by the instrument control software and present an alternative water vapour correction based on a set of laboratory-derived empirical factors. The accuracy of the instrument for measurements of CO₂ and CO is evaluated with a cavity ring-down spectrometer (Picarro Inc., CA, USA). Besides that, we tested the ability to do flask sample measurements with the QCL analyser and validated these QCL measurements with gas chromatography - mass spectrometry (GC-MS) instrumentation by NOAA/ESRL. We have found that with frequent calibrations and a well-controlled temperature environment the system provides high precision measurements of COS, CO₂, and CO in field applications.

T30 A SYSTEM FOR CONTINUOUS MEASUREMENTS OF ATMOSPHERIC O₂/N₂ AND AR/N₂ RATIO, STABLE ISOTOPIC RATIOS OF N₂, O₂ AND AR AND ITS APPLICATION IN PREPARING GRAVIMETRIC STANDARDS FOR ATMOSPHERIC O₂/N₂ RATIO

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We have conducted continuous measurements of atmospheric O₂/N₂ and Ar/N₂ ratios, CO₂ concentration and stable isotopic ratios of N₂, O₂ and Ar at Tsukuba, Japan since 2012 using a mass spectrometry method developed by Ishidoya and Murayama (2014). The measurement system is equipped with an original inlet system, allowing sample and reference air flow through the inlet at a flow rate of 5-10 mL min⁻¹, with only a miniscule amount of the flow transferred to the ion source through thermally insulated fused silica capillaries with 25 micro-m ID. The values of O₂/N₂, Ar/N₂, stable isotopic ratios of N₂, O₂ and Ar of standard air stored in 48-L high-pressure cylinders have remained stable to within ±3.7, ±5.3, ±1.1, ±2.4 and ±10 per meg, respectively, for the last 3 years. Since we are planning to evaluate gravimetric standards for atmospheric O₂/N₂ ratio by using the measurement system, we are developing a method to prepare gravimetric standards of ambient O₂ level with a precision better than 1 ppm of O₂ mole fraction, by weighing masses of O₂ and N₂ using two mass comparators. This will involve determining the masses of O₂ and N₂ with precisions better than 0.3 mg and 1 mg, respectively, using a small mass comparator (maximum capacity: 2 kg, readability: 0.01 mg) for O₂ and a large mass comparator (maximum capacity: 26 kg, readability: 1 mg) for N₂. We will present an overview of our measurement system, along with preliminary observational results of atmospheric O₂/N₂ and Ar/N₂ ratios, and a plan for development of the gravimetric standards for atmospheric O₂/N₂ ratio.

T31 INTERFEROMETRIC AND MASS SPECTROMETRIC MEASUREMENTS OF O₂/N₂ RATIO AT THE SCRIPPS INSTITUTION OF OCEANOGRAPHY

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Since 2002, routine measurements of O₂/N₂ ratio at the Scripps Institution of Oceanography have been made simultaneously on an interferometric analyzer and an Isoprime mass spectrometer. Both analyzers are connected to the same calibration gas system and share a rack for analysis of 5L glass flasks. Flasks collected from the 10-station Scripps O₂ network have been analyzed concurrently on both systems. The long-term external precision of flask replicates on the interferometer and mass spectrometer are $\sim \pm 3.6$ and $\sim \pm 2.7$ per meg, respectively. A detailed comparison of the methods will be presented based on more than 8000 overlapping flask measurements and more than 2000 overlapping tank calibrations. Results will also be reported from a 15-year flask stability test, involving 39 flasks which were sampled at the end of the Scripps Pier in 1994-1995 and then stored in the dark until analysis in 2009-2010, when they were analyzed for CO₂, O₂/N₂ and Ar/N₂.

T32 REGIONAL AND GLOBAL ATMOSPHERIC CO₂ MEASUREMENTS USING 1.57 MICRON IM-CW LIDAR

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Atmospheric CO₂ is a critical forcing for the earth's climate, and knowledge of its distribution and variations influences predictions of the Earth's future climate. Accurate observations of atmospheric CO₂ are also crucial to improving our understanding of CO₂ sources, sinks and transports. To meet these science needs, NASA is developing technologies for the Active Sensing of CO₂ Emissions over Nights, Days, and Seasons (ASCENDS) space mission, which is aimed at global CO₂ observations. Meanwhile an airborne investigation of atmospheric CO₂ distributions as part of the NASA Suborbital Atmospheric Carbon and Transport – America (ACT-America) mission will be conducted with lidar and in situ instrumentation over the central and eastern United States during all four seasons and under a wide range of meteorological conditions.

In preparing for the ASCENDS mission, NASA Langley Research Center and Exelis Inc./Harris Corp. have jointly developed and demonstrated the capability of atmospheric CO₂ column measurements with an intensity-modulated continuous-wave (IM-CW) lidar. Since 2005, a total of 14 flight campaigns have been conducted. A measurement precision of ~0.3 ppmv for a 10-s average over desert and vegetated surfaces has been achieved, and the lidar CO₂ measurements also agree well with in-situ observations. Significant atmospheric CO₂ variations on various spatiotemporal scales have been observed during these campaigns. For examples, around 10-ppm CO₂ changes were found within free troposphere in a region of about 200×300 km² over Iowa during a summer 2014 flight, and inter-annual variations of cornfield CO₂ drawdown could be larger than 5 ppm.

This paper presents results from recent flight campaigns. The ability to achieve the science objectives of the ASCENDS mission with an IM-CW lidar is also discussed, along with the plans for the ACT – America aircraft investigation that begins in the winter of 2016.

T33 IN SITU METHANE IN THE THIRD DIMENSION – USING DRONES TO 3000M IN ASCENSION ISLAND, TO SAMPLE TROPICAL AIR.

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Ascension Island (7°58'S, 14°4'W) is a remote central Atlantic island, superbly located for atmospheric sampling. The marine boundary layer air is almost invariably the SE Trade Wind, typically about Beaufort Force 5, gusting at times. This wind originates in the remote South Atlantic and has very little influence from Africa. Thus it delivers integrated deep Southern hemisphere air. Above the very well-developed Trade Wind Inversion, at around 1500m (varying diurnally and with season, and about 500-800m above Ascension's summit), the air is variably tropical, typically from equatorial or savanna central Africa (depending on season) but sometimes from South America. This air characteristically last encountered the African or S. American surface in thunderstorm systems.

Thus sampling this well-mixed air is a very attractive target for monitoring: ideally, an Ascension monitoring station that could regularly access air above 1500m would be able both to track the deep Southern Hemisphere and also sample the equatorial tropics. We here report on Unmanned Aerial Vehicle (UAV) experiments to develop a sampling system consisting of three eight motor multirotor octocopter platforms developed at Bristol Robotics Laboratory (BRL). Two campaigns have been carried out, in 2014 and 2015, successfully retrieving airbag samples from above the Trade Wind Inversion up to 3000m. The samples were analysed immediately for mole fraction, using the Picarro analyser, and then offline for ¹³C CH₄ at Royal Holloway. The results demonstrate clearly that, if regular drone collection could be supported, this is a successful way to monitor air composition both in the boundary layer and in the tropical mid-troposphere. For atmospheric chemical transport models, Ascension thus potentially offers an extremely powerful location to monitor a very wide sector of the Southern Hemisphere.

A brief movie will be shown.

T34 LONG OPEN PATH FOURIER TRANSFORM SPECTROSCOPY MEASUREMENTS OF GREENHOUSE GASES IN THE ATMOSPHERE

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How representative are in situ measurements at a point in an inhomogeneous atmospheric environment? Open path measurements offer spatial averaging and continuous measurements of several trace gases (including CO₂, CH₄, CO and N₂O) simultaneously in the same airmass over paths of hundreds to thousands of metres. Spatial averaging over kilometre scales improves comparability with the finest scale atmospheric models becoming available, and helps bridge the gap between models and in situ measurements. With what precision, accuracy and reliability can such measurements be made? We pooled our experience in open path measurements and remote sensing by Fourier transform spectroscopy (FTS) in the infrared (Wollongong) with long path DOAS techniques in the UV-visible (Heidelberg) to make open path measurements across a 1.5 km one-way path in urban Heidelberg, Germany. Direct open-atmosphere measurements of trace gases CO₂, CH₄, CO and N₂O as well as O₂ were retrieved from several near-IR absorption bands between 4000 and 8000 cm⁻¹ (2.5 – 1.25 micron). At one end of the path an in situ FTIR analyser simultaneously collected well calibrated measurements of the same species for comparison with the open path-integrated measurements. The measurements ran continuously from June – November 2014. We introduce the open path FTS measurement system and present an analysis of the results, including assessment of precision, accuracy relative to co-incident in situ measurements, reliability, and avenues for further improvements and extensions. Short term precision of the open path measurement of CO₂ was better than 1 ppm for 5 minute averages and thus adequate for studies in urban and other non-background environments. Measurement bias relative to calibrated in situ measurements was stable across the measurement period. The system operated reliably with data losses mainly due to weather conditions. In principle the system can be improved to provide longer pathlengths and higher precision.

T35 AN UPDATE ON RECENT RESULTS FROM OCO-2 AND THE TCCON NETWORK

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Total column observations of CO₂ and CH₄ provide a new tool for diagnosing the Earth's carbon cycle. For a decade, the Total Carbon Column Observing Network (TCCON - see: <https://tcon-wiki.caltech.edu/>) has obtained measurements of the mean dry mole fraction of CO₂ and CH₄ using ground-based remote sensing. The measurements are tied to the broader global carbon monitoring system using simultaneously measured in situ profiles obtained periodically over the network sites. In addition to their direct use in carbon cycle science investigations, the TCCON measurements are used for evaluation of column observations made from space from both the Japanese GOSAT and NASA's OCO-2 missions. Comparisons between TCCON and OCO-2 retrievals during the first year of operations will be shown.

T36 TRACE GAS MEASUREMENTS BY GC-PDD

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We will present results from some of our recent applications of the Valco pulsed discharge detectors for gas chromatographic analyses of selected atmospheric trace gases.

T37 COMPLEMENTARY OBSPACK DATA PRODUCTS: A NEW WAY TO THINK ABOUT COOPERATIVE DATA PRODUCTS

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ObsPack is a framework designed to bring together atmospheric GHG observations from a variety of sampling platforms, prepare them with specific applications in mind, and package and distribute them in a self-consistent and well-documented product. ObsPack products are intended to support GHG budget studies and represent a new generation of cooperative value-added GHG data products. Considerable progress has been made since GGMT-2013. Products may now include original data reformatted using the ObsPack framework. We continue to enhance and standardize metadata to help ensure data are used appropriately, calibration and quality assurance histories are clearly described, and individuals responsible for the original data are properly acknowledged. The distribution strategy, designed to improve communication between data providers and product users, continues to be refined. Products have a required citation which includes a DOI to ensure unambiguous identification when cited and to facilitate citation searches in the literature. Products are freely available from www.esrl.noaa.gov/gmd/ccgg/obspace/. In 2014, we began thinking about ObsPack products in a new way [Masarie et al., 2014; www.earth-syst-sci-data.net/6/375/2014/]. Instead of creating a single product that includes data from many laboratories, we consider a suite of complementary ObsPack products each containing similarly prepared data from a single laboratory or subset of laboratories. Laboratories can prepare complementary products provided they adhere to ObsPack protocols and ensure no two products include the same original data. Complementary products will improve our ability to provide timely updates of some products without impacting products whose original data remain unchanged. Further, laboratories can distribute their products as they choose. This new approach will require that products are fully compatible so that users can easily and unambiguously merge products without introducing duplication or inconsistencies. Recently, NOAA has teamed with ICOS Carbon Portal and WDCGG to explore the feasibility of complementary ObsPack products.

T38 PROPOSAL OF NEW INTERFACE FOR METADATA INPUT AT THE WDCGG WEBSITE

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Recent development for new operations and service at WDCGG (World Data Centre for Greenhouse Gases) is demonstrated. For last few years, WDCGG has provided its fundamental reform plans to serve data contributors and users better. The progress is not so fast with our limited resources, although, several new directions and proto-types are produced. Data and metadata are submitted separately under the current WDCGG system. In addition, the version history of metadata set cannot be held. This could lead to undermine the connection between history of datasets and their metadata. We would like to connect them in a more reliable and efficient way. A new data submission system will be set up to ensure one-to-one correspondence of data to metadata. As well as data, metadata are essential in WDCGG. However, our current metadata input interface is not necessarily convenient for data contributors to input and update their metadata. How we can collect metadata and keep them updated have become a key issue. The proto-type metadata input interface was designed to be user-friendly and to alleviate data contributors' burden. It will be demonstrated in the presentation. WDCGG has a wide variety of data formats now. Its data format will be changed to a single consolidated format for fixed stations and mobile platforms (aircraft and ship), exploring potential collaborations with NOAA ObsPack. We will introduce a new data browsing interface where data users can easily reach their target dataset with a sophisticated visual aid. For 25 years after its establishment in 1990, WDCGG has pursued the increasing role in greenhouse and reactive gas measurements and their application community. WDCGG will continue to operate the reformed services to better bridge data contributors and users.

T39 INFORMING POLICY WITH OBSERVATIONS AND MODELING – AN OPPORTUNITY

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Global society faces the major challenge of reducing greenhouse gas emissions by at least 80%, most notably those of CO₂, while at the same time facing variable and potentially overwhelming Earth System feedbacks. It is currently failing miserably, heading toward an average 3C (6-7C average over continents) increase in temperature before 2050. Starting with discussions in Jena (2009), followed by New Zealand (2011) and Beijing (2013), the GGMT has recommended what to improve in order to help society succeed in reducing greenhouse gas (GHG) emissions. These discussions, driven “organically” from within the community, by decisions made by WMO’s Commission for Atmospheric Sciences (2009, 2013), and by the fact that atmospheric GHGs continue to rise at increasing rates, have largely focused on observing systems and modeling, but also included information delivery. Simultaneously, several of us have been working within WMO and other international organizations to gain approval and funding to prepare an implementation plan, based largely on discussions among members of this group and on several national documents seeking a similar outcome. With final approval by WMO Congress this past June, an international writing team has now been identified and assembled to begin developing an implementation plan for an Integrated Global Greenhouse Gas Information System (IG3IS) with realizable goals. The plan aims to provide guidance for WMO and its member nations (185) and territories (6) in enhancing observations and improving transport modeling, Earth-system analysis, and information delivery. This brief presentation will address the overall approach for this plan and solicit comments and contributions from the community.

T40 A 21ST CENTURY SHIFT FROM FOSSIL-FUEL TO BIOGENIC METHANE EMISSIONS INDICATED BY $^{13}\text{CH}_4$

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The stable carbon isotopes ($\delta^{13}\text{C}(\text{Atm})$) of methane provide important constraints on the global methane budget during times of changing atmospheric methane concentration $[\text{CH}_4]$. For example, a $[\text{CH}_4]$ -plateau between 1999 and 2006 could be caused by a temporary reduction in industrial or climate sensitive sources or by sink variability. We have combined ($\delta^{13}\text{C}(\text{Atm})$)-measurements from the laboratories at the Institute for Arctic and Alpine Research, USA, University of Heidelberg, Germany, and the National Institute of Water and Atmospheric Research, NZ, which form a global network of clean air monitoring stations. Inter-laboratory offsets are quantified using Antarctic data following Levin et al. (2012). Global mean $\delta^{13}\text{C}(\text{Atm})$ -values were calculated while accounting for temporal and geographic gaps in the record. The resulting trend parallels the $[\text{CH}_4]$ -history until the end of the $[\text{CH}_4]$ -plateau but then decreases while $[\text{CH}_4]$ rises again. Box model calculations show that diminishing thermogenic emissions, probably from fossil-fuel mining and reticulation, and/or variations in hydroxyl, the dominating CH_4 -sink are the most plausible causes of the $[\text{CH}_4]$ -plateau. Our results indicate that the renewed $[\text{CH}_4]$ -increase after 2006 is most likely driven by biogenic sources and not by resumed thermogenic emissions.

Reference: Levin, I. et al. No inter-hemispheric $\delta^{13}\text{CH}_4$ trend observed. *Nature* **486**, E3-E4, doi:10.1038/Nature11175 (2012).

T41 60 YEARS OF SOUTHERN HEMISPHERE $\Delta^{14}\text{CO}_2$ OBSERVED AT WELLINGTON, NEW ZEALAND

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Atmospheric $\Delta^{14}\text{CO}_2$ measurements have been made at Wellington, New Zealand (41°S, 175°E) since December 1954. This is the longest atmospheric $\Delta^{14}\text{CO}_2$ record from anywhere in the world, predating the ^{14}C “bomb spike” by several years and documenting the movement of bomb ^{14}C into the Southern Hemisphere and throughout the global carbon cycle. In more recent times, the spatial and temporal changes in $\Delta^{14}\text{CO}_2$ are dominated by two main drivers: (i) the addition of ^{14}C -free, fossil-fuel derived CO_2 , emitted mainly over Northern Hemisphere continents, and (ii) the ocean-to-atmosphere flux of ^{14}C -depleted CO_2 , most strongly from the Southern Ocean. Southern Hemisphere $\Delta^{14}\text{CO}_2$ records in particular have the potential to elucidate the mechanisms that drive Southern Ocean carbon exchange, a key component of the global carbon cycle.

We will present a revised Wellington $\Delta^{14}\text{CO}_2$ record, updated to span 60 years from 1954 to 2014. The record is primarily based on ~2 week integrated samples collected by static absorption of CO_2 into NaOH solution. We have thoroughly reviewed and revised the entire record, through which there have necessarily been many changes in methodology. In particular, the ^{14}C measurement method was changed from gas counting to AMS in 1995, and the first ten years of this period is noisy and possibly biased high; we are re-measuring this period using archived material from the same NaOH samples with improved precision. A series of anomalously high $\Delta^{14}\text{CO}_2$ values from 1990-1992 has been re-examined with archived CO_2 from flasks and tree rings from two nearby locations; the anomaly appears to be a measurement artifact and the record has been revised. We will discuss the updated record, comparison to other atmospheric $\Delta^{14}\text{CO}_2$ records and use new modeling tools to examine the causes of the temporal variability in the Wellington $\Delta^{14}\text{CO}_2$ record.

T42 MEASUREMENTS OF THE STABLE ISOTOPES ^{13}C AND ^{18}O IN ATMOSPHERIC CO AT IMAU, UTRECHT UNIVERSITY (NL)

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A fully automated system for the determination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in atmospheric CO has been developed at IMAU, using continuous flow isotope ratio mass spectrometry (CF-IRMS). First, the CO_2 present in the air sample is removed completely, using Ascarite / $\text{Mg}(\text{ClO}_4)_2$ followed by a cryogenic trap. The CO is then converted to CO_2 using Schütze reagent, and it is analyzed as CO_2 in an isotope ratio mass spectrometer (IRMS).

The system is able to perform measurements at typical atmospheric mole fractions and below, relatively fast (20 min / analysis), and needs small quantities of sample air (150 ml / analysis). It can thus be used for atmospheric samples, but also for e.g. ice core, stratospheric, soil air and other normal or low CO mole fraction samples. At normal atmospheric CO mole fractions, the typical repeatability is 0.1 ‰ for $\delta^{13}\text{C}$ and 0.2 ‰ for $\delta^{18}\text{O}$. The lower limit for the CO mole fraction in air that can be analyzed is currently about 30 ppb.

We will present an overview of the system setup and the main quality check means, and will give some examples of data from measurements performed so far.

A1 GAS ADSORPTION AND DESORPTION EFFECTS ON CYLINDERS AND THEIR IMPORTANCE FOR LONG-TERM GAS RECORDS

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It is well known that gases adsorb on many surfaces, in particular metal surfaces. There are two main forms responsible for these effects (i) physisorption and (ii) chemisorption. The reverse process is called desorption and follows similar mathematical laws, however, it can be influenced by hysteresis effects. In the present experiment we investigated the adsorption/desorption phenomena on three steel and three aluminium cylinders containing compressed air in our laboratory and under controlled conditions in a climate chamber, respectively. We proved the pressure effect on physisorption for CO₂, CH₄ and H₂O by decanting one steel and two aluminium cylinders completely. The CO₂ results for both cylinders are in excellent agreement with the pressure dependence of a monolayer adsorption model. However, adsorption on aluminium (< 0.05 ppm and 0 ppm for CO₂ and H₂O) was about 10 times less than on steel (< 0.41 ppm and about < 2.5 ppm, respectively). Furthermore, adsorption/desorption effects were minimal for CH₄ and for CO, yet measured on one aluminium cylinder only with a very low mole fraction and requires further attention. In a climate chamber the cylinders were exposed to temperatures between -10 to +50 °C to determine the corresponding temperature coefficients of adsorption. Again, we found distinctly different values for CO₂ ranging from 0.0014 to 0.0184 ppm / °C for steel cylinders and -0.0002 to -0.0003 ppm / °C for aluminium cylinders. The reversed temperature dependence for aluminium cylinders point to significantly lower desorption energies than for steel cylinders and might at least partly be due to temperature and gas consumption induced pressure changes. Temperature coefficients for CH₄, CO and H₂O adsorption were, within their error bands, insignificant. These results do indicate the need for careful selection and usage of gas cylinders for high precision calibration purposes such as requested in trace gas applications.

A2 LONG-TERM CO AND OZONE MEASUREMENTS ON A GLOBAL SCALE FROM IAGOS IN-SERVICE AIRCRAFT.

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The In-Service Aircraft for a Global Observing System (IAGOS) is a European Research Infrastructure for routinely sample the atmospheric composition at high resolution and on a global scale using commercial aircraft (<http://www.iagos.org>). It is the continuation of the former CARIBIC (since 1997) and MOZAIC (1994-2014) programmes. The latter has provided a unique scientific database using five aircraft operated by European airlines over twenty years. IAGOS started in July 2011 with the first IAGOS-CORE instrument installed on a Lufthansa Airbus 340 and has expanded its fleet with six aircraft already in operation (A340/A330), with the goal to operate up to twenty aircraft worldwide and over decades.

We present a technical overview of this IAGOS-CORE instrumentation that continuously sample carbon monoxide, ozone, water vapor and cloud droplets. Optional instruments for measuring either NO_y, NO_x, Aerosols or carbon dioxide and methane are also currently under development within IAGOS. Here, we focus on carbon monoxide and ozone measurements which are performed by optimized, but well known, methods such as UV absorption and IR correlation, respectively. We describe the data processing/validation and the data quality control. Using the two overlapping years, we show that the IAGOS data for ozone and carbon monoxide can be considered as the continuation of the MOZAIC data with the same quality assurance. With already more than 20 and 13 years of continuous ozone and carbon monoxide measurements, respectively, the IAGOS data are particularly suitable for climatologies and trends. Since commercial aircraft are daily operated and several time a day, the near-real time IAGOS-CORE data are also used to observe pollution plumes and to validate air-quality models (see examples in <http://www.iagos.fr/macc>, as done in the frame of the Copernicus atmospheric service, CAMS) as well as satellite products.

ESTIMATION IN CO₂ FLUX IN FOREST OF REGIONAL SCALE BY OBSERVATION OF ATMOSPHERIC CO₂ CONCENTRATION BY TOP-DOWN METHODS

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We estimated the CO₂ flux in forest of regional scale where have a stable wind direction, flat terrain, no anthropogenic emission and to be covered forest by observations that are to measure the CO₂ concentration on ground of a plurality of sites using by CO₂ continuous measurement and the CO₂ concentration of vertical profile from ground to 10,000m at the windward site and the lee site using by CO₂ sonde.

The continuous measurement was composed the CO₂ measurement unit (Li-840 (NDIR)), the switching device of outside air/standard gases and 4 cylinders of standard gas (NIES95 scale). The CO₂ sonde was composed a sonde for measuring temperature, humidity and location information, the balloon filled with helium gas and the CO₂ sensor (NDIR) for measuring the CO₂ concentration. We performed that study at Teshio in the north part of Japan in 2012, at Iriomote Island in the southwest part of Japan in 2013 and at Danum Valley in the Northeast part of Borneo Island in 2014 and 2015.

The CO₂ concentration from an altitude of 0 to 200m in early morning at the lee site was higher than that at the windward site. On the other hand, the CO₂ concentration from an altitude of 0 to 300m in noon at the lee site was lower than that at the windward site.

CO₂ flux in the forest between windward site and lee site was calculated by the distance of the both sites and the CO₂ concentration difference between the both sites. As a result, a value close to CO₂ flux which was determined by bottom-up method was calculated.

A4 Withdrawn

A5 INFERRING 222RADON SOIL FLUX FROM AMBIENT 222RADON ACTIVITY AND EDDY COVARIANCE MEASUREMENTS

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222Radon (^{222}Rn) is a radioactive noble gas that is produced at a constant rate from $^{226}\text{Radium}$, which is relatively uniformly distributed in all soils. When released into the atmosphere ^{222}Rn is transported and mixed in the atmosphere similar to all other gases emitted from, or close to, the surface. This makes ^{222}Rn a very useful tracer in atmospheric sciences. If, for a given area, the ^{222}Rn surface flux is known, ambient measurements of its activity from, for example, a tall tower can be used to ‘calibrate’ the transport component in atmospheric transport models and to calculate the surface flux of a second constituent such as CO_2 . This methodology is known as the ^{222}Rn tracer inversion method. But how to determine the ^{222}Rn surface flux for a large area? Current approaches are either limited by spatial resolution (e.g. chamber measurements), or rely fully on process models.

We propose a novel approach that utilises and combines in-situ measurements of ^{222}Rn activity and CO_2 eddy covariance observations. First we analyse these observations for events where we observe both CO_2 fluxes (i.e. ΦCO_2 ; using eddy covariance) and significant ^{222}Rn and CO_2 mole fraction enhancements above local background values. Then we calculate the ^{222}Rn surface flux from the mole fraction ratio of D^{222}Rn to DCO_2 , scaled by ΦCO_2 , and finally we estimate the observed area influencing our observations using footprint analysis.

To test our approach, we have applied our methodology to synthetic data from an atmospheric transport model (Weather Research and Forecasting model (WRF)) to confirm our method returns the surface fluxes we have put in the model. We also applied the method to ambient observations of CO_2 (both mole fraction and eddy covariance) and ^{222}Rn activity from two measurement sites (Cabauw and Lutjewad, the Netherlands) and we compared these results with estimates from chamber measurements and surface models.

A6 ICOS ATC METROLOGY LAB: METROLOGICAL PERFORMANCE ASSESSMENT OF GHG ANALYZERS.

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In the framework of ICOS, an European research infrastructure aiming to provide harmonized high precision data for advanced research on carbon cycle and greenhouse gas (GHG) budgets over Europe, the Atmosphere Thematic Centre (ATC), located at LSCE in Gif-sur-Yvette, France, includes the Metrology Lab, a facility mainly dedicated to elaborating measurement protocols and evaluating performance of GHG analyzers. The Metrology Lab assesses the ICOS compliance of the analyzers before deployment in the ICOS monitoring station network, but also carries out a technology watch by testing the performance of new instrument, prototype and emerging technology from company and research group. The current species handled by ICOS for continuous measurement are CO₂, CH₄ and CO. However ICOS is targeting in a near future other species such as N₂O and isotopologues of CO₂ and CH₄. Most of the analyzers tested at the Metrology Lab are based on Cavity Enhanced Spectroscopy. The conducted tests consist in characterizing the metrological performance in term of short and long term repeatability, linearity, drift, cross sensitivity with other species, thermal sensitivity, water vapor correction (to derive the dry mixing ratio) among others. For that purpose, the Metrology Lab has at its disposal a lot of sources of stable air (tanks) with different mixing ratios of the targeted trace gas and all the required equipment such as a humidifying bench able to humidify a known mixing ratio gas at different stable H₂O levels without artifact. The presentation will give an overview of the results of the tests conducted at the ATC Metrology Lab and will focus on the water vapor correction performance which will be compared to the use of drying systems.

A7 NETWORK OF CARBON DIOXIDE MEASUREMENTS IN THE SOUTHEAST UNITED STATES – RESULTS FROM THE GULF COAST INTENSIVE

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The Southeastern United States is a dynamic and relatively poorly constrained contributor to the terrestrial carbon balance of North America. Furthermore, the forests of this region are important for the North American carbon balance because they are one of the most productive biomes on the continent, have large biological fluxes, and are sensitive to climate change. The Gulf Coast Intensive (GCI) project seeks to apply recent advances in atmospheric inversion methodology and observational technology to study the carbon balance of North America as a whole with special emphasis, including new terrestrial inventory assessments, on the dynamic and relatively understudied southeastern United States. As part of the GCI, five cavity ring-down spectrometers were deployed on communications towers (~100 m AGL) in March 2015. The network design strategy included minimization of anthropogenic influences (e.g., power plants) while maximizing the data impact of each site. Factors that were taken into consideration were existing observations, land coverage, net ecosystem productivity, fossil fuel emission estimates from Vulcan, and large emission sources such as power plants. Here we present calibration procedures and accuracy assessment, as well as early results from the network.

EVALUATION AND QUALITY ASSESSMENT OF 8 YEARS (2006-2013) OF N₂O AND SF₆ OBSERVATIONS AT LUTJEWAD MONITORING STATION, THE NETHERLANDS

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We evaluate 8 years of continuous observations of N₂O and SF₆ from Lutjewad monitoring station in the Netherlands (6.3529° E, 53.4037° N, 1 m asl) starting from May 2006 onwards. The coastal location of the station provides that relatively clean marine background air can reach the sampling tower in contrast to more polluted air masses coming with the prevalent south-westerly and westerly winds. Ambient air samples are collected from the top of the 60 m monitoring tower, and are cryogenically dried and analysed by an Agilent 6890N GC-system equipped with a μ -ECD, offering about 7 measurements per hour. The data between 2006 and 2012 have been recalculated and quality assessed following the InGOS project (Integrated non-CO₂ Greenhouse gas Observing System) QA/QC protocols aiming at correcting and harmonizing historical non-CO₂ data sets. We obtained an overall measurement precision based on the Target tank reproducibility of <0.4 ppb for N₂O and <0.1 ppt for SF₆ during optimal performance of the GC-system. Instrumental mal-performance and leaks affecting the air sampling and GC-system, as well as data gaps, resulted in the omission and flagging of about 40% of the data. An absolute off-set in the ambient N₂O data between 2006 and 2012 of about -2 ppb has been identified and corrected for, adding ± 0.4 ppb to the total uncertainty. Laboratory tests in order to understand and re-produce this off-set indicated that the problem was associated with different mass flow settings between the ambient and reference sample flows through the sampling loop. The lower boundary of the final corrected time series from Lutjewad follows the general trend observed at the Mace Head continental background station with a mean annual growth rate of ~ 0.7 ppb for N₂O. Also similar to the Mace head results a small positive trend of ~ 0.3 ppt is observed in the SF₆ time series. Episodes of elevated N₂O concentrations in the range of 340-350 ppb are predominantly found with background conditions for SF₆ pointing to a large role for regional emissions from agricultural activities (e.g. use of fertilizers).

A9 ISOTOPE RATIO INFRARED SPECTROMETER TO CONTINUOUSLY MONITOR CARBON AND OXYGEN ISOTOPOLOGUES OF CO₂

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Abstract text: Laser-based Isotope Ratio Infrared Spectrometers (IRIS) offer the potential to perform precise, continuous, in-situ monitoring of isotopologues of trace gases at ambient concentration. We are presenting a middle-infrared laser-based sensor platform that is capable of simultaneously determining both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope ratios of carbon dioxide to precision as low as 0.05‰. Specifically, we access the fundamental bands of CO₂ at 4.2 microns using a difference frequency generation (DFG) laser combined with a simple, direct absorption approach that makes use of a robust multi pass cell and a cryogen free setup.

We will present data from simulations of ambient measurements as well as real world data collected at a greenhouse gas monitoring station. Pure CO₂ was diluted with synthetic air to simulate different applications. A simulation of ambient measurement conditions with a 75 ppm/hour change in CO₂ concentration from 350-650 ppm showed a precision of <0.05‰ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ over 24 hours with 30 min averaging time. Comparison with Isotope Ratio Mass Spectrometer (IRMS) showed differences of 0.046 ‰ and 0.047 ‰, for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively.

The analyzer was deployed to the Lutjewad station (60 m, 6°21'E, 53°24'N, 1 m a.s.l.) in the Netherlands from January 14 to May 28, 2015. The data shows periods of advected urban pollution with enhanced CO₂ concentration. We will show the comparison of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ to flask analysis performed using IRMS as well as a comparison of CO₂ concentrations with in situ measurements from other analyzers.

A10 CHARACTERIZATION OF CONTINUOUS OCS, CO, AND CO₂ MEASUREMENTS AT A TOWER SITE IN LIVERMORE, CA USA

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Carbon monoxide (CO) and carbonyl sulfide (OCS) are promising tracers for partitioning individual flux components of the carbon dioxide (CO₂) budget in areas where strong anthropogenic and biogenic activity can confound the atmospheric CO₂ signal. We have recently deployed a Los Gatos Research, Inc. ® OCS/CO/CO₂/H₂O analyzer at a tower site located at the southeastern edge of Livermore, California USA (Lon: -121.71°, Lat: 37.67°; Alt: 27 m a.g.l., 224 m a.s.l.) with the goal of providing a more informed interpretation of CO₂ variability downwind of the San Francisco Bay Area, a large metropolis of around 7 million people. Here, we present an evaluation of the performance of the Los Gatos OCS, CO, and CO₂ measurements based on calibrations performed using an in situ, automated calibration system over a 5 month period during the first half of 2015. The calibration system delivers multiple calibration source gases to the OCS/CO/CO₂/H₂O analyzer and to other instruments at the site. Standard gases include synthetic whole air standards (with CO₂ referenced to the NOAA/WMO scale) as well as concentrated standards for CO and OCS that are precisely and accurately diluted with zero air to give controllable concentrations in the range of ambient observations. We will report on the design and performance of the multi-source calibration system, short-term (hourly to daily) and long-term (monthly) variability in instrument bias for the different measurement channels, water-vapor corrections for CO and OCS measurements, and an inter-comparison of the CO and CO₂ measurements with those collected simultaneously at the site using different techniques, including a direct comparison with the widely used Picarro CO₂ analyzer (G1301) against a set of three WMO-certified whole air standards.

A11 AMAZON BASIN: AN IMPORTANT SOURCE OF METHANE?

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Tropical land regions have until recently been poorly observed with large-scale integrating in-situ observations. Considering that the Amazon Basin represents 50% of the world tropical rainforest and Methane (CH₄) is the second most important anthropogenic greenhouse gases, contributing with around 18% to radiative forcing, and in 2012 the CH₄ mixing ratio increases of 5ppb in comparison with the previous year, reaching 1819ppb, is important understand the behavior of the Amazon Basin in relation to this greenhouse gas. Then, observing the global importance of CH₄ and uncertainties in the emission of this greenhouse gases this study aimed to determine CH₄ emission in the Amazon Basin. We used regular vertical profiles in 4 sites distributed over the basin from east to west, Alta Floresta (ALF; 8.80°S, 56.75°W), Rio Branco (RBA; 9.38°S, 67.62°W), Santarem (SAN; 2.86°S; 54.95°W) and Tabatinga (TAB; 5.96°S, 70.06°W). Since 2010 samples are collected, fortnightly, aboard light aircraft between 300m and 4.4km. From the flux estimates we calculated basin wide budgets with some differentiation of underlying processes based on carbon monoxide from fires. The results showed that the Amazon Basin was a source of CH₄ during the study period, but the CH₄ emission variable in the different regions and variability with the years, these can be related with the climatological variations, 2010 and 2012 was driers years and 2011 and 2013 was wet years. With these results is possible to observe the importance of conducting studies on a regional scale to elucidate the behavior of the entire Amazon Basin. And the importance of long-term studies due the variation in emissions year by year, so that the results can be assumed to average behavior a long time series is necessary to take into account the methane balance from the Amazon Basin.

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A12 STUDY OF SF₆ CONCENTRATIONS IN AMAZON BASIN AND BRAZILIAN COAST

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SF₆ is one of the most potent greenhouse gases known. Its surface fluxes include anthropogenic emissions from applications in industry and very minor uptake by the oceans. SF₆ is inert throughout the troposphere and stratosphere and is slowly photolyzed in the mesosphere, resulting in an estimated atmospheric lifetime of 3200 years¹. Our interest in SF₆ concentrations is to use this gas as a transport tracer to calculate CO₂, CH₄ and N₂O fluxes over the Amazon Basin. SF₆ atmospheric measurements were started with vertical profiles using small aircrafts, since 2000 in Santarém (SAN; 2.86°S; 54.95°W), 2009 in Rio Branco (RBA; 9.38°S, 67.62°W), 2010 in Alta Floresta (ALF; 8.80°S, 56.75°W) and Tabatinga (TAB; 5.96°S, 70.06°W), all these sites located in Brazilian Amazon Basin. Since 2010, we started flask measurements at two sites located at the Brazilian Atlantic coast: in Salinópolis (SAL; 0.60°S, 47.37°W) and in Natal (NAT; 5.48°S, 35.26°W). The purpose of this study is to present and discuss these measurements. Consistent with other existing records our results show that SF₆ concentrations increased nearly 3.3ppt (71%) between 2000 and 2013, with a mean increase rate of 0.25ppt per year. The concentrations at all our stations are generally similar to other Southern Hemisphere records with the exception of the January to April period for SAL and SAN and the January to March period for RBA, ALF and TAB when concentrations are more similar to Northern Hemisphere records. Examination of air parcel paths using HYSPLIT² for these periods confirmed that some air parcels arriving at these stations have travelled from the Northern Hemisphere to the sites. The NAT concentrations differ and are all year round influenced entirely by Southern Hemisphere air. Finally there are no significant differences between coastal and inland stations confirming the absence of SF₆ sources in the Basin.

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2 Draxler, R.R. and G.D. Rolph (2013), HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://ready.arl.noaa.gov/HYSPLIT.php>), NOAA Air Resources Laboratory, Silver Spring, MD.

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A13 FOUR YEARS CARBON MONOXIDE VERTICAL PROFILES STUDY AT THE AMAZON BASIN

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The Carbon monoxide (CO) has been used like atmospheric biomass burning tracer in different scales. To elucidate the actual contribution and the flux of carbon produced from biomass burning in the Amazon Basin, determine the concentrations of CO is an important tool. Were performed vertical profiles at 4 sites in the Amazon Basin (SAN -Santarém, TAB -Tabatinga, RBA -Rio Branco and ALF -Alta Floresta) 2 times per month over the period 2010-2013 and to calculate the CO flux it was applied the Column Integration Method (Miller et al, 2007). At the 4 locations were identified a correlation between the CO flux, precipitation and counts of fire spots. In ALF, located at Arc of Fire (Arco do Fogo), was observed that the peak of CO emission coincides with the maximum of fire spots and precipitation decreases, thereby making evident the emission from the wet and dry season. This is the site where the highest concentrations of CO were observed and, unlike TAB and SAN, were determined a strong vertical mixing. At the sites, where there is a predominance of forest like TAB and RBA, the observed flux showed the same behavior than ALF, however in a minor emission. SAN, located in the Amazon northeast region, receives a great influence of anthropogenic emissions from the northeast Brazil region. The relation between the concentrations of CO and CO₂ (carbon dioxide) in the profiles was performed, considering only the profiles with a clear plume to determine the emission ratio, where it was used only the portion of profile above 1.5km, approximately the PBL (Planetary Boundary Layer). The 3 sites with fewer anthropic impacts had similar ratio CO/CO₂, in contrast to what was determined in Santarém.

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A14 CO MEASUREMENT ISSUES ENCOUNTERED BY MPI-BGC GASLAB

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The atmospheric variability of carbon monoxide in background atmospheric air is much bigger than for long-lived greenhouse gases like CO₂, CH₄, and N₂O. Therefore, the relative accuracy requirements for CO to capture atmospheric signals as seasonality, regional and inter-hemispheric gradients are less demanding. However, there are complications specific to CO analysis that make accurate CO analysis a challenge, in particular the increase of CO mole fractions in reference gases over time. This problem has been observed by many laboratories including the Central Calibration Laboratory and this has affected the consistency of assignments on the X2004 scale and entails that CCL assignments on the X2014 scale remain tentative since 2012.

In this contribution we will present information on the CO measurements at the GasLab of the Max-Planck-Institute for Biogeochemistry since 2002. We will focus on CO specific issues that have been encountered in the measurement operation like non-linear detector behavior, drifting detector sensitivity, and growth of CO in containers (high pressure cylinders and glass flasks).

A15 A STUDY OF EXTERNAL FACTORS PROMOTING VARIABILITY IN μ ECD RESPONSE

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Previous studies demonstrated that external factors could influence in nitrous oxide (N_2O) analysis performed by gas chromatography (GC) with Electron Capture Detector (ECD). Together with these past studies, to minimize the interferences effects on analyses, since 2012, the analysis were performed in triplicate, enabling a better understanding of the detector variability as it is more than 3500 samples per year in average and to obtain more reliable concentrations. Suspecting that the covariance of N_2O and CO_2 concentrations could be a technical ECD problem, a new detector was acquired to substitute the old one, and the experiments were repeated to verify the interference of external factors in the N_2O analysis. The new detector is a micro Electron Capture Detector (μ ECD), which use Argon – Methane (5%) as carrier gas. This gas provides a higher ECD sensitivity than N_2 or Ar gases (Wang et al., 2010). The pre-column and column used were both stainless steel 3/16" ED, 183cm length, packed with HayeSep® Q 100/120 mesh. Loop with 15ml volume and oven with constant temperature of 70°C. The μ ECD temperature was 350°C. The tests involved variation in the room temperature and carbon dioxide (CO_2) concentrations. The room temperature is controlled by a regular air conditioning system which varies $\pm 1^\circ C$ of the set temperature. The CO_2 source used was dry ice as it is moist and heat free. Both the studied external factors showed interferences in μ ECD response. These studies are relevant as N_2O is the third most important natural greenhouse, then the efforts in produce a better precision is very valuable and ECD is the most used detector to analyze N_2O in reference laboratories.

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A16 A SENSITIVITY STUDY ON THE ESTIMATION OF CONTINUOUS ANTHROPOGENIC CO₂ USING CO₂, CO, $\delta^{13}\text{C-CO}_2$, O₂/N₂ AND $\Delta^{14}\text{C-CO}_2$

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In order to close the greenhouse gas budget on regional scale, inverse transport models use greenhouse gas measurements at different stations. For CO₂, a differentiation of measured CO₂ concentration into contributions from the biosphere and from fuel CO₂ burning is necessary to allow separating biogenic and anthropogenic CO₂ emissions. Various tracer-based approaches exist to estimate anthropogenic CO₂ continuously, such as CO₂ alone, as well as the additional surrogate tracers CO, $\delta^{13}\text{C-CO}_2$, O₂/N₂ and potential future continuous $\Delta^{14}\text{C-CO}_2$. Simulated concentration records of these surrogate tracers are used to investigate different approaches of anthropogenic CO₂ estimation at three hypothetical stations representing rural, urban and polluted conditions. We find that tracer-based anthropogenic CO₂ cannot reliably be estimated continuously at rural sites due to the low signal-to-noise ratio. However, at more polluted sites, different tracer configurations are possible: $\Delta^{14}\text{C-CO}_2$ with a precision of 5 ‰ as may potentially be available in near future seems most promising in terms of precision (precision of anthropogenic CO₂: 10-20 ‰), but the inability to detect biofuel emissions may lead to significant biases if not accounted for. A good alternative are precise $\delta^{13}\text{C-CO}_2$ measurements (precision of anthropogenic CO₂: 30%) if all CO₂ sources in the catchment area are well characterized with respect to their isotopic signature. CO and O₂/N₂ are slightly less promising for fuel CO₂ estimation due to non-fuel CO contributions and measurement imprecision of O₂/N₂, respectively. Finally, we compare different calibration strategies for the surrogate tracers and find using a limited number of precise $\Delta^{14}\text{C-CO}_2$ measurements on grab samples is most promising and leads to mean biases of anthropogenic CO₂ of typically below 10% without significant diurnal discrepancies. This should allow for a significant improvement in terms of validation and bias reduction of highly resolved emission inventories using atmospheric observations and regional modelling.

A17 AIRCORE OBSERVATIONS OF CO₂ /CH₄/CO OVER THE SODANKYLÄ TCCON SITE

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As an essential network to validate satellite observations, Total Carbon Column Observing Network (TCCON) observations of CH₄, CO, and CO₂ need to be tightly linked to ground-based observations, i.e. on the WMO reference scale. AirCore, a long coil of tubing with one end open and the other closed flown with a balloon, has been demonstrated to be a reliable tool for vertical profile measurements from the surface up to ~30 km and has a great potential for accurately linking in situ with space-based remote sensing measurements (e.g. S5P, GOSAT, and OCO-2).

We report the recent development of the AirCore technique, with an automatic valve that is capable of closing the coil a couple of seconds after landing to prevent the loss of air sample. We use a fill gas with a high CO concentration of 8,000 ppb to mark the top and the bottom of the AirCore profile. Furthermore, the fill gas remaining in the AirCore after each flight is accurately determined and is used to calculate the equivalent altitude ceiling at which air sample starts flowing into the coil, which demonstrates the importance of reducing the pressure drop across the dryer of the AirCore to effectively collect air sample at the top of the balloon flight. We also compare AirCore profiles from multiple AirCores that were either flown on the same flight or on two flights that were launched next to each other. Moreover, we present nearly two-year AirCore profiles of CO₂ /CH₄/CO over Sodankylä since September 2013 and evaluate the TCCON retrievals with the integrated AirCore column averages.

A18 COMPARISON OF CARBON DIOXIDE MIXING RATIOS FROM IN-SITU MEASUREMENTS BY NDIR AND CRDS ANALYZERS AND BOTTLE SAMPLING MEASUREMENTS AT HATERUMA ISLAND

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We compared mixing ratios of the atmospheric carbon dioxide (CO₂) measured by several techniques at Hateruma monitoring station (HAT, 24.06°N, 123.81°E) during a period of January to March 2015. Two NDIR analyzers (Shimadzu XURA-207 and LI-COR LI-7000) and a CRDS analyzer (Picarro G2401) were used for the in-situ CO₂ measurements. The air samples were also collected into 2.5L glass bottles by using two sampling systems: an automated regular sampling system at intervals of 4 days and a remote-controlled event sampling system. The bottle samples were sent back to our laboratory and the CO₂ mixing ratios were determined by another NDIR analyzer (LI-COR LI-6252). The sample air, drawn by diaphragm pumps from the top of tower (46 m a.s.l.), was introduced into the CRDS analyzer and the two bottle sampling systems through three individual sampling lines and into the two NDIR analyzers through another one sampling line. Before the in-situ measurements and the bottle samplings, the sample air was dried to dew points of -80°C and -40 °C for the NDIR analyzers and the sampling systems by cold traps and to a dew point of -40 °C for the CRDS analyzer by a Nafion dryer. The NDIR and CRDS analyzers were calibrated against NIES 09 CO₂ scale every 3 and 25 hours, respectively. We achieved some improvements for the measuring systems until the end of 2014. The measured CO₂ mixing ratios agree with each other within +0.1 ppm. Average of the CO₂ mole fraction differences were -0.04 ± 0.14 ppm (LI-7000 - XURA-207) and -0.02 ± 0.11 ppm (G2401 -XURA-207).

A19 NOAA/GMD STANDARDS PREPARATION AND CO₂ CALIBRATION TRANSFER

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Designated by the World Meteorological Organization as the Central Calibration Laboratory for ambient measurement of CO₂, CH₄, CO, and N₂O. Atmospheric trace gas in-natural-air standards are prepared in aluminum high pressure cylinders and calibrated for high precision trace gas measurement. The mixing ratios of CO₂, CH₄, CO, N₂O and SF₆ and the isotopic ratios of CO₂ can be targeted, providing a set of differing mole fraction working standards for precision measurement of ambient air. Standards preparation, use considerations, stability, and CO₂ calibration transfer are now ISO compliant. Historically this program has grown to produce more than 450 standards per year for NOAA/GMD and WMO/GAW atmospheric measurement groups.

A20 RESULTS OF FLASK AIR SAMPLING INTERCOMPARISON PROGRAMS AT THEALERT, NUNAVUT GHG COMPARISON SITE

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High precision atmospheric measurements in greenhouse gas concentrations and CO₂ isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) provide valuable information in determining the magnitude and distribution of carbon sources and sinks and of various controlling processes on both regional and global scales. Systematic biases amongst various data sets (obtained from different laboratories) may lead to improper scientific understanding and carbon budget estimates. For more than a decade, WMO has set a global network compatibility target goal for CO₂ of ± 0.1 ppm (± 0.05 ppm in the southern hemisphere). In order to provide long-term estimates appropriate to certain emission scenarios, target goals have been set for other trace gases and isotopes as well, including $^{13}\text{C}\text{-CO}_2$ and $\delta^{18}\text{O}\text{-CO}_2$. Scientists present at the 13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, September 19-22, 2005 in Boulder, CO, U.S.A., recommended the WMO/GAW sites at Alert, Mauna Loa and Cape Grim serve as Greenhouse Gas Comparison Stations. These flask air sampling intercomparison programs can provide a mechanism to monitor differences between individual network global data sets and to indicate whether WMO compatibility goals have been achieved. At Alert, flask sampling inter-comparison programs have been conducted between seven different international laboratories. Results from the years 2005-2013, will be summarized in this presentation.

A EUROPEAN-WIDE INTERCOMPARISON OF ATMOSPHERIC ²²²RADON AND ²²²RADON PROGENY MEASUREMENTS

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²²²Radon (²²²Rn) is a short-lived radioactive noble gas (half-life time $T_{1/2} = 3.8$ days) that is produced in all soils from the radioactive decay of ²²⁶Radium (²²⁶Ra), a member of the primordial ²³⁸Uranium decay series. As the first gaseous constituent in this series, ²²²Rn has a chance of escaping from the (unsaturated) soil zone into the atmosphere. The only sink of ²²²Rn is its radioactive decay. The ²²²Radon flux from ocean surfaces is almost zero. As the continental ²²²Rn exhalation rate and its spatial and temporal variability are relatively well known, ²²²Rn can serve as a quantitative tracer for atmospheric boundary layer mixing and transport model validation. Due to its increasing use in these applications, the number of atmospheric ²²²Rn measurements has greatly increased in the last decade, with several fundamentally different analysis systems applied, either measuring ²²²Rn directly or via its short-lived progeny in the atmosphere. Comparable calibration of the different measurement systems is, however, principally impossible. Therefore, within the EU-funded project InGOS, we conducted a European-wide ²²²Radon/²¹⁴Polonium intercomparison of the various types of monitors in use at European atmospheric monitoring stations. Our aim was to determine correction factors that could be applied to existing (and future) observations to harmonise the data as input for regional atmospheric transport model validation in Europe. Two compact and easy-to-transport Heidelberg Radon Monitors (HRM) (one-filter systems) were sent around to run for at least one month at each of the eight European measurement stations included in the intercomparison. Linear regressions of the resulting parallel atmospheric ²²²Rn data sets were calculated, yielding correction factors relative to the HRM ranging from 0.68 to 1.45. For the stations that use one-filter systems, preliminary ²¹⁴Po/²²²Rn disequilibrium factors were also estimated, which decreased with height above local ground. Our study clearly demonstrates that significant corrections need to be applied to existing ²²²Rn and ²¹⁴Po activity concentration data in order to obtain a consistent European ²²²Radon data set for model validation.

A22 COMPARISONS OF CO₂ AND OTHER GREENHOUSE GASES SAMPLED BY THREE DIFFERENT METHODS IN THE CONTRAIL PROJECT

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Since 2005, we have conducted an observation program for greenhouse gases using the passenger aircraft of the Japan Airlines named Comprehensive Observation Network for TRace gases by AirLiner (CONTRAIL). We now use 3 types of equipment onboard the Boeing 777: 1) Continuous CO₂ Measuring Equipment (CME), 2) Automatic air Sampling Equipment (ASE), and 3) Manual air Sampling Equipment (MSE). Over the past 10 years, CMEs have collected more than 6 million in-situ CO₂ data from about 12000 flights between Japan and Europe, Australia, North America, or Asia. The large number of CME data enable us to well characterize spatial distributions and seasonal changes of CO₂ in wide regions of the globe especially the Asia-Pacific regions. Observations by ASE and MSE address monitoring spatial distributions and temporal changes in mixing ratios of other important greenhouse gases such as CH₄, N₂O and SF₆. These air samplings have been conducted mainly along two flight routes over the Pacific (between Sydney and Tokyo) and the Eurasia continent (between Paris and Tokyo). We started MSE samplings in 2014 to fill the data gap along the above flight routes when ASE sampling cannot be operated due to changes of aircraft assignment. Japan Airlines personnel or a researcher onboard the aircraft manually collects air samples using a manual diaphragm pump through the air-outlet nozzle in the cockpit. We compared CO₂ data obtained from ASE, MSE and CME during the same flights, finding good agreements within 0.5 ppm. In this presentation, we also show time series of the other greenhouse gas mixing ratios obtained by ASE and MSE with clear seasonal variations and long-term trends in the upper troposphere/lower stratosphere over the Eurasia continent.

A23 INTER-COMPARISON EXPERIMENTS OF STANDARD GASES FOR JMA/WCC ACTIVITY

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Japan Meteorological Agency (JMA) serves as the World Calibration Centre (WCC) for methane (CH₄) and the Quality Assurance/Science Activity Centre (QA/SAC) in Asia and the South West Pacific within the framework of the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO). The WMO/GAW program has set a goal for all participating institutions measuring atmospheric CH₄ to report data on the internationally common CH₄ standard scale. Thus, the JMA/WCC has carried out intercomparison experiments of CH₄ reference gases in co operation with NOAA/ESRL (WMO/CCL, USA), CSIRO (Australia), NIWA (New Zealand), CMA (China), KMA/KRISS (the Republic of Korea), IITM (India), and several Japanese laboratories. The purpose of the JMA/WCC intercomparisons is to determine the differences of their CH₄ standard scales as well as to monitor the long term stability of standard gases in Asia and the South West Pacific regions. We report the all results of the past intercomparison experiments of CH₄ since 2002, which are posted on the JMA/WCC web site (<http://ds.data.jma.go.jp/gmd/wcc/wcc.html>).

On the other hand, the JMA and major observation laboratories in Japan have established a domestic alliance with the National Metrology Institute of Japan (NMIJ/AIST) in harmony with the BIPM/WMO MOU in the international sector. Base on this alliance, we started a series of intercomparison exercises named iceGGO (Inter Comparison Experiments for Greenhouse Gases Observations) in 2012. Not only CH₄ but also CO₂ and CO reference gases were circulated to compare their measurements. The iceGGO results could provide more detailed information about the standard gas scales as well as calibration methods used in the Japanese community.

We would like to acknowledge all participants for supporting our JMA/WCC activities.

A24 RECENT ACTIVITIES OF WMO GAW WORLD CALIBRATION CENTRE-SF₆

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Korea Meteorological Administration (KMA) was designated as World Calibration Centre for sulfur hexafluoride (WCC-SF₆) in 2012 and has conducted its roles for WMO GAW communities. The key tasks of WCC-SF₆ are i) developing of guidelines for SF₆ measurements, ii) performing audits for GAW stations of SF₆, iii) conducting inter-comparison experiments (e.g., round robin experiments), and iv) training of station personnel to make the GAW station keep compatibility goals and traceability for their data quality control for SF₆. During last 2 years WCC-SF₆ has developed a technical note named as Various analytical methods of atmospheric SF₆ using GC- μ ECD, which deals with a conventional Gas Chromatography coupled with Electron Capture Detector (GC-ECD) using pre-concentrator and fore-cutting/back flush method. It can be accessed on webpages of WMO GAW and WCC-SF₆. We have prepared for audit procedures, check-lists, and travelling standard gases. We have a plan to have an audit on the Cape Point station in South Africa in 2016 and support the Pune station in India build up the SF₆ measurement system in 2015. The 1st round-robin experiment on SF₆ will be started in 2015. We prepared tertiary standard gases for the experiments, whose concentration values are in an excellent agreement with those of GAW Central Calibration Laboratory for SF₆. Since 2009 KMA has held Asia-Pacific GAW Workshop on Greenhouse gases (APGG). WCC-SF₆ has implemented the task for training and education through this workshop as supporting those people who are interested in greenhouse gas measurements. From last year we extended its period as including training and education course to offer an opportunity to learn practical and applicable skills of SF₆ analysis. We will provide 3-day WCC-SF₆ training and education course before the APGG this year. The information can be accessed on webpages of the WMO GAW as well as WCC-SF₆.

A25 ASSESSING THE IMPACT OF C₂H₆ ON ATMOSPHERIC δ¹³CH₄ MEASUREMENTS AT INDUSTRIAL SITES WHEN USING A CAVITY RING DOWN SPECTROMETER

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CRDS is now a common technique used to make methane (CH₄) isotopic measurements ranging from biogenic to anthropogenic sources [Phillips et al. 2013, Fisher et al. 2011]. The ability to distinguish between different sources is essential for correctly quantifying CH₄ anthropogenic emissions which are important due to their high global warming potential and large emission uncertainties [Allen et al. 2014]. Many fossil fuel based CH₄ sources have a large ethane (C₂H₆) content [Rudolph 1995]; however, during laboratory tests we discovered that C₂H₆ has the potential for cross-sensitivity on the measured δ¹³CH₄. In order to use CRDS to characterize sources it is vital to understand and quantify interferences on δ¹³CH₄ measurements. Our instrument, a G2201i Picarro (Santa Clara, USA) measures C₂H₆ with sensitivities to CO₂ and H₂O. We performed controlled experiments varying these parameters to calculate the corresponding correction factors: [C₂H₆]Corrected=[C₂H₆]Raw+0.89%H₂O +0.00014ppmCO₂. A dilution series was performed using a C₂H₆ standard (51.6ppm in nitrogen) and C₂H₆-free air to characterize the δ¹³CH₄ correction which has been calculated as: δ¹³CH₄=[δ¹³CH₄]Raw+3.44‰. These results agree well with that of a recently published independent study [Rella et al. 2015] however also demonstrate the heterogeneous character of CRDS instruments in regards to the C₂H₆ cross-sensitivity and highlights the requirement for determining correction factors for each instrument individually. The correction has been utilized on measurements taken at a natural gas site to assess their impact in a real-world application. Isotopic signatures calculated using the Keeling plot method display a shift of up to -4. The dilution series was subsequently used to calibrate the C₂H₆ measurements with an existing gas chromatograph [Chrompack Varian 3400, Varian Inc, USA], this facilitated the calculation of the C₂H₆:CH₄ ratio for both observations and sources: Robs= 0.012 – 0.049, Resource= 0.057 – 0.092 which is compared to existing inventories.

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A26 FOSSIL FUEL AND BIOGENIC PARTITIONING IN CO₂ EMISSIONS FROM EAST ASIA DETERMINED BY HIGH-FREQUENCY RADIOCARBON MEASUREMENTS AT HATERUMA ISLAND

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We developed and installed a remote-controlled air sampling system at Hateruma Island, Japan (HAT, 24°03'N, 123°48'E) to collect air samples of Asian outflow with high CO₂ concentrations in winters. We made high-frequency air samplings (several-hour intervals) to capture the rapid CO₂ variations and analyzed radiocarbon in CO₂ using the Compact AMS (Accelerator Mass Spectrometry; NEC 1.5SDH 500kV) performed by Paleo Labo Co., Ltd., Japan.

We analyzed $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in ~100 samples of 13 high-CO₂ events. We observed CO₂ increases of 10–20 ppm from the background level (d[CO₂]) in these events. Fossil fuel-derived CO₂ component (Cff) was calculated as, $\text{Cff} = \text{Cobs}(\Delta^{14}\text{C}_{\text{bg}} - \Delta^{14}\text{C}_{\text{obs}}) / (\Delta^{14}\text{C}_{\text{bg}} + 1000)$, where Cobs is the observed CO₂ mixing ratio (ppm), $\Delta^{14}\text{C}_{\text{bg}}$ and $\Delta^{14}\text{C}_{\text{obs}}$ is the background and observed $\Delta^{14}\text{C}$ (‰), respectively. We found regional differences in the Cff/d[CO₂] ratio: The Cff/d[CO₂] ratio was lower for the air from China (61% in average) than from others (Japan and Korea) (81% in average). This suggests larger CO₂ emissions from biosphere over China in winter. We also used $\delta^{13}\text{C}$ and Keeling plot approach to identify the source of Cff. The results show that the $\delta^{13}\text{C}$ value in the air from East China and Yellow Sea is higher than the other events, but with some exceptions. The result is consistent with larger CO₂ emission from cement productions (limestone) in China than in Japan and Korea.

A27 TESTING THE DELTA RAY INSTRUMENT TO MEASURE ISOTOPE RATIOS OF CARBON DIOXIDE IN AIR UNDER LABORATORY CONDITIONS AND AT BARING HEAD, NEW ZEALAND

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New technologies enable in situ measurements of stable isotope ratios in atmospheric carbon dioxide. These technologies may open the window to future observations in remote locations with unprecedented temporal resolution. The Delta Ray instrument (Thermo Fisher Scientific, Bremen, Germany) measures carbon and oxygen isotope ratios in carbon dioxide at atmospheric levels with a maximum temporal resolution of 1Hz. The measurement precision of the Delta Ray is specified with 0.05 ‰ for both isotope ratios, which sits between the compatibility and the extended compatibility goals formulated during the WMO GGMT - 2013 meeting.

In this study, we test the performance of the Delta Ray instrument in the laboratory and during a 26 day trial period at Baring Head, NIWA's remote atmospheric monitoring station. We found a minimum Allan variation of 0.03 ‰ for both isotope ratios and of <0.01 ppm for mole fractions of carbon dioxide at integration times of 200 and 300 s, respectively. One laboratory experiment was designed to measure air from two high pressure cylinders by switching back and forth between the two cylinders. These measurements show paralleling variations which suggests that external factors, such as room temperature, impacted identically on the measurements of each cylinder. Further analysis of the measurements including diagnostic data is needed to evaluate the robustness of our atmospheric observations. So far, the Delta Ray seems a promising tool for autonomous observations of stable isotope ratios in atmospheric carbon dioxide at remote locations. The corrected carbon isotope ratio data from the deployment at Baring Head show interesting variations with amplitudes of up to 0.5 ‰. We present our referencing scheme and discuss our results in the context of synoptic changes and further instrumental records from Baring Head.

A28 CHARACTERIZATION OF THE RESPONSE OF CAVITY RING-DOWN SPECTROMETER METHANE STABLE ISOTOPIC RATIOS TO CHANGES IN METHANE CONCENTRATION

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The impact of increased natural gas activities on the atmosphere through fugitive emissions is largely unknown and unmonitored. An ongoing study measures methane concentrations using cavity ring-down spectrometers (CRDS) from four tower locations in the Marcellus Shale region of northeast Pennsylvania. The CRDS is capable of measuring the methane stable isotope ($^{13}\text{CH}_4$) with a precision of 0.4 ‰ (5 min. average), which can be used to deduce the array of sources (cattle, landfill, natural gas) likely to impact the tower measurements. We developed laboratory and field calibration standard procedures to characterize the response of the isotope measurement to ambient concentrations of methane. We describe these approaches and discuss their utility for potentially improving the precision of the $^{13}\text{CH}_4$ isotope measurement to below 0.1 ‰, and interpreting the in situ concentration measurements from the towers.

A29 INSTALLATION AND CURRENT STATUS OF CAMS SYSTEM AT NIES

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^{14}C measurement is useful to estimate fossil carbon contribution on atmospheric CO_2 . In 2014, compact carbon AMS (NEC 1.5SDH) were put into operation at NIES to be applied for our observational projects on global and regional carbon cycle, including GOSAT/GOSAT2 projects. NIES-CAMS system is based on a 0.5MV tandem pelletron accelerator with a cesium sputtering ion source and a 134-sample holder.

We analyzed IAEA reference materials (C-1 ~ C-8) for accuracy evaluation of measurements by CAMS. The measured values were close to IAEA consensus values with a maximum difference of 0.64 pMC (C-2), suggesting that CAMS covered fairly wide range of Libby age 60,000 to present.

We produced two whole air reference cylinders, KAS (CO_2 381.5 ppm) and TH1 (CO_2 418.5 ppm, added industrial ^{14}C -free pure CO_2), to keep consistency on ^{14}C scale for atmospheric $^{14}\text{CO}_2$ measurement. We had been analyzed atmospheric $^{14}\text{CO}_2$ at Paleo Labo Co., Ltd, including KAS and TH1 reference air samples. This time, we re-evaluated KAS and TH1 using NIES-CAMS and found that those values agreed with the previous values by Paleo Labo although our data had relatively larger variations than their data.

Furthermore, as $^{14}\text{CO}_2$ inter-comparison activity we joined, two CO_2 samples (FARI-A, FARI-B) distributed by NOAA were converted to graphite by our newly designed compact vacuum line and measured by NIES-CAMS with our reference CO_2 . Measured values for inter-comparison samples matched reasonably with reported values from other laboratories. Thus, it was concluded that the $^{14}\text{CO}_2$ measurements using NIES-CAMS were considerably reliable by our initial experiments.

In order to get higher accuracy measured values from NIES-CAMS, it is important to improve method of making graphite and to search for optimal condition of CAMS analysis.

A30 STABLE ISOTOPE MEASUREMENTS ON AIR SAMPLES FOR THE ICOS NETWORK

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The Integrated Carbon Observation System (ICOS) is a European monitoring network designed to provide long-time harmonized, high accuracy data on greenhouse gases (CO₂, CH₄, N₂O...) with high spatial and time resolution. Supplementary information to quantify greenhouse gas sources and sinks can be obtained from the isotopic composition of these gases. One task of the central analytical laboratory ICOS-CAL is therefore to measure the isotopic composition CO₂ in air samples collected at the European measurement stations.

We report on measurements of stable CO₂ isotopes in air samples ($\delta^{13}\text{C}(\text{CO}_2)$ and δ^{18}

O(CO₂)) and present the analytical system for the measurements of O₂ /N₂ , Ar/N₂ and CO₂ /N₂ ratios in air samples that is currently set up. The CO₂ stable isotope scale is currently synchronized with the primary scale at the MPI-BGC Isolab (IRAS06). most recent results will be presented.

A31 RADIO-METHANE PROCESSING AND MEASUREMENT AT CU-INSTAAR

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We report here on method development and initial results of a new radio-methane processing capability at CU-INSTAAR, for AMS measurement at UC-Irvine.

The INSTAAR methane conversion line is similar to those described by Lowe et al. [1991] and Petrenko et al. [2008], but scaled up to provide for high-precision $\Delta^{14}\text{C}$ measurement at ambient atmospheric methane levels without pre-concentration. Briefly, ~ 400 L of air is extracted from high-pressure cylinders at 1.5 L/min and flowed across a series of high-efficiency cryogenic traps to remove water and CO_2 . CO is oxidized over SOFNACAT and the resultant CO_2 removed by additional cryogenic trapping. Residual air is then combusted over platinized glass wool to yield CO_2 from (primarily) CH_4 . The yield is quantified and the process CO_2 transferred to flame-sealed tubes for eventual graphitization and measurement using procedures optimized for high precision measurement of atmospheric $\Delta^{14}\text{CO}_2$ [Turnbull et al., 2007]. Small excess process yields of $\sim 1\%$ are attributable to breakthrough of native CO_2 and possible condensation of ambient CO_2 via leaks- constituting a potential $\Delta^{14}\text{C}$ measurement bias of ~ 0.4 per mil, which is small relative to ambient atmospheric $\Delta^{14}\text{CH}_4$ of $\sim +350$ per mil. Reproducibility of the measurement is evaluated primarily by analysis of replicate extraction aliquots of authentic samples.

Initial results include replicate $\Delta^{14}\text{CH}_4$ measurements in whole air samples collected in high-pressure cylinders at Niwot Ridge, CO and samples obtained approximately every three weeks at two locations in Alaska (Barrow Observatory and near Fairbanks) from mid-2012 to present, in collaboration with investigators of the NASA-supported Carbon in Arctic Reservoirs Vulnerability Experiment (CARVE) project at JPL and NOAA/ESRL. Using a simple one-dimensional interpretative model, the CARVE $\Delta^{14}\text{CH}_4$ measurements and companion measurements of CH_4 mole fraction and $\delta^{13}\text{CH}_4$, we attempt to quantify the fraction of aged, warm-season methane emissions from wetlands and/or degrading permafrost.

A32 RISING GLOBAL METHANE – USING $\delta^{13}\text{C}$ IN CH_4 TO DECIPHER THE CAUSES

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High-precision measurement of stable isotopes offers powerful tools in understanding why the atmospheric methane burden is increasing. Isotopes can help characterize inputs into local and regional air masses, to identify sources, and to apportionate the regional source mixes into global budgets. Growth in atmospheric methane began in 2007, both in the southern hemisphere and the Arctic, and has continued since then, with an extremely strong rise in 2014. With the growth came a marked shift in $\delta^{13}\text{CCH}_4$, to more negative values. This shift implied either a change in source mix, or a change in the OH sink. Globally, destruction rates of methane by the OH radical appear to have been stable: thus the likely implication is that isotopically depleted sources have increased.

A key problem is that, away from the developed northern hemisphere, isotopic characterization of methane sources is lacking. In particular, in the tropics there has been very limited measurement of characteristic $\delta^{13}\text{CCH}_4$ values from tropical wetlands, biomass burning, and ruminants in low intensity agriculture. The 'Keeling plot' technique is extremely valuable here: by collecting a suite of air samples up and downwind from sources, or in diel campaigns, the $\delta^{13}\text{CCH}_4$ values of methane actually emitted to the air can be determined (and may be somewhat different from results from chambers or other conventional methods). This method can be applied in swamps, near fires, and also from aircraft, both close to source or at distances of thousands of kilometres. However, the method needs high-precision (0.05‰) offline analysis by mass spectrometry: unless the source is very close, the precision of continuous optical methods is inadequate.

Using $\delta^{13}\text{CCH}_4$ values from Keeling plots of tropical and boreal/Arctic sources, and the geographic distribution of growth, the most likely interpretation of the recent rise in methane is that increases may have come from boreal wetlands during the anomalous Arctic summer of 2007, and then from tropical wetlands after heavy rainfall in the S. American and African tropics, from 2010-11 onwards. Tropical agricultural emissions may also have grown. In 2014, it is possible that South American wetlands may have contributed, as well as the global high temperatures. While fossil fuel emission may also have grown, the isotopic shift and the tropical and Southern Hemisphere origins of much of the growth, suggest direct anthropogenic sources were not the dominant factor in the recent increase.

A33 ONLINE MEASUREMENTS OF GREENHOUSE GASES AND CARBON ISOTOPES IN A CO₂ EXTRACTION SYSTEM USING A CAVITY RING-DOWN SPECTROMETER

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Cavity ring-down spectrometers are now commonly used for isotopic measurements of CO₂ with applications ranging from paleoclimate research (e.g. Onac et al., 2013) to urban atmospheric studies (e.g. Turnbull et al., 2011). With the emergence of more robust and compact table-top accelerator mass spectrometers (Synal et al. 2007) there is a large potential for increased use of radiocarbon in atmospheric studies. In preparation of the installation of the ECHO-MICADAS system at LSCE in 2015/2016, a new CO₂ extraction system for whole-air samples was developed. At first the extraction efficiency and fractionation of the system was determined. Afterwards, a cavity ring-down spectrometer (G2201i, Picarro INC, Santa Clara, USA) was coupled to the system to allow online measurements of CO₂, CH₄ and $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$ during the extraction process. The coupled setup allows extracting of ca. 10 samples per day and typically yields 0.2mgC to 0.6mgC when optimizing for extraction time and measurement time for the G2201i. The fractionation (lack thereof) was verified by analyzing the pure samples using an Optima IRMS (Isoprime INC, Manchester, UK). The typical precision for GHG and carbon isotope measurements was determined in previous tests to be ca. 1ppb for CH₄, 0.07ppm for CO₂, 0.1permil for $\delta^{13}\text{C-CO}_2$ and 0.6permil for $\delta^{13}\text{C-CH}_4$ for 5 minute averages. The system was tested extensively and used to extract multi-samples of an urban measurement campaign in 2015 to validate the routines.

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Synal et al. 2007, MICADAS: a new compact radiocarbon AMS system 2007 *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*

B1 AN ASSESSMENT OF AIR POLLUTION LEVELS IN ATHI RIVER TOWNSHIP AND OLKARIA ECOSYSTEMS, KENYA

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Air pollution monitoring and modelling has evolved in the recent past into a fully-fledged branch of atmospheric science with various environmental institutions setting up divisions in charge of air quality. The increased concentration of greenhouse gases (GHGs) in the atmosphere is central to environment, weather and climate monitoring and ultimately contributes to global climate change. The Global Atmospheric Watch (GAW) program runs air pollution monitoring activities in Kenya through the Kenya Meteorological Service (KMS). This presentation traces the evolution of air pollution monitoring activities by KMS, since 1999 to the latest analysers for various gases such as Ozone (O₃), Carbon Monoxide (CO), Carbon Dioxide (CO₂), Nitrogen Oxides, Sulphur Dioxide (SO₂), Hydrogen Sulphide (H₂S), Black Carbon (soot), Ammonia (NH₃), Suspended Particulate Matter and others. In the end, this presentation will examine two case studies of air quality assessment campaigns in two ecosystems (urban and rural) in Kenya; Athi River Township and KenGen Olkaria Geothermal Power Station (KOGPS). Data from field experiments will be presented showing variation of various GHGs, hydrocarbons, nitrogen and sulphur compounds among others. Preliminary results obtained indicate that there is high concentration of some pollutants in the urban site far much beyond the WHO air quality guidelines such PM₁₀ and PM_{2.5} particulate matter, while the KOGPS indicates very low concentration of some pollutants. These pollutants have adverse health impacts on human. Although the other pollutants are below the WHO set standards, this study finds that there is need to reduce their prevalence, particularly, exposure to residents over considerable longer time duration

B2 GGMT-2015 IZAÑA STATION UPDATE: INSTRUMENTAL AND PROCESSING SOFTWARE DEVELOPMENTS, SCALE UPDATES, AIRCRAFT CAMPAIGN, AND PLUMBING DESIGN FOR CRDS

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Izaña observatory (IZO) is a GAW Global station located at 2373 m a.s.l. on Tenerife (Canary Islands, Spain). Several atmospheric greenhouse gases (CO₂, CH₄, N₂O and SF₆; and the related tracer CO) are measured in situ and continuously at this station. The recently published WMO/GAW report N. 219 (“Izaña Atmospheric Research Center Activity Report 2012-2014”) provides detailed information about the different measurement programmes of this supersite. Firstly, we summarize the changes/developments introduced in the IZO GHG measurement systems and data processing software operative at Izaña station. Secondly, we briefly discuss the stability of the IZO laboratory standards after their recent recalibration at the GAW CCLs (NOAA-ESRL-GMD), and the impact of the scale updates we have recently implemented (for CO₂, N₂O and SF₆) in the time series of IZO GHG measurements. Thirdly, it is briefly mentioned that after GGMT-2013 we finished adapting the IZO GHG in situ measurement systems to be able to measure also discrete samples collected on board aircrafts using a quasi-automatic sampler (a PCP with a PFP) and we participated in the MUSICA-AMISOC aircraft campaign: 7 scientific flights were carried out between 21th July and 1st August 2013 above the ocean to the south of IZO. Finally, we detail the plumbing scheme we have designed for the GHG CRDS we are going to install at IZO, which takes advantage of the fact that there are technical personnel at the station every day; and the improvements that are going to be implemented in the inlet systems of the rest of instruments are briefly mentioned.

GREENHOUSE GASES MONITORING AT CHACALTAYA GAW STATION, BOLIVIA

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The Chacaltaya GAW Station (CHC) in Bolivia (16.21°S / 68.08°W / 5240 m.asl), operated by the Laboratory for Atmospheric Physics (LFA) at Universidad Mayor de San Andres (LFA-UMSA), was equipped in 2011 by an international scientific consortium with many analyzers for high precision monitoring of aerosols properties and greenhouse gases. Atmospheric CO₂ mole fraction was first measured with NDIR instrument (Licor-6252) from December 2011 to August 2014. From May 2014 onwards, measurements are made with a CRDS analyzer (ESP-1000) which enable additional measurements of CH₄ and H₂O. Both instruments are regularly calibrated with standard gases traceable to the WMO reference scales. Since 2014 air samples are also regularly collected in bags for analysis of $\Delta^{13}\text{C-CH}_4$ at RHUL. Our presentation will summarize the observed CO₂ and CH₄ variabilities from diurnal to interannual scale. Based on collocated measurements we will evaluate the influence of La Paz urban conglomerate located approximately 20 km in straight line from the station, and by using back-trajectories we will differentiate signals of air masses originating from the Pacific Ocean from air masses lifted up from the Amazon basin.

B4 THE DETERMINATION OF REGIONAL CO₂ MOLE FRACTIONS AT THREE WMO/GAW REGIONAL STATIONS IN CHINA

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The identification of atmospheric CO₂ observation data which is minimally influenced by very local emissions / removals is essential for the estimation of trend analysis, regional sources and sinks, and for modeling of long-range transport of CO₂. Four data filtering approaches were applied to flag the observed CO₂ data series at three WMO/GAW regional stations in China (Lin'an in Zhejiang province, Longfengshan in Heilongjiang province and Shangdianzi in Beijing), which were based on a statistical approach (REBS), on the atmospheric black carbon (BC) and, using CH₄ as auxiliary tracer (AUX) and on meteorological parameters (MET). All the approaches do suitably well to capture the seasonal CO₂ cycle at the three stations. At LAN station, the REBS may overestimate the regional CO₂ mole fractions, while the BC may underestimate the values. At Longfengshan station, the REBS and CT apparently induce errors on the regional CO₂ mole fractions, and the BC and MET are better to select the regional CO₂ events. Relatively, the MET method seems to be the most favorable to all the three regional stations because it mainly focuses on the influence of potential local sources and sinks and considers diurnal variations, local topography, and meteorological conditions.

By using the MET method, the variations of atmospheric CO₂ and CH₄ mole fractions at Shangdianzi station was analyzed. The results indicated that 81.4% of CO₂ and 75.6% of CH₄ records observed at Shangdianzi station were influenced by very local sources and sinks. The filtered regional mole fractions were influenced by air masses from south-southwest region of Shangdianzi (Beijing-Tianjin-Hebei area, BTH) and northwest (Russia, Mongolia, and Inner Mongolia autonomous region, RMI). The annual growth rates were 3.8 ± 0.01 ppm yr⁻¹ for CO₂ and 10 ± 0.1 ppb yr⁻¹ for CH₄ in BTH, which were apparently higher than those in RMI and global means.

GREENHOUSE GAS OBSERVATION NETWORK OF JAPAN METEOROLOGICAL AGENCY IN THE WESTERN NORTH PACIFIC

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The Japan Meteorological Agency (JMA) has been operationally monitoring atmospheric greenhouse gases in the western North Pacific region under the Global Atmosphere Watch (GAW) Programme using 3 ground-based stations, 2 research vessels and an aircraft.

Since 1987, the JMA has operated a continuous CO₂ measurement at Ryori (RYO, GAW regional station) located at the northern part of Japan, and has expanded the observation to measure other trace gases such as CH₄, CO, N₂O, halocarbons, and O₃. In 1993, we established a background air monitoring station at Minamitorishima (MNM, GAW global station), where is a remote coral island, about 2000 km southeast of Tokyo. Several co-operative research groups have joined us at MNM for in-situ observations of radon-222 and H₂ by Meteorological Research Institute (MRI) and flask measurements of HCFCs, O₂/N₂, and isotopic composition of CO₂ by National Institute for Environmental Studies (NIES) and National Institute of Advanced Industrial Science and Technology (AIST). In 1997, Yonagunijima (YON, GAW regional station) observation has started as the third monitoring station of JMA.

Since 2011, the JMA has carried out an operational aircraft observation in the mid-troposphere at an altitude of about 6km. The aircraft observation is conducted by using a cargo aircraft C-130H of the Japan Ministry of Defense, which flies from Atsugi air base near Tokyo to MNM once a month (Niwa et al., 2014). Air samples are collected in flasks during a cruising flight as well as a descending over MNM station. Mole fractions of CO₂, CH₄, CO, and N₂O in the flask air samples are measured using a high-precision analysis system with two laser-based instruments (Tsuboi et al., 2013). The 5-year aircraft data could capture the spatial variations of their seasonal cycles in the mid-troposphere as well as the climatology of their vertical profiles over MNM.

In this presentation, we will introduce the JMA/GAW observation activities, particularly showing the aircraft observation results.

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**MOBILE LABORATORY AS A PART OF INTERNAL QUALITY CONTROL OF ICOS
ATMOSPHERIC STATION NETWORK**

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ICOS (Integrated Carbon Observation System) is a pan-European research infrastructure providing data on carbon cycle and greenhouse gas budget and perturbations. ICOS concept is a high precision long-term network of stations measuring greenhouse gas concentrations in the atmosphere and greenhouse gas fluxes from ecosystems and oceans, designed around central facilities (CF). The main tasks of CFs are provision of calibration gases, standardized data processing, technical support and training, and quality control. As part of the Atmospheric Thematic Centre, one of the CFs, Finnish Meteorological Institute operates a mobile laboratory (MobileLab). The MobileLab is responsible for atmospheric station audits and independent quality control.

The MobileLab has a fully equipped and air-conditioned van providing space for several greenhouse gas analysers: Picarro G2401 (CO₂, CH₄ and CO), Ecotech FTIR (CO₂, CH₄, CO and N₂O) and LGR (CO and N₂O) along with a set of calibration gases. Even though it is preferred to operate the equipment in the monitoring station side-by-side with the local analysers, it is also possible to run the analysers when installed in the van. The MobileLab visits 3–5 stations per year. An audit includes a multi-day station evaluation visit, a cross-check of the calibration gases and comparison measurements for one to two months, depending on the local circumstances. The MobileLab has standard operating procedures for all its operations that ensure reproducible audit visits from station to station, still enabling to adapt the operations to the local specialities. After the audit visit, the MobileLab operators write a report including possible recommendations.

In 2014, the MobileLab developed methods for the field site visits and visited two stations: Hyytiälä (Finland) and OPE-Andra (France). Jungfraujoch (Switzerland) was visited in the beginning of 2015. The MobileLab has also developed the layout and content for the reports and the first report (Hyytiälä) is now finalized.

QUANTIFYING THE NET EXCHANGE ECOSYSTEM FOR DIFFERENT LAND USE IN PAMPA BIOME IN SOUTHERN BRAZIL

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The Pampa is the newest and most unknown Brazilian Biome. It is located in the Southern portion of the country, as well as part of Argentina and the entire Uruguay, and is formed principally by natural grasslands that have been used for centuries for grazing livestock. In recent decades it has gone through a process of intense land use change and degradation, with the replacement of natural vegetation by rice paddy crops, soybean and exotic forests. Recent studies show that the Pampa has only 36% of its original vegetation in Brazil. Research on carbon and greenhouse gas emissions in Pampa Biome are recent. It is known that the Pampa natural areas contain high stocks of soil organic carbon, and therefore their conservation is relevant for climate change mitigation. However, the net exchange of Carbon between the surface and the atmosphere are unknown. To fill this gap, a flux tower network, SULFLUX – www.ufsm.br/sulfux, was created. Currently, SULFLUX comprises three flux towers in the Pampa biome, two of them being over natural vegetation and the other one over a rice paddy. The flux tower are nearly 100 km apart from each other. We examine the effects of climate on carbon fluxes since 2013. Analysis of temporal variability in CO₂ fluxes is examined at daily to annual scales. Overall, regional variability in climatic drivers, land use and soil proprieties have a considerable effect on net carbon exchange.

NEW CRDS OBSERVATIONS (CO, CH₄, CO₂) AT THREE PERMANENT OBSERVATORIES IN THE SOUTH OF ITALY IN THE FRAMEWORK OF THE I-AMICA PROJECT

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The Mediterranean Basin is considered a hot-spot region in term of air-quality and climate change due to the impact of anthropogenic and natural processes. Nevertheless, permanent infrastructures for the observation and the recognition of the atmospheric composition variability changes are still too sparse in this region. To contribute to a more accurate and wide-spread observation system, in the framework of the Project "I-AMICA" (Advanced Infrastructure for the Environmental-Climatic Monitoring), four Climatic-Environmental Observatories have been set up in the southern Italy: Lecce (Apulia Region, 40° 20' 8" N, 18° 07' 28" E, 37 m a.s.l.), Lamezia Terme (Calabria Region, 38° 52' 34" N, 16° 13' 56" E, 6 m a.s.l.), Capo Granitola (Sicily, 37° 34' N, 12° 39' E, 5 m a.s.l.) and Mount Curcio (Calabria Region, 39° 31' N, 16° 42' E, 1796 m a.s.l.). They can provide information about greenhouse gas variability and related impact from anthropogenic and natural sources.

These observatories were equipped with homogeneous and standardized experimental set-up for measurements of aerosol properties (number size distribution, absorption and scattering coefficients, mass, equivalent black carbon), reactive gases (O₃, NO, NO₂, SO₂, CO) and greenhouse gases (CO₂, CO, CH₄). In particular, the continuous investigation of CO, CO₂ and CH₄ variability is based on the use of CRDS systems (Picarro G2401).

In this work, we provide a characterization of the three coastal observatories in terms of location, meteorology and transport patterns. We also present and discuss the experimental set-up (sampling systems, calibration strategies, gas standards) used to implement the CO, CO₂ and CH₄ measurement programmes at each of these stations. Moreover, the first 6 months (January – June 2015) of continuous observations will be presented, providing a preliminary assessment of winter-spring variability and background levels at the measurement sites.

B9 NATIONAL GREENHOUSE GASES MONITORING NETWORKS IN INDIA

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The quantification of interactions among the atmosphere, biosphere, hydrosphere and lithosphere i.e. bio-geo chemical cycle is necessary to accurately estimate sources and sinks of Greenhouse Gases (GHGs). It requires accurate determination of concentration of these gases and their trends with adequate spatial coverage so as to improve estimates of radiative forcing and addressing the climate change issues. India has become one of the largest and fastest growing economies in South Asia and is emerging as a significant contributor to CO₂ emissions among developing nations. As per report of the Ministry of Environment, Forests and Climate Change, Government of India (2010), the total GHGs emissions in India have grown from 1252 million tons in 1994 to 1905 million tons in 2007 at a compounded annual growth rate of 3.3%. Between 1994 and 2007, some of the sectors indicate significant growth in GHG emissions such as cement production (6.0%), electricity generation (5.6%), and transport (4.5%). LULUCF (Land use, land-use change and forestry) sector was a net sink and sequestered 177.03 million tons of CO₂ during this period. As such, there is need for long term monitoring of atmospheric GHGs and establishment of dedicated national network. Sinhagad (SNG) Pune, India station for GHG concentration measurement is functioning since 2009 with weekly flask sampling which has been augmented with in-situ instrument in June 2014. Calibrations are done with NOAA standards. Flux measurements are being carried out at six sites since 2013. All these sites measures carbon and methane fluxes including soil temp, soil moisture etc. In addition, airplane campaign has been conducted over Ganga basin during September, 2014, and over Maharashtra and Arabian sea during July 2015 to measure CO₂, CH₄, CO, H₂O concentration vertical and horizontal profiles. In order to improve the understanding in this field, India is augmenting its GHG observational and research facilities such as i) ambient CO₂ and other GHG monitoring at the surface ii) air sample analytical technique development using WMO/GAW calibration standards, iii) cruise and airborne campaigns, iv) CO₂ transport as well as lagrangian particle dispersion model simulations, etc. It is also analyzing available CO₂ and other trace gases observation and model simulations over India to improve the flux estimates and GHG budget over this region.

B10 IMPLEMENTATION OF LONG-TERM GREENHOUSE GAS OBSERVATION CAPACITIES IN CHILE AND VIETNAM

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The provision of reliable scientific data of the chemical composition of the atmosphere is crucial for understanding climate change and for a sound assessment of the environmental players and impacts. Data must be long-term, consistent, of adequate quality, and have to be available world-wide. Despite the ongoing considerable improvement in spatial data coverage and the large number of GAW stations measuring greenhouse gases around the globe, data sparse regions still exist in some regions of the world.

Among other recent international efforts, the project Capacity Building and Twinning for Climate Observing Systems (CATCOS), funded by the Swiss Agency for Development and Cooperation and coordinated by the Federal Office of Meteorology and Climatology MeteoSwiss, aims at establishing and resuming systematic observations of greenhouse gas and other atmospheric and terrestrial Essential Climate Variables in developing and emerging countries where the availability of observations is currently insufficient. Within CATCOS, Empa – as one of the Swiss implementing partners – is in charge of establishing sustainable and high-quality greenhouse gas (carbon dioxide, methane, carbon monoxide and ozone) measurement capabilities in Chile and Vietnam. In Chile, the implementation took place at the regional GAW station El Tololo (30.17degS, 70.80degW, 2220m asl) in the foothills of the Andes in April 2013 in collaboration with MeteoChile. The equipment in Vietnam was implemented in collaboration with the Vietnamese National Hydro-Meteorological Service (NHMS) at the Pha Din climate station (21.57degN, 103.52degE, 1466m asl), a rural site in a hilly forested area in Northern Vietnam, in February 2014.

The presentation will give a comprehensive overview of the CATCOS project and its goals in general, and the first results after 2 ½ and 1 ½ years of continuous operation at El Tololo and Pha Din, respectively.

B11 **THREE YEARS OF CONTINUOUS VERTICALLY RESOLVED CO₂/CH₄/CO MEASUREMENTS AT THE AMAZON TALL TOWER OBSERVATORY SITE (ATTO, BRAZIL)**

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At the Amazon Tall Tower Observatory site (ATTO, Brazil; 2°08'S, 59°00'W), a 330 m-tall tower is in its final constructing and equipping phase. The ATTO tall tower extends above the atmospheric surface layer and the nocturnal stable boundary layer, and aims at delivering ground breaking findings that will be the basis for improved climate models.

While awaiting completion of the tall tower, a number of campaign and continuous pilot measurements are ongoing at a walk-up tower and a mast (both 80 m tall). Since March 2012, we run continuous high precision CO₂/CH₄/CO measurements in an air-conditioned lab container at the foot of the 80 m tower. The sample air is drawn from inlets installed at five levels (79, 53, 38, 24, and 4 m a.g.l.) through 8 liter buffer volumes towards two frequently calibrated CRDS analyzers (G1301 and G1302; Picarro Inc.) to measure CO₂/CH₄ and CO/CO₂, respectively. On the CO/CO₂ analyzer, part of the operating time different Nafion dryers were used to test their drying efficiency under high ambient humidity conditions (up to 4 % vol. H₂O) in unattended conditions.

Furthermore, we used the opportunity to compare the parallel CO₂ measurements on the two instruments (with Nafion dryers and without drying). While due to measuring relatively close to the canopy (~ 35 m a.g.l.) the data is influenced by local sources and sinks, it still provides a valuable insight into the diurnal and seasonal variations of the measured gas species. A first analysis of the available data and tests is presented.

Our work was performed within the frame of the German-Brazilian project ATTO and supported by the federal government agencies BMBF and MCT (Grant number BMBF 01LB1001A). We acknowledge the fundamental support by the Max Planck Society, INPA and UEA. Special thanks go to the Amazonas State SDS/CEUC-RDS Uatumã.

B12 OBSERVATION NETWORK FOR GREENHOUSE GASES AND RELATED SPECIES IN THE NEW ZEALAND REGION.

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The observational programme of atmospheric composition in New Zealand has evolved over time as scientific knowledge and challenges have developed. Initially, observations were made to monitor background air, while more recent observations aim to inform on regional to global scale processes.

We present the geographic scale of the New Zealand regional network ranging from Arrival Heights, Antarctica (78 °S) to Raoul Island (29 °S) with three observation sites within New Zealand where continuous analyses are conducted. The range of observations of greenhouse gases and related species made at these stations will be presented. The measurement programme started with observations of atmospheric $^{14}\text{CO}_2$ (1954), and from 1970 continuous analyses of greenhouse gas concentrations were added, followed by total column measurements in the last decade. The capability in isotope measurements has seen the continual inclusion of stable isotope techniques within the programme ($^{13}\text{C-CO}_2$, $^{18}\text{O-CO}_2$, $^{13}\text{C-CH}_4$, $^{13}\text{C-CO}$) and also radiocarbon measurements ($^{14}\text{CO}_2$, $^{14}\text{CH}_4$, ^{14}CO). The measurement of in situ atmospheric oxygen at Baring Head provides additional information on carbon cycling in the Southern Hemisphere. The network of CO_2 observations has recently been used in the development of an inverse model to inform on air parcel origin and regional (especially terrestrial) carbon source/sink distribution. This is now being supported by in situ observations of atmospheric radon at the Baring Head site and a developing programme of regional oceanic pCO_2 observation. Preliminary data from a recently deployed nitrous oxide isotopomer instrument will also be discussed.

B13 ICOS ATMOSPHERE THEMATIC CENTER

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ICOS is a recently-launched, world-class research infrastructure dedicated to the monitoring and improved understanding of carbon sources and sinks. It consists of complementary, harmonized networks of long-term monitoring stations focusing on Europe and adjacent regions. The ICOS networks will comprise about 40 operational atmospheric stations (measuring atmospheric composition in greenhouse gases and other core parameters), 40 ecosystem stations (measuring fluxes from ecosystems) and about 20 oceanic measurement platforms. The networks are coordinated through a set of central facilities: three thematic centres respectively for atmospheric, ecosystem and ocean data, and a central analytical lab. The Atmospheric Thematic Center (ATC) has two main functions:

1. Operate the atmospheric data processing chains, going from data transmission from stations to the routine delivery of quality checked data-stream
2. Carry out regular measurement technology survey, analysis and enable development of new sensors and their testing prior to field deployment in ICOS

The presentation will describe state of the art of atmospheric GHG measurement and data processing with a special focus on quality assessment. It will also present new measurement technique, like isotopic measurement, that can attribute GHG concentration changes to different emission sources.

B14 INITIAL OPERATION OF THE FLASK AND CALIBRATION LABORATORY FOR ICOS (INTEGRATED CARBON OBSERVATION SYSTEM)

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The Integrated Carbon Observation System (ICOS) is a European-wide research infrastructure that aims at providing high quality observational data for the long-term monitoring of the European greenhouse gases balance. Since 2013 we are building up the Flask and Calibration Laboratory (FCL) in Jena (Germany), a central facility for the ICOS research infrastructure. It will be responsible for measurements of CO₂, CH₄, N₂O, CO, H₂, SF₆ and O₂/N₂ ratios as well as stable isotope analyses (CO₂ and CH₄) of flask air samples collected at atmospheric platforms of the ICOS monitoring network.

In addition, the FCL is in charge to provide real air reference standards calibrated relative to the respective WMO calibration scales for operation of continuous measurement systems at the monitoring stations. Therefore a standard filling facility including a compressor and a spiking system for the production of user-defined reference air mixtures was established.

Within our contribution we will present the actual state of analytical instruments and their respective performance as well as the systems for preparation of standard gases.

We have explored the possible application of a Los Gatos Research Inc. Trace Gas Analyzer (Enhanced Performance model) for CO and N₂O for flask air analyses and will present preliminary test results.

**B15 MONITORING OF ATMOSPHERIC CARBON DIOXIDE AND OTHER GHG'S IN INDIA:
IMPLICATIONS FOR CONSTRAINING INDIAN EMISSIONS**

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India has one of the largest and fastest growing economies in South Asia and is emerging as a major contributor to CO₂ emissions among developing nations. However, there has been relatively little monitoring of atmospheric CO₂ over India to date. The Carbon Dioxide Information Analysis Center (CDIAC), USA, estimates the total fossil-fuel CO₂ emissions from India as 189 TgC in 1990, 324 TgC in 2000, 385 TgC in 2005 and 508 TgC in 2009, and the annual rate of increase as ~7% per year during 2005-2009. Some of these emissions may be compensated by vegetation uptake. According to a report published in May 2010 by the Ministry of Environment and Forest (MoEF), Govt of India, the total greenhouse gases emissions in India have grown from 1252 million tons in 1994 to 1905 million tons in 2007 at a compounded annual growth rate of 3.3%. Between 1994 and 2007, some of the sectors indicate significant growth in GHG emissions such as cement production (6.0%), electricity generation (5.6%), and transport (4.5%). In order to improve our understanding in this field, we are involved in: i) ambient CO₂ and other GHG monitoring at the surface ii) air sample analytical technique development using WMO/GAW calibration standards, iii) cruise and airborne campaigns, iv) CO₂ transport as well as lagrangian particle dispersion model simulations, etc. The present study is an attempt to analyze available CO₂ and other trace gases observation and model simulations over India which may help to improve the flux estimates and GHG budget over this region.

B16 CONTINUOUS MEASUREMENTS OF CO₂ AND CH₄ DURING 2011-2014 AT PONDICHERRY, INDIA

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- 12. CSIR Fourth Paradigm Institute*
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The work here shows continuous CO₂ and CH₄ measurements made along with wind speed and direction between 2011-2014 at Pondicherry (12.0159° N, 79.8585° E) which is in the eastern coast of Southern India. Pondicherry is influenced both by Southwest monsoon during June-Aug and Northeast monsoon during Oct-Dec and samples air from the Indian Ocean, South India and SE Asia during the year. The instrument used for continuous measurement of CO₂ and CH₄ is Picarro 2301 which is calibrated with four tanks traceable to WMO primary scale. Hourly values of CO₂ and CH₄ are derived for this period and are interpreted in conjunction with the wind direction and wind speed data from diurnal to seasonal scales. There is a sharp decline in CO₂ and CH₄ values at the onset of sea breeze. The growth rates of CO₂ and CH₄ at Pondicherry during 2011 to 2014 are discussed in comparison with measurements at Port Blair (11.6683° N, 92.7378° E) which is on the same latitude band. These results when used in conjunction with those from the other Indian station at Hanle can lead to a better understanding of the distribution of carbon sources and sinks over Indian subcontinent.

B17 LONG-TERM MEASUREMENTS OF ATMOSPHERIC TRACE GASES (CO₂, CH₄, N₂O, SF₆, CO, H₂), O₂, AND δ¹³CH₄ ISOTOPES AT WEYBOURNE ATMOSPHERIC OBSERVATORY, UK: PAST, PRESENT AND FUTURE.

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The Weybourne Atmospheric Observatory (WAO) is a component of the National Centre for Atmospheric Science (NCAS) Atmospheric Measurement Facility (AMF). WAO is situated on the north Norfolk Coast (52.95°N, 1.13°E) in the United Kingdom and is run by the University of East Anglia with support from NCAS. Since 2008 we have been collecting high-precision long-term in situ measurements of atmospheric carbon dioxide (CO₂), oxygen (O₂), carbon monoxide (CO) and molecular hydrogen (H₂), as well as regular bag sampling for δ¹³CH₄. In early 2013, the measurement of atmospheric methane (CH₄) commenced, and nitrous oxide (N₂O) and sulphur hexafluoride (SF₆) began in 2014. Here we summarize the CO₂, O₂, CH₄, N₂O, SF₆, CO, H₂ and δ¹³CH₄ measurements made to date and highlight some key features observed (e.g. seasonal cycles, pollution events and deposition events). We summarize how the long-term measurements fit into other broader projects which have helped to support the long term time-series at WAO over the years, and highlight how we contribute to broader global atmospheric observation networks.

B18 AMAZON AND COAST BRAZILIAN GREENHOUSE GAS MEASUREMENT PROGRAM AND THE EFFORTS IN CONSTRUCT THE GHG NETWORK

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With the goal of building The Brazilian Greenhouse Gas Network we changed the Atmospheric Chemistry Laboratory (LQA) from IPEN to INPE in order to join two Brazilian groups to build the National GHG Laboratory and improve conditions to build the Brazilian network. In October it will be a workshop to define the structure of this network, based on the experience that we already have in action in Brazil and guests from other networks (NOAA and IGOS) that will bring their experiences to us.

By now the efforts in to construct a GHG network is doing by many projects funded by Brazilian, UK, US, EC agencies. We start this effort with NASA project performing vertical profiles aircraft at SAN (2.86S 54.95W), started in 2000 with monthly/biweekly sampling (300m to 4400m a.s.l.). In 2010 we added three more aircraft sites: TAB (5.96S 70.06W), RBA (9.38S 67.62W) and ALF (8.80S 56.75W). And in 2013 we added 2 new high vertical profiles sites (up to 7.3km to 300m) RBA and in a new site in coast (SAH: 0.76S 47.84W). This project had the objective to compare with GOSAT. Coastal studies are conducting actually at 3 sites: SAL (started 2010), NAT (started 2010) and CAM (started 2014). Since 2010 until 2014, we performed 400 vertical profiles from 300m to 4400m above sea level, measuring CO₂, CH₄, N₂ O, CO and SF₆ on WMO mole fraction scales. SAN is the longest time series, where it was performed 221 vertical profiles since 2000.

It will be showed the results since 2010 until 2014 with new high profiles for CO₂ the flux calculated by Column integration technique.

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B19 THE CARBON RELATED ATMOSPHERIC MEASUREMENT (CRAM) LABORATORY: A UNITED KINGDOM NATIONAL REPORT

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Since 2007, we have been developing UK national capability for high precision greenhouse gas measurement at the School of Environmental Sciences, University of East Anglia (UEA), with a multi-faceted programme:

CRAM Laboratory: Our analysis system measures air from suites of high pressure cylinders as well as from flask samples collected in the field. The system comprises of the following analysers in a contiguous series: a custom-built vacuum ultraviolet O₂ analyser; a Siemens Ultramat 6F CO₂ analyser; a Perkin Elmer Clarus 500 gas chromatograph equipped with a flame ionisation detector, methaniser, and electron capture detector for measuring CH₄, CO, N₂O and SF₆; and an Isoprime 10-collector isotope ratio mass spectrometer for measuring Ar/N₂ ratios. All analysers are calibrated with a suite of 14 primary calibration gases purchased from NOAA/ESRL and Scripps Institution of Oceanography.

Calibration Cylinder Filling Facility (CFF): This facility is used to fill and prepare high pressure cylinders for working standards to be used in both laboratories and at field stations. The facility can prepare sub- and above-ambient concentrations for all the major greenhouse gases and related species, and can fill cylinders of dry air (<1 ppm H₂O) up to pressures of 300 bar.

In situ measurements: From the Weybourne Atmospheric Observatory, UK, we collect measurements of O₂, CO₂, CO, H₂, CH₄, N₂O and SF₆ (poster by G.L. Forster); from Mace Head, Ireland, O₂ and CO₂; from Kjølnes, northern Norway, CO₂, CH₄, N₂O and CO; from Tacolneston, UK, CO₂ and CH₄; and from a Hamburg Süd container ship travelling from Germany to Argentina, O₂ and CO₂. In early 2016, we will install an O₂ and CO₂ system at Halley Research Station, Antarctica.

Software tools: Bespoke software programs for data acquisition and automation, as well as data processing and analysis tools, support our measurements. We include comprehensive near-real-time diagnostic capability.

B20 EIGHT YEARS OF IN SITU MEASUREMENTS OF CH₄, N₂O AND CO MADE WITH A PROTOTYPE FOURIER TRANSFORM TRACE GAS ANALYSER AT LAUDER, NEW ZEALAND.

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We present an eight year (2007-2015) time series of in situ measurements of CH₄, N₂O and CO made by a prototype in situ Fourier transform trace gas analyser (FTS) operated at Lauder, New Zealand (45.04S, 169.68E, 370m AMSL). The operational methodology, measurement precision, accuracy and long term stability are reported here. FTS measurements are then compared to trace gas concentrations derived from GC analysis of flask air samples acquired routinely (weekly) at the site since May 2009. The Lauder time series are also compared to clean air measurements taken from Baring Head, New Zealand (41.4S, 174.9E, 87m AMSL).

The FTS time series captures the seasonal variations in CH₄ and CO, the secular rise in CH₄ since 2006, an increase in the upward trend in N₂O since mid-2009 and the downward trend in CO. Comparing FTS and co-located flask measurement shows that the bias in CH₄ of -0.8nmol mol⁻¹ +/- 3.0 (FTS - flask) is within the GAW Inter-Laboratory comparability limit of 2nmol mol⁻¹ whilst the FTS-flask bias in CO and N₂O of -1.9nmol mol⁻¹ +/- 2.1 and -0.13nmol mol⁻¹ +/-0.75 respectively are bordering on the accepted comparability limits of 2nmol mol⁻¹ and 0.1nmol mol⁻¹ .

We introduce a bespoke scale transfer standard gas tank suite with a customized atmospheric composition matrix consisting of prescribed CO₂, CH₄, N₂O and CO mole fractions tailored to this particular type of FTS with concentration ranges spanning the sampled atmosphere at Lauder. The composition matrix is configured to reduce any gas measurement cross sensitivity/covariance in the FTS.

B21 GROUND AND AIRBORNE BASED OBSERVATIONS OF GREENHOUSE GASES MIXING RATIOS AT US-DOE ATMOSPHERIC RADIATION MEASUREMENT FACILITIES.

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We report on ground-based and airborne-based measurements of atmospheric greenhouse gases from continuous analyzers and flask samplers, collected between 2002 and 2015 over the Atmospheric Radiation Measurement Program Climate Research Facilities in the US Southern Great Plains (SGP), the Eastern north Atlantic (ENA), and the North Slope of Alaska (NSA). These observations were designed to quantify trends and variability in atmospheric concentrations of CO₂ and other greenhouse gases with the precision and accuracy needed to evaluate ground-based and satellite-based column CO₂ and CH₄ estimates, test forward and inverse models, and help with the interpretation of ground-based measurements.

**B22 THE FRENCH METROPOLITAN GREENHOUSE GASES MONITORING NETWORK:
SNO-ICOS FRANCE.**

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6. CEA / LSCE, 7. UVSQ / LSCE, 8. CEA / LSCE, 9. UVSQ / LSCE, 10. UVSQ / LSCE

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Greenhouse gases (GHG) have been identified as the main driver of current climate change. Future evolution of the atmospheric composition will determine the intensity of current climate warming and will depend on our ability to modify/diversify our energy sources and/or moderate its consumption.

In order to follow these different aspects as well as to increase our knowledge on carbon cycle and refine carbon budget (from global to local scale), it is crucial to continuously monitor the atmospheric composition. Since the late fifties and the Mauna Loa first record, atmospheric monitoring stations have been set up over most of the world, and then organized into harmonized and structured networks at the national or international level. The Integrated Carbon Observation System (ICOS) research infrastructure gathers the GHG atmospheric monitoring efforts at the European level (mainly focusing on CO₂, CH₄, CO and N₂O species). As a member and contributor to the ICOS infrastructure, France has a major role on the atmospheric component of the project through its GHG national monitoring network (SNO ICOS-France) and the atmospheric thematic center based at LSCE.

We will present the French metropolitan GHG monitoring network based on 9 ground observation stations and the two airborne platforms including the aircraft ATR42 from SAFIRE, a joint research facility of CNRS, MeteoFrance and CNES, recently equipped with GHG analyzers. Station design and location, instrumental set up and characteristics as well as measurement protocol will be depicted. Example of data records from the French facilities and associated scientific interpretation such as altitudinal gradients from high tower, airborne validation, long term and/or seasonal trends will also be shown and analyzed. Results from an attempt to apply a methodology to filter high frequency variability to the GHG records (local spikes for example) will also be shown for one or two sites.

B23 DEVELOPMENTS IN THE CSIRO AUSTRALIAN GREENHOUSE GAS OBSERVATION NETWORK

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CSIRO Ocean & Atmosphere Flagship

The Cape Grim Baseline Air Pollution Station (CGBAPS) is the central reference observation site in the Australian regional Greenhouse Gas Observation Network (AGGON). Recent developments in the GHG program at CGBAPS include new in-situ analysers for N₂O/CO and ¹³CO₂/12CO₂ using Quantum Cascading Laser (QCL) instruments (Aerodyne, QC-TILDAS). Recently, two additional observation sites were added to this network (“Burncluith” and “Ironbark”), associated with the atmospheric monitoring of fugitive emissions from Coal Seam Gas (CSG) extraction projects, being developed in the Australian state of Queensland. Currently each site is limited to a single Cavity Ring Down Spectrometer (CRDS) (Picarro, G2300 & G2400).

In addition, a new Australian Marine National Facility blue water research vessel RV Investigator was recently commissioned (2015) with dedicated atmospheric observation capability on-board. This includes in-situ N₂O/CO (Aerodyne, QC-TILDAS) and CO₂/CH₄ (CRDS) (Picarro, G2300) analysers in the GHG program.

A key research application of AGGON is to monitor changes in the efficiency of the Southern Ocean CO₂ sink using a well inter-calibrated, high precision, Southern Ocean atmospheric observation sub-network. The atmospheric data from this network is dominated by regional ocean-atmosphere exchange, making this an important top-down complement to ocean-based Southern Ocean carbon observation and modelling research. Recent analysis of this data has revealed small but consistent diurnal and seasonal variations that will improve our understanding of Southern Ocean CO₂ exchange such as that related to biological production.

In addition to an expansion of the network, the research programs at other network sites have also been developing. The pilot Australian Tropical Atmospheric Research Station (ATARS) established at Gunn Point, near Darwin in Australia’s Northern Territory (12.249S, 131.045E, elevation 25 metres). A key research application of this site is to understand the impact on the atmosphere from the regular (mostly controlled) seasonal biomass burning events that occur over the large expanse of tropical savannah in this region. The GHG program consists of in-situ CO₂/CH₄ and ¹³CO₂/12CO₂ CRDS analysers (Picarro G1300 & G2100i) and a flask air samples collection program. In addition, there are research programs for reactive gases, aerosols, radon (ANSTO), gaseous mercury (Macquarie University) and short lived biogenic halocarbons (University of Cambridge).

The status of these new sites will be presented here, including a selection of data and results from recent network developments.

B24 5 YEARS OF BRAZILIAN GREENHOUSE GASES BACKGROUND CONCENTRATIONS

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In 2010 studies were initiated at two sites on the Brazilian coast Salinópolis/PA (SAL: 00°36'15.03"S; 47°22'25.02"W), and Natal/RN (NAT: 05°29'22.05"S; 35°15'39.64"W). Air samples were collected in the surface weekly and analyzed at the Atmospheric Chemistry Laboratory of IPEN, quantifying the gases: carbon dioxide, methane, nitrous oxide, sulfur hexafluoride and carbon monoxide. Results showed that SAL presents higher seasonality when compared to NAT. Simulations of backward trajectories, allowed to observe how each study site is influenced by air masses arriving in them. Then, in SAL air masses were from Atlantic ocean North (NAO) and South (SAO), depending on time of year, and in NAT only from the SAO. These behaviors were related to the position of the Intertropical Convergence Zone, suffering changes throughout the year. In SAL was observed that the main greenhouse gas (GHG), CO₂, suffered absorption processes by the ocean, a phenomenon also observed in flights using aircraft profiles. The second most important, CH₄, presented seasonally throughout the year and was similar behavior to the concentrations of the Barbados global station (RPB: 13°16'50.00"N, 59°43'20.00"W). And the third most important, N₂O, presented dispersions which may be related to marine productivity. And the burning tracer, CO, showed periods of high concentrations from August to October and this was related to biomass burning in Brazil and in Africa, due to transport by air masses. In NAT, it was observed that the GHG concentrations, were similar behavior to the Ascension global station (ASC: 07°96'67.00"S; 14°0'00.00"W), since SAO concentrations are lower than the NAO. The concentrations of measured gases showed seasonality and periods of high concentrations, which were also associated with biomass burning on another continent. Overall, both study sites, SAL and NAT showed an increase in their concentrations over the years in the Brazilian coast following the world growth.

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B25 IMPROVEMENTS OF THE SPECTRONUS FTIR INSTRUMENT FOR APPLICATION IN STATIC MODE AT TALL TOWERS

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The Spectronus instrument uses FTIR spectroscopy to measure simultaneously and at high reproducibility the most important greenhouse gases CO₂, CH₄, N₂O and also CO and δ¹³CO₂ in dry air at ambient concentrations (Esler et al, 2000, Hammer et al, 2013). Several improvements have been applied to adapt the system for use at (remote) tall tower sites in order to reduce gas consumption and improve stability at static mode in order to measure gradients along the tall towers. Compared to the standard 3.5 L glass cell this instrument is equipped with a metal cell with a volume of 2.5 L and temperature control up to 10 mK accuracy. After laboratory testing (reproducibility results in Table 1) the instrument has now been tested for six months at Cabauw tall tower (Netherlands), measuring vertical gradients at four heights along the tower, with all inlets connected to a buffer volume system. Data coverage in the period was 98% (see figure 1 for CO₂ timeseries).

B26 IMPROVEMENTS TO PICARRO'S G2401 AND G2301 – ICOS-COMPLIANT REPRODUCIBILITY, AND IMPROVED DRIFT SPECIFICATIONS IN RESPONSE TO RESULTS FROM ICOS INSTRUMENT COMPARISON

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2. Picarro

3. Picarro

4. Picarro

5. Picarro

6. Picarro

7. Picarro

Europe's Integrated Carbon Observation System (ICOS) makes extensive use of Picarro's G2401 and G2301 greenhouse gas (GHG) analyzers for the long-term measurement of background carbon dioxide, methane, and carbon monoxide (the latter, G2401 only). ICOS demands stringent reproducibility specifications for analyzers reporting concentrations of these gases. These specifications present a particular challenge for carbon monoxide, where the required reproducibility is <1 part per billion (10 minute average, 1 σ), with typical atmospheric concentrations being less than 1 part per million (ppm). We report on software and hardware improvements made to our G2401 greenhouse gas analyzer resulting in compliance with ICOS specifications for our standard production unit, over a guaranteed measurement range of 0-1 ppm.

Scientists at ICOS' Atmospheric Thematic Centre, Laboratoire des Sciences du Climat et de l'Environnement (France), recently completed a comparison of 47 laboratory-based Picarro analyzers and 15 in-the-field instruments. Results of this study revealed a previously unknown deterioration in drift performance when comparing earlier, 1000 generation analyzers with those built on the current 2000 platform. This is clearly illustrated by an Allan variance plot presenting methane averaging for Picarro's ESP 1000, G1301, G2301, G2401, and G2401-m (flight applications model) analyzers. An initial analysis attributed the concentration measurement drift to a drift in cavity pressure measurement. Further investigation revealed that the pressure sensor itself did not change between the 1000 and 2000 platform. But changes to the pressure measurement electronics in our system were found to have impacted the long term drift performance of the analyzer. The issue was resolved with the application of new, high performance electronics in the pressure measurement and control sub-system. An analysis and conclusions of this investigation are presented here for G2301 and G2401 analyzers.

B27 JAPAN METEOROLOGICAL AGENCY'S SHIP-BASED OBSERVATION FOR THE PARTIAL PRESSURE OF CARBON DIOXIDE IN THE WESTERN NORTH PACIFIC

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Japan Meteorological Agency (JMA) has been conducting a series of hydrographic and biogeochemical observations in the western North Pacific to understand the changes in the ocean circulation, air-sea interactions, and biogeochemistry associated with the global change. Data of partial pressure of CO₂ in surface seawater (pCO₂sea) and in overlying air (pCO₂air) have been acquired along the 137°E and 165°E repeat lines since early 1980s and mid-1990s, respectively, on board R/V *Ryofu Maru* and R/V *Keifu Maru*. For the measurement of pCO₂, we have been using a non-dispersive infrared (NDIR) gas analyzer, a showerhead-type equilibrator and a set of CO₂ standard gases calibrated with WMO mole fraction scale. We have also been making precise measurements of dissolved inorganic carbon (DIC), pH and total alkalinity (TA) in the water columns since 1994, 2003 and 2009, respectively.

The trend of pCO₂sea increase has been observed along 137°E and 165°E repeat lines together with the increase of pCO₂air. It is mainly ascribed to the uptake of anthropogenic CO₂ by the ocean, but the rate of pCO₂sea increase changes year by year, depending on the variations in the physical and biogeochemical conditions in the respective regions. The CO₂ data we obtained are publicly available from the WMO's World Data Centre for Greenhouse Gases (WDCGG) operated by JMA (<http://ds.data.jma.go.jp/gmd/wdcgg/wdcgg.html>) and from SOCAT database (<http://www.socat.info/>). Additionally, using these data of carbonate system parameters, we are providing various information regarding ocean carbon cycle such as ocean CO₂ uptake, change in the column inventory of anthropogenic CO₂ and the trend of ocean acidification in the western North Pacific (http://www.data.jma.go.jp/gmd/kaiyou/english/oceanic_carbon_cycle_index.html).

B28 THE IN-SITU MEASUREMENT OF GREENHOUSE GASES (CO₂, CH₄, N₂O & CO) DISSOLVED IN INLAND WATERS AND THEIR WATER-ATMOSPHERE EXCHANGE

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Global greenhouse gas (CO₂, CH₄ and N₂ O) emissions from inland waters are significant yet estimates remain highly varied and are quoted with large uncertainty^{1, 2}. Recent CO₂ estimates range from 0.6 – 3.3 Pg C yr⁻¹ and are comparable in magnitude to the global land or ocean anthropogenic CO₂ sink¹⁻⁹. However, these estimates are not adequately constrained by small scale measurement data, particularly for CH₄, N₂ O and CO, which have received far less attention than CO₂^{9, 10}. Here we investigate and present in-situ measurements of inland water-atmosphere greenhouse gas exchange examined on rivers, lakes and reservoirs within Europe and Australia. Gas analysis was conducted using a Fourier-Transform InfraRed (FTIR) Trace Gas Analyser, which allowed simultaneous and continuous measurement of CO₂, CH₄, N₂ O, CO and δ¹³C in CO₂. Coupling the analyser to an equilibrators and a floating chamber facilitated either continuous measurement of gas partial pressures within the waters and the overlying atmosphere or the direct measurement of water-atmosphere gas exchange. Where these measurements coincided, gas transfer velocities were derived and compared to those modelled from water and/or air turbulence parameters. We provide an overview of the employed measurement techniques and their capabilities and a selection of the results from various field campaigns.

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B29 CONTINUOUS MEASUREMENTS OF $x\text{CO}_2$ AND $x\text{CH}_4$ IN THE SEAWATER AND OVERLYING AIR IN THE WESTERN ARCTIC OCEAN

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Underway measurements of the mole fraction of CO_2 ($x\text{CO}_2$) and CH_4 ($x\text{CH}_4$) in surface seawater and overlying air were made continuously in the western Arctic Ocean during the cruise of the R/V Mirai (JAMSTEC) in September–October 2012. The measurements were carried out with a system that consists of a WS-CRDS analyzer (Picarro G2301) and a shower-head-type equilibrator. The system was calibrated once a day using three working standard gases of the mixture of CO_2 and CH_4 in air. The data were compared with those from the measurements made in parallel using NDIR analyzer (LI-COR LI-7000) that have been calibrated every 1.5 hour using four working standard. Temperature, salinity, and dissolved oxygen were also measured simultaneously.

$x\text{CO}_2$ in the surface seawater measured by CRDS was higher than that by NDIR (0.48 ± 0.71 ppm). The difference in the surface water $x\text{CO}_2$ was well below its target precision of 1 ppm. It is known that the $x\text{CO}_2$ determined with CRDS is affected by the O_2/N_2 ratio of the air. In this cruise, $x\text{O}_2$ of the air equilibrated with seawater varied largely (0.194–0.239%). However, its effect on the analytical result of $x\text{CO}_2$ was unclear because of the large variation of surface water $x\text{CO}_2$ in space and time.

The high-resolution measurements of $x\text{CH}_4$ using CRDS revealed several spots of high- $x\text{CH}_4$ (~ 6.22 ppm) in near-surface water. They were positively or negatively well correlated with that of $x\text{CO}_2$ depending on the controlling mechanisms, i.e., upwelling of continental shelf bottom water and biological activities.

These results indicate that the CRDS analyzer can be applied successfully to the shipboard CO_2/CH_4 measurements and serve as a powerful tool to clarify the changes in CO_2 and CH_4 in the ocean, in particular the regions like the Arctic where spatial variation in $x\text{CO}_2$ and $x\text{CH}_4$ is large.

**B30 IMPROVEMENTS IN SHORT-TERM ATMOSPHERIC OXYGEN MEASUREMENT
PRECISION BY FASTER SAMPLE-REFERENCE SWITCHING**

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High-precision, atmospheric O₂ measurement employing the lead fuel cell technique involves switching sample and reference gases between two fuel cells, in order to improve measurement precision and accuracy (Stephens et al., 2007). The switching frequency of the two gases is typically on the order of 1 minute, of which the first ~30 seconds of data are ignored (known as the sweep-out time), in order to account for flushing of the fuel cells and tubing, and the fuel cell response time (not particularly fast owing to the need for diffusion of sample/reference across a gas-permeable membrane). We have investigated the effect of changing the switching frequency on the short-term precision and accuracy of atmospheric O₂ measurements, using two atmospheric O₂ measurement systems that employ Oxzilla II (Sable Systems Inc.) lead fuel cell analysers.

The Allan deviation of the differential O₂ signal with no switching indicates that the optimum averaging time is about 14 seconds. We found that reducing the switching frequency from 60 to 30 seconds with a sweep-out time of 15 seconds reduced the mean O₂ mole fraction standard deviation (SD) by up to 55% while measuring cylinder air, and by 25% while measuring ambient air.

To mitigate compromising the accuracy of the O₂ measurement when reducing the sweep-out time, we minimized the residence time of air in the tubing between the switching valve and the fuel cells, by installing the switching valve as close as possible to the fuel cells and using 0.04" internal diameter tubing. We found no change in O₂ accuracy as a result of reducing the sweep-out time to 15 seconds (from 30 seconds). Reducing the sweep-out time to 10 seconds, however, did result in a bias in the O₂ mole fraction values.

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B31 PRELIMINARY RESULTS ON O₂/N₂ SCALE COMPARISON BETWEEN SIO AND NIES BASED ON FLASK SAMPLING AT LA JOLLA

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We present preliminary results on comparison of O₂/N₂ scales between the Scripps Institution of Oceanography (SIO) and the National Institute for Environmental Studies (NIES) based on simultaneous flask samplings at La Jolla during a 5-year period 2010 to 2014. Although there are about 200 per meg differences in the $\delta(\text{O}_2/\text{N}_2)$ values between SIO and NIES data because both institutes have independent O₂/N₂ scales, the temporal variations measured by NIES agree well with those by SIO. The correlation coefficient between the SIO and NIES data is 0.995 and the correlation slope of the scatter plot determined by a reduced major axis (RMA) regression analysis is 1.045 ± 0.015 (SIO/NIES). This result seems to suggest that the span sensitivity of NIES is slightly lower than that of SIO. Therefore, the spatiotemporal variabilities measured by NIES may be slightly underestimated in comparison with those by SIO. In fact, the ratios of the seasonal amplitudes and decreasing trends based on the simultaneous data at La Jolla for the 5-year period between SIO and NIES (SIO/NIES) are 1.038 ± 0.059 and 1.056 ± 0.073 , respectively. Assuming that the above span sensitivity difference is applicable to the NIES data during the whole observation period, the average changing rate of the O₂/N₂ ratios observed at HAT and COI during 2000-2013 by NIES is changed from -21.1 per meg yr⁻¹ (NIES scale) to -22.1 per meg yr⁻¹ (SIO scale). This change in the decreasing rates corresponds to the change in the global carbon uptake of about 0.4 PgC yr⁻¹ (the larger decreasing rate corresponds to the larger ocean uptake). It should be noted, however, that since our inter-comparison data at La Jolla are still limited we need careful attention to assess the implication for the long-term trends of our data.

B32 OBSERVATIONS OF AN INTERHEMISPHERIC GRADIENT, AND STRATOSPHERIC DEPLETION IN THE ATMOSPHERIC AR/N₂ RATIO DURING THE HIPPO GLOBAL

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Argon has the potential to play a critical role in ocean and atmospheric sciences as a constraint on physical and carbon-cycle processes in the oceans and stratospheric mixing. As a noble gas, argon is inert—its atmospheric concentration is governed by its solubility in the world's oceans, and changes in its concentration are a function of the solubility temperature dependence.

The HIAPER Pole to Pole Observations (HIPPO) airborne sampling campaign ran between 2009 and 2011, profiling the atmosphere at five points in the seasonal cycle from the surface to 14 km, from 67 S to 87 N, along the middle of the Pacific Ocean. Measurements from HIPPO provide evidence of two predicted, but previously poorly observed Ar/N₂ signals—an interhemispheric gradient favoring higher Ar/N₂ ratios in the Southern Hemisphere, and depletion in lower stratospheric air.

The interhemispheric gradient is thought to exist as a result of heat flow in the world's oceans, and while Scripps sampling stations have shown evidence of annual mean offsets in surface Ar/N₂ over the last decade, these offsets were measured on flasks collected from distinct sampling systems, with the potential for site specific biases. HIPPO flasks were collected with a single system, allowing confirmation that station offsets in the Scripps network are largely real.

Lower stratospheric depletion is predicted to occur due to gravitational settling of the heavier Ar atom (M40) relative to the lighter N₂ molecule (M28). Though measurements deep into the stratosphere have shown the latter effect to occur over areas of the upper stratosphere, the HIPPO data show clear depletions in the first kilometer above the tropopause with a much larger number of samples. We relate this depletion to tracers of the age of stratospheric air to estimate the rate at which stratospheric air loses Ar.

B33 PROGRESS IN DATA MANAGEMENT AND INFORMATION PROVISION OF WDCGG

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The progress of service improvement at the World Data Centre for Greenhouse Gases (WDCGG) mainly for last two years is presented. The preliminary reform plan of WDCGG was already shown and discussed in the last meeting, and some changes in the plan have been made.

The current WDCGG system cannot hold the version history for metadata. The new database structure for metadata is designed with the support of NILU/EBAS and the proto-type database has been developed methodically to cover all categories and species in the current WDCGG archive, which has been historically expanded sometimes in ad hoc manner. The new structure is carefully designed in order to be expanded flexibly to meet potential demands for new species and categories. The harmonization of the WDCGG archive with NOAA ObsPack data package is also discussed.

Relating to the new strategic implementation plan for the Global Atmosphere Watch (GAW) Programme, the data management of the World Data Centres is now afoot for some transformation. In this connection, WDCGG is planning to hand over the data-centre function for reactive gas species (CO, NO_x, SO₂, VOC, tropospheric O₃, etc.) to other GAW WDC, then WDCGG can concentrate on the services for long-lived GHGs (CO₂, CH₄, CFCs, N₂O, halocarbons etc.) The opinions for the demarcation of covering gas species between datacentres for GHGs and RGs are invited from GHG science community. Although this transformation discussion has started, some progress has been made on the VOC archive data and their visualization in the WDCGG.

We ask each data contributor for cooperation on the metadata input task, therefore, our efforts to alleviate this burden is beneficial to all contributors. Another presentation from WDCGG staff will show a proto-type design of the new data submission procedure and interface.

B34 ESTIMATING CO₂ SINKS AND SOURCES IN NEW ZEALAND FROM ATMOSPHERIC MEASUREMENTS AND LAGRANGIAN MODELLING

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Over the Kyoto period (2008-2012), New Zealand exceeded its emissions target by about 20%, but these emissions are thought to have been offset by nearly equal forest uptake over this period. Due to the key role that forest uptake plays in New Zealand's national greenhouse gas inventory, independent top-down estimates underpinned by our atmospheric data are needed to verify New Zealand's carbon sinks. We present the first results from a regional inversion method developed to determine the spatial and temporal distribution of CO₂ sinks and sources across New Zealand between 2011 and 2013. This method estimates regional air-sea and air-land fluxes from in situ measurement records from two stations, Baring Head (41.4S, 174.9E) and Lauder (45.0S, 169.7E), and back-trajectory simulations from a Lagrangian dispersion model. The impact of regional fluxes on atmospheric CO₂ mole fractions is calculated as the difference between the in situ data and an observationally determined baseline that accounts for latitudinal variability in background air entering the domain. The sensitivities of the inversion method to several modelling assumptions are reported.

The results indicate a strong seasonal cycle in the South Island of New Zealand, especially in western regions covered by indigenous forest, suggesting higher photosynthetic and respiratory activity than suggested by land process models. On the annual scale the terrestrial biosphere in New Zealand is estimated to be a net CO₂ sink, removing 98 (± 37) Tg CO₂ yr⁻¹ from the atmosphere on average during 2011-2013. This sink is much larger than the reported 27 Tg CO₂ yr⁻¹ from the national inventory for the same time period. The differences to the bottom-up estimates can in part be reconciled when factors related to tree harvesting, grassland growth and soil uptake are considered, but some differences are likely to remain.

B35 REVISIT THE GLOBAL AVERAGE OF GHGS ABUNDANCES BY THE WDCGG METHOD

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The difficulties to determine a global mean mole fraction are caused by the sparsity and irregularity on distribution of in-situ greenhouse gas (GHG) observations. We revisit WDCGG global average of GHGs abundances to make it more spatially representative and more useful.

For long years, The Global Monitoring Division of NOAA/Earth System Research Laboratory has provided the global means of GHGs with selected well-mixed marine boundary layer (MBL) data using their globally deployed flask sampling network. Whereas, in 2006, WMO World Data Centre for Greenhouse Gases (WDCGG) started to compute another global mean including carefully screened data from inland stations in addition to the MBL selections.

To better estimate and utilize the global average of atmospheric CO₂ abundance, we examine inland stations' representativeness further from the current WDCGG method by which MBL and inland data are equally weighted in a zonal average before calculating the global mean. We will show the result of our examination with modified method of global mean calculation. Some comparisons with the global surface average computed by an inversion analysis using a newly developed CO₂ transport model (GSAM-TM) are also presented.

B36 THE TRICKS OF THE CLIMATE POLITICIANS

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On 27 November 2014 the widely circulated German newspaper, Die Zeit, posted an article on various tricks used by politicians in negotiating greenhouse gas emission reductions (<http://www.zeit.de/2014/49/klimakonferenz-klimagipfel-lima>). The article was a prelude to the 20th Conference of Parties (COP-20) to the United Nations Framework on Climate Change, to be held in Lima, Peru, in December 2014, but it has particular relevance to the upcoming COP-21 scheduled to take place in Paris, December 2015, where decisions and specific agreements are largely anticipated. While the article was informative, the most compelling part was a full page display of how the various stances and negotiations would affect the ultimate outcome these efforts. Needless to say, the prognosis is not good – unless much tighter restrictions are not only agreed to, but enacted upon and monitored. Current commitments could lead us to a 3.6°C world if those commitments are held. This article is a good example of communicating the issue of emissions to an informed public, though it relies to some extent on an ability to understand fundamental data plots. We have taken the liberty to translate the graphic into English for GGMT attendees to ruminate over. Key to a successful future will be enhanced measurement and analysis systems to inform decisions as time goes by, leading to better policy decisions and responsible management. Communicating this issue will continue to be a struggle.

(Note: A world warmed by 2°C by 2100, the Kyoto Protocol (1990) target, would be substantially different than today, in that in such a world, one would expect an average of 6°C (11°F) warming over the continents. Of course this would not be distributed evenly. But, what's worse is that the current state of negotiations would lead to a +3.6°C (6.5°F) average global warming, or +10.8°C (19.5°F) average over the continents.)

B37 PROCESSING OF CO₂, CH₄ AND CO MOLE FRACTIONS AT THE ICOS ATMOSPHERIC THEMATIC CENTER

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The ICOS Atmospheric Thematic Center (ATC) started to operate processing chains of atmospheric greenhouse gases mole fractions in 2009 as part of the ICOS preparatory phase. Four sites have been participating to the demonstration experiment and the results provide the basis for improvement of the facility and tools set up at the ATC. The facility which has been developed includes servers to receive raw data files at least once per day, to archive and process the data, and to provide data products updated daily in order to support the quality control of the dataset which is done by the scientists and engineers in charge of the instruments. The tools provided by the ATC include two graphical applications which enable to configure the station/instrument setup at the stations, and to quality control the time series.

The ICOS atmospheric database is the backbone of the system. It has been developed with an emphasis on the traceability of the data processing. As soon as the data are received, they are automatically processed with calibration and water vapor corrections. The mole fractions calculated in near real time are automatically re-evaluated as soon as the next instrument calibration has been processed, or when the station supervisors perform the quality control.

The poster presents the different steps of the automatic data processing and the tool developed to allow the manual quality control of the data.

References:

ICOS ATC demonstration: <https://icos-atc.lsce.ipsl.fr>