Uncertainties of NOAA GHG measurements from discrete air samples and zonal means

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Measurements of atmospheric greenhouse gases (GHG) can not be effectively compared nor properly analysed unless they include estimates of uncertainty. At NOAA, our earliest measurements of CO_2 from discrete samples began in the 1960s when few accompanying quality assurance (QA) data were collected, hampering efforts to estimate uncertainties.

I will describe a method to calculate uncertainties for discrete samples that includes a common framework of multiple terms combined in quadrature. We estimate uncertainty in each measurement from the following: $\sigma_u^2 = \sigma_{st}^2 + \sigma_{lt}^2 + \sigma_{sp}^2$. σ_{st} is short-term measurement noise (i.e., repeatability). We can assess it from the variance in measurements of test flasks filled simultaneously, from the mean difference between pairs of air samples collected simultaneously at sites with low natural variability (e.g., South Pole), and from the variance in measurements of air from a cylinder. σ_{lt} is the long-term variability of the analytical system (reproducibility); it is an assessment of how compatible measurements are over times scales of months to years. This is difficult to assess. Neither "test" flasks nor target cylinder measurements reveal significant long-term biases, but in both there may be periods when measurements are significantly different from assigned values. We use the mean difference between measurements of a target cylinder and its assigned value as a proxy for this parameter. σ_{sp} is a measure of our ability to propagate the WMO standard scales (reproducibility of standard scale propagation), and it is based on repeat calibrations, more than one year apart, on an independent analytical system dedicated to propagating the standard scales. Additional uncertainty terms are added when necessary. For example, early measurements of CO_2 were made against standards of CO_2 in N_2, and these were later corrected to account for pressure broadening effects. In this case, we include a term for the uncertainty in this correction.

We've historically assessed uncertainty in zonal averages from our network distribution with a "bootstrap" method. To account for potential intermittent bias lasting over variable periods, we've developed a Monte Carlo (MC) approach to compliment our bootstrap method. The MC method is designed to realistically account for periods of bias by modifying actual data based on bias randomly selected from a Gaussian distribution and applying it to a randomly selected analysis period from 3 to 24 months. One hundred sets of time series are produced, each with a unique, randomly-selected bias and time-period. As with the network bootstrap method, the 100 time-series are smoothed temporally and spatially to produce zonal means, and each of those are averaged to produce the statistics of interest. As an example, the uncertainty on the annual increase for N_2O is about a factor of 10 larger when determined with the MC method compared to the bootstrap. Because N_2O is very well mixed in the background atmosphere, there is little spatial variability to exploit in the network bootstrap analysis, and uncertainties are unreasonably small, so this new method produces more believable uncertainties.

Efforts to separately report random and systematic measurement uncertainty for continuous measurements in the NOAA Global Greenhouse Gas Reference Network

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We have developed a multi-species framework for separately reporting time-dependent random and systematic uncertainties for continuous measurements of CO_2, CH_4, and CO [Andrews et al., 2014]. Knowledge of systematic errors enables reliable trend detection and confident interpretation of spatial gradients, and information about random errors is needed to correctly propagate uncertainties when computing time averages and to estimate atmospheric variability. We will show that in most cases, random and systematic errors can be estimated using straightforward diagnostics, and we will describe modifications for measurements of humid air streams. We will also discuss challenges encountered in applying the framework to historical data records.

References

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An update of comparisons of non-CO_2 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 of greenhouse and ozone depleting gases often require data from more than one network's group of stations. It is therefore 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 comparisons (now more than 400 individual comparisons) of non-CO_2 greenhouse gases (now totalling more than 45 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 six common measurement sites are: Cape Grim, Australia; Cape Matatula, American Samoa (includes some NOAA in situ data); Ragged Point, Barbados; Trinidad Head, USA; Mace Head, Ireland; and Zeppelin, Norway.

This presentation will give an update of the comparisons presented at GGMT-2015 (La Jolla, USA) summarising the methodology and resultant output, with detailed results from selected comparisons, including the results from the new N_2O scales. 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.

Revision of the WMO CO_2 calibration scale

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The NOAA Global Monitoring Division serves as the Central Calibration Laboratory for the WMO Global Atmospheric Watch program for carbon dioxide (along with CH_4, CO, N_2O, and SF_6). The WMO CO_2 scale, identified as WMO-CO_2-X2007, is defined, maintained, and linked to the SI using a manometric method. Since the last scale revision in 2007, we have identified two issues that impact the accuracy of the CO_2 scale: 1) we discovered a minor calculation error in the 2nd Virial coefficient for CO_2, and 2) apparent loss of CO_2 during the measurement process. While our primary objectives are consistency and reproducibility, we should also correct for bias when possible. In addition to these issues which affect accuracy, operational changes such as implementing a new laser spectroscopic methods for CO_2 analysis (Tans et al., 2017) and expansion of the core mole fraction range from 250-520 μmol mol^{-1} to 250-600 μmol mol^{-1} also justify a scale update.

We recalculated the CO_2 mole fractions derived from NOAA's manometric measurements (1996-2015) for the 15 WMO primary standards, making corrections for the 2nd Virial coefficient and apparent CO_2 loss. We then harmonized the manometric values by correcting for the residuals following analysis by the laser spectroscopic method. Since the applied corrections are mole fraction dependent, the scale update is also mole fraction dependent. The net change in scale is approximately equal to 0.0008179*X – 0.153, where X is the X2007 scale. Hence, at 400 μmol mol^{-1}, the net change is +0.17 μmol mol^{-1}. We have also re-examined uncertainties and find that the total, expanded (~2-sigma), uncertainty is ~0.22 μmol mol^{-1} (0.056%) at 400 μmol mol^{-1} (previous estimate was 0.14 μmol mol^{-1}). We will present our proposed scale revision, including updated mole fraction assignments for the primary standards as well as propagation to secondary and tertiary standards.

References

Tans, P. P., A. M. Crotwell, and K. W. Thoning (2017), Abundances of isotopologues and calibration of CO_2 greenhouse gas measurements, *Atmos. Meas. Tech. Discuss.*

An update on the WMO CO X2014A scale

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With the release of the WMO CO X2014A scale revision, NOAA changed the method of maintaining the WMO CO in air scale. Previous scales were defined by repeated gravimetric sets made every 4-6 years. With X2014A, we maintain a single set of primary standards and all calibrations since January 2011 are traceable to this single set. This is more consistent with how other calibration scales are maintained by NOAA. However, the lack of stability of CO standards in high pressure aluminium cylinders means we had to develop a method for evaluating drift in the primary standards. We use an internal tracer technique to monitor the slow growth of CO in the primary standards. Percent-level gravimetric mixtures of CO and CH_4 in air are used as "parent" tanks. We assume growth of CO has no significant impact on the gravimetrically determined CO:CH_4 ratio. Static dilutions from these parent tanks were made to create suits of standards with CO covering the range of interest (30 – 1000 nmol mol^{-1}). CH_4 in these daughter products is measured and CO is calculated using the known CO:CH_4 ratio of the parent. The parents are considered stable and by making fresh daughter standards periodically, we can determine the growth rate of CO in the primary standards.

At GGMT-2015 we described the internal tracer method, and the X2014A scale revision was released shortly thereafter. We have continued measuring the primary standards twice per year using the internal tracer technique since then. At the time of the X2014A scale revision we felt the applied drift rates were probably too high. Subsequent measurements since 2015 have confirmed this. While still data limited, current best estimates of drift rates are approximately 0.1 – 0.2 nmol mol^{-1} yr^{-1} lower than the X2014A assignments. We present an update on the most recent determinations of the drift rates in the CO primary standards, implications for the WMO CO scale, and future plans to ensure scale stability.

The result of the first SF_6 inter-comparison Experiment (SICE) 2016-2017

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One of main activities of World Calibration Centre for SF_6 (WCC-SF_6) is to assist WMO members operating GAW station to link their SF_6 observations to the WMO reference scale through comparisons with standards calibrated against CCL (Central Calibration Laboratory for SF_6, NOAA/ESRL) in the GAW quality assurance system (WMO GAW no 228). According to a memorandum of understanding (MoU) between World Meteorological Organization (WMO) and Korea Meteorological Administration (KMA), which was designated as WCC-SF_6, the first SF_6 inter-comparison Experiment had been implemented from 2016 to 2017 The 12 laboratories participated this activity and three of them had their own standard scale while the others used WMO scale (NOAA scale). There were two circuits, which consist with 8 labs in Europe and 3 labs in Asia-Pacific region, and CCL contributed to each circuit as a participant. In this presentation, the result of the first SF_6 inter-comparison experiment will be summarized.

And also, WCC-SF_6 has an inter-comparison with CCL biennially to confirm the differences between two labs. We will also present last results in 2013, 2015 and 2017 respectively in this presentation.

References

WMO/GAW, 2017, WMO Global Atmosphere Watch (GAW) Implementation Plan: 2016-2023, GAW report No.228

A new method to produce SI-traceable, primary calibration standards for halogenated greenhouse gases

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For many years, comparability of measurements obtained with various instruments over the globe within a monitoring network has been ensured by anchoring all results to a unique suite of reference gas mixtures, or so called “primary calibration scale”. Such suites of reference gas mixtures are usually prepared and then stored over decades in pressurised cylinders by a designated laboratory. For halogenated gases, this anchoring method is still highly relevant as measurement reproducibility is currently much better (<1%) than the expanded uncertainty of a reference gas mixture (usually >2%, k=2 or 95 % confidence interval). However, newly emitted halogenated gases (such as HFC-1234yf) are already measured in the atmosphere at sub-pmol/mol levels [e.g. 1], while still lacking an established reference standard. For compounds prone to adsorption on material surfaces, it is difficult to evaluate mixture stability and thus variations in the level of uncertainty over time in cylinders at pmol/mol levels.

To support atmospheric monitoring of halogenated gases, we present here a method to produce an SI-traceable reference gas mixture at near atmospheric molar fraction, combining gravimetric and dynamic preparation. The generation process consists of four successive steps. In the first step the matrix gas, nitrogen or synthetic air is purified. In a second step, this matrix gas is spiked with the pure substance using a permeation device from which the pure substance (e.g., HFC-1234yf), liquefied in a reservoir, permeates through a polymer membrane. This process occurs in a temperature and pressure controlled chamber, with a constant matrix gas flow. The resulting linear mass loss rate is precisely calibrated using a magnetic suspension balance. In a third step the desired molar fraction is reached by dilution of the high concentration mixture exiting the permeation chamber with a chosen flow of the matrix gas in one or two subsequent dilution steps. All flows are piloted by thermal mass flow controllers. All surfaces in contact with the gas mixture are passivated with a silica-based, inert surface coating (SilcoNert2000®, SilcoTek Inc.) in order to reduce adsorption/desorption processes. In the last step the mixture is pressurized into Silconert2000®-coated stainless steel cylinders by cryo-filling. The final mixture has an expanded uncertainty of no more than 3% (k=2).

We present the realisation of a suite of multi-component reference gas mixtures for HFC-1234yf, HFC-125, SF_6, CFC-13 and HCFC-132b, composed of 11 cylinders each at a slightly different molar fraction, the associated uncertainty budget according to GUM [2] and first results of comparison to other existing primary calibration scales.

References

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Quality assurance and quality control of the upcoming ICOS-RI atmospheric dataset

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The Integrated Carbon Observation System European Research Infrastructure (ICOS-ERIC) was launched by the European Commission on November 2015. It integrates atmosphere, ecosystem and ocean greenhouse gas observations to provide timely and reliable data for research, policy making, and the general public. In 2016 the official station labeling process of the ICOS stations has been initiated, and first ICOS atmospheric stations will be announced during the autumn general assembly.

In this presentation we will first present the specifications established for the ICOS atmospheric stations. Those specifications have been defined during the preparatory phase and are annually revised by the Monitoring Station Assembly (MSA) which gathers station principal investigators (PIs) of the ICOS national networks, and responsible of the ICOS central facilities. The two central facilities of the atmospheric components are the Atmospheric Thematic Center (ATC) ensuring that all data are treated in near-real time (24hr) and quality controlled with the same algorithms, and the Central Analytical Laboratories in charge of providing calibration references and analyzing flasks sampled at the stations. ICOS distinguishes two classes of stations. Both class 1 and 2 stations have the same requirements in terms of quality assurance plan for continuous CO2 and CH4 measurements, but class 1 stations have to measure more parameters and to perform regular flask sampling. In a second part we will present the continuous time series obtained in 2016/2017 by the most advanced candidate stations to the ICOS labelling, with particular emphasis on quality control aspects of the measurements (e.g. regular target gases measurements).

QA/QC of IAGOS NRT GHG data

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Within the European research infrastructure IAGOS, the In-service aircraft for a global observing system, globally distributed measurements of greenhouse gases (GHG) CO2 and CH4, as well as CO will start in 2017. A supplemental type certificate for installation of the CRDS system including two calibration gas cylinders in the avionics bay of Airbus A340 and A330 has been issued by EASA in late 2016. First integration is scheduled for June 2017 aboard an A330 (tail sign D-AIKO) operated by Lufthansa. Within the next years, about five aircraft from various airlines operating out of different parts of the world will be equipped. Near-real time (NRT) data transmission is foreseen for utilization of observations by the Copernicus Atmosphere Monitoring Service (CAMS) and by other users.

Due to the increasing use of NRT data for validation of data assimilation systems and their products, it is important to properly quantify the uncertainty of NRT observations so that the information can be utilized quantitatively. The presentation will discuss the various steps involved in ensuring traceability of NRT data to WMO calibration scales. Before each installation on board the aircraft for an observing period of several months, the CRDS system together with its two calibration cylinders is calibrated against in-house reference gases. During the deployment period, the system performs self-calibrations approximately every two hours using the two calibration cylinders installed within the aircraft, with longer (10 min. per cylinder) calibration on ground, and shorter (3 min. per cylinder) calibrations during flights. After each flight the data are transferred via GSM to the central IAGOS database in Toulouse, and a series of automated processing steps to assess housekeeping data and instrument drift are performed, including provisional uncertainty propagation for the NRT data. Data are then made available to users in NASA Ames 1001 format. The multiple calibration gas measurements during each deployment period will be used to assess instrument drift, and to quantitatively propagate uncertainties into the dry air mole fractions reported to the users. After an initial testing phase, it is envisioned to fully automate such assessments for the NRT data stream.

WCC-Empa – Activities and Achievements

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Empa operates the World Calibration Centre for Carbon Monoxide (CO), Methane (CH_4), Carbon Dioxide (CO_2) and Surface Ozone (WCC-Empa) since 1996 as a Swiss contribution to the Global Atmosphere Watch (GAW) programme and has conducted over 80 system- and performance audits over the past 20 years. To increase the number of N_2O audit at GAW stations. WCC-Empa collaborates with the World Calibration Centre for Nitrous Oxide (WCC-N_2O) hosted by the Karlsruhe Institute of Technology (KIT), Institute of Meteorology and Climate Research (IMK-IFU).

WCC-Empa is responsible for verifying the traceability of the measurements to the designated GAW reference maintained by Central Calibration Laboratories. The activities of WCC-Empa are a key element 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 (Zellweger et al., 2016).

The paper will give a comprehensive overview of WCC-Empa activities and summarise results and achievements of system- and performance audits at GAW stations. The focus will be on CO and N_2O comparisons, which will be analysed according to the method described by Zellweger et al. (2016). Audit results of these two parameters show that the WMO/GAW compatibility goals are often not met, and further improvements both on analytical techniques and calibration standards are needed to solve this issue. Furthermore, the results will be discussed in the context of comparisons made within the European Metrology Research Programme HIGHGAS project.

References

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Data Quality Objectives for stable isotopes in greenhouse gases: current status and future needs.

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GAW-Data Quality Objectives (DQOs) are based on the requirements related to the meaningful use of the data. For stable isotopes in greenhouse gases, DQOs mean metrological compatibility of the data obtained at different labs, stations and in different years (discrepancies not larger than XXX). This in turn implies correctness of calibrations (no lab-to lab biases in calibrations) as well as the long-term consistency (no drifts) of the isotope scales themselves which are currently based on artefacts. All that can be achieved based on the proper use of high quality Reference Materials (RMs) only. All in all DQOs may be considered as the combined uncertainty requirements, which includes (i) uncertainty of the reference materials in use, including primary RMs, (ii) uncertainty of lab' calibrations and (iii) typical (averaged) uncertainty due to sampling and measurements.

In particular DQOs for delta-13C give values (0.01 permil for air CO2 and 0.02 permil for air methane) which are hardly possible to reach in practice as the combined uncertainty, even by using the best analytical instruments. The situation needs a revision and potentially adapting approaches as developed in other areas.

This presentation aims to start the stable isotope section at the meeting. This will also review the most critical aspects and introduce topics for discussion as following:

- Components of uncertainty. Why in some cases increased number of measurements cannot improve the uncertainty anymore?
- 2-point data normalisation on the delta-13C scale aimed at the scale consistency - implications for the uncertainty propagation;
- Uncertainty needed for reference CO2-mixtures;
- Uncertainty reported by end-users: to be propagated to the scale level, based on the combined uncertainty of RMs in use (including reference CO2-mixtures).
- Which components of uncertainty are relevant to DQOs?
- Recommendations / SOPs on the use of reference mixtures and performing measurements at user-labs;
- Quality Assurance and Quality System at all levels (RM providers, CCL, analytical labs);
- Future and developments.

Delta-13C scale realisation based on the primary Reference Materials in the form of carbonates.

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The presentation will address the most important aspects of delta-13C scale realisation based on primary Reference Materials (RMs) from the IAEA as following:

- Release of IAEA-603, replacement of NBS19 (info on its uncertainty, consistency of the scale realisation);
- Large uncertainty found for LSVEC (second primary RM defining the scale-span for delta-13C scale). Replacement of LSVEC is urgently needed, the steps planed.
- Metrological requirements for RMs to be used in the atmosphere monitoring.
- A range of RMs needed for optical isotopic analysers – pure CO2 gases and gas mixtures.
- Collaborations and expected results (e.g. gas mixtures planned by EMPIR project leaded by NPL).

An overview of strategic plan and developments will be given.

JRAS-06: Keeping up with changing internationally-distributed, light-element stable isotopic reference materials

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One of the most critical aspects of measuring carbon isotopic signatures of atmospheric CO_2 is the stringent standardisation procedure which is required. Without it, inter-laboratory $\delta^{13}C$ comparisons of atmospheric CO_2 are difficult at best, and impossible at worst. Following the "principle of identical treatment" (IT principle; Werner and Brand, 2001), isotopic reference materials for atmospheric CO_2 analysis should be chemically identical to analysed samples. For the last 10 years, the stable isotope laboratory at the Max-Planck-Institute for Biogeochemistry (BGC-IsoLab) has offered the Jena Reference Air Set (JRAS-06) to the scientific community. CO_2 for this set of reference materials is evolved from carbonates, including NBS 19 calcite ($\delta^{13}C \equiv +1.95$ mUr and $\delta^{18}O \equiv -2.2$ mUr) that anchors one end of the VPDB-LSVEC carbon-isotope scale and LSVEC lithium carbonate ($\delta^{13}C \equiv -46.6$ mUr), and it is diluted into CO_2-free matrix air. Thus, an air-CO_2 scale has been produced that is linked directly to the VPDB-$CO_{2(gas)}$ scale. Use of JRAS-06 enables laboratories to follow the identical treatment principle and report their findings on the VPDB-$CO_{2(gas)}$ scale.

The year 2016 was a turbulent year for the VPDB oxygen-isotope scale and the VPDB-LSVEC carbon-isotope scale. The distribution of NBS 19 was discontinued because its supply was nearly exhausted. A new calcite, IAEA-603 (Carrara marble; https://nucleus.iaea.org/rpst/referenceproducts/referencematerials/Stable_Isotopes/13C18and7Li/IAEA-603/index.htm; $\delta^{13}C = +2.46 \pm 0.01$ mUr and $\delta^{18}O = -2.37 \pm 0.04$ mUr) was introduced by the International Atomic Energy Agency as an internationally-distributed, secondary isotopic reference material to anchor measurement results to the carbon- and oxygen-isotope scales. Furthermore, LSVEC was deemed inappropriate as a second scale anchor because it can react with atmospheric CO_2, thereby affecting its carbon isotopic signature. BGC-IsoLab is currently involved in a collaborative effort to quantify the $\delta^{13}C$ value of a high purity calcium carbonate with a $\delta^{13}C$ value of ~−42 mUr that is intended to serve as an internationally-distributed, secondary isotopic reference material to anchor measurement results to the VPDB-LSVEC carbon-isotope scale. This new material also can be used to anchor the JRAS-06 scale. Here, we present preliminary results on this new high purity calcium carbonate whose $\delta^{13}C$ value does not change with exposure to atmospheric CO_2. Additionally, we discuss some considerations that need to be made when determining isotope-delta values of secondary isotopic reference materials.

Maintaining quality with quantity: lessons learned in the corrections and calibrations of INSTAARs large isotopic dataset

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The Stable Isotope Laboratory at CU-INSTAAR works with NOAA Global Monitoring Division's Global Greenhouse Gas Reference Network to measure stable isotopes of carbon dioxide and methane. We have 27 years of isotopic measurements of $\delta^{13}C$ and $\delta^{18}O$ of CO_2 and 19 years of measurements of $\delta^{13}C$ of CH_4. Here we highlight ongoing challenges to maintaining the world's longest continuous monitoring program for stable isotopes of these greenhouse gases.

Recently, krypton (Kr) has been shown to interfere with measurement of atmospheric $\delta^{13}CCH_4$, assumed to result from tailing of doubly charged $86Kr^{2+}$ and scattering of singly charged Kr ions (Schmidt et al. 2013). One method of removing this interference is by installation of a post-combustion column (PoraBond Q, 12 m) in-line with the GC-IRMS sample stream to separate Kr from CH_4-derived CO_2. Measurement of a suite of standards of different methane mixing ratios shows the effect to be between 0.017 and 0.03 permil per 100 ppb increase in CH_4. Interpolation over the last 19 years of INSTAAR measurements, when globally-averaged atmospheric methane increased from 1772-1840 ppm, indicates that the effect of the Kr interference on $\delta^{13}CCH_4$ is likely no more than -0.03 ‰, compared with the global long term decline in globally-averaged $\delta^{13}CCH_4$ of 0.25 ‰. We are working to better quantify this effect and correct the $\delta^{13}CCH_4$ time-series record accordingly.

We have also seen new challenges in recent years maintaining our INSTAAR isotopic CO2 scale (our independently established tie to VPDB) within our lab, as we now measure samples on four different instruments. A standard cylinder measured periodically on all instruments and with different working references between 1996 and 2015 has a reproducibility (1 σ standard deviation) of 0.023 permil for $\delta^{13}CCO_2$ and 0.123 for $\delta^{18}OCO_2$; since 2005 it is 0.019 and 0.042 permil respectively. Considering the long time frame, the magnitude of this variance is respectable; however, our past strategy of "bootstrapping" our scale between working references is inadequate to stay within our targeted precision of 0.015 and 0.03 permil. We are in the process of switching to the JENA-06 scale (established by MPI-BGC, the Central Calibration Laboratory for CO_2 isotopes), and establishing standard operating procedures to propagate the scale to multiple working references. The resulting change in our dataset will be modest: INSTAAR data are too positive by about 0.02 permil for $\delta^{13}C$ and 0.06 permil for $\delta^{18}O$. We are assessing our agreement at more negative isotopic values, where INSTAAR measurements are less precise both within and between instruments, possibly due to instrument-specific scale contraction or expansion. We will discuss our efforts to resolve these issues, our timeline and methods for reprocessing our large data set to the JENA-06 scale, our estimation of uncertainties, and our adoption of best practices going forward.

Measurement and Calibration Uncertainty in the CSIRO atmospheric CO2 Stable Isotope Program

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The CSIRO atmospheric CO_2 stable isotope measurement program has been running for nearly 40 years. Early measurements focused on samples collected at Cape Grim, Tasmania, but the program expanded during the 1980s to a global flask collection program with numerous international partners. Two independent programs were run by CSIRO at Cape Grim for almost 30 years that provided a unique opportunity to assess sample collection, measurement and calibration procedures and test new procedures.

Initial measurements were calibrated using a high purity CO_2 gas calibrated against NBS19 carbonate. As the measurement program developed a series of high-purity CO_2 gases were intercalibrated to provide a calibration strategy for the measurements. With the acquisition of a new mass spectrometer in 1990 a new strategy was developed around whole air standards that were integrated with the CO_2 gases and the carbonate calibrations. The result of this measurement and calibration strategy is a high quality 35 year record of the stable isotopic composition of atmospheric CO_2.

An integral component of the calibration strategy was the establishment of a Quality Assurance system that enables any required corrections to be applied retrospectively to any measurement. Every step in the strategy has been assigned an uncertainty or a method for calculating the associated uncertainty. Some components of the final uncertainty assigned to a measurement come from values "assigned" to standards, while other components are calculated from measurements performed on a daily basis. Two recent developments to the system are (1) an automated recalibration procedure that assesses current and past calibrations and revises, when necessary, all measurements and determines an uncertainty for every measurement, and (2) a link to the WMO-CCL for the stable isotopes of CO_2. As almost all whole air and pure CO_2 standards are still available for analysis, the revised calibration procedure allows us to demonstrate consistency of the long-term trends observed in the atmosphere.

This talk will present the “production” version of this procedure and the newly developed, and soon to be implemented, revised procedure. Topics to be covered include:

Determination of instrumental effects
Development of ion correction procedures
The long-term atmospheric $\delta^{13}C$ record
Flask same-air comparisons with NOAA(INSTAAR) & ECCC
Round-robin exchanges, such as the IAEA funded CLASSIC program
Implications for carbon cycle modelling

On the calibration of isotopologue-specific optical trace gas analysers

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In recent years optical spectroscopic analysers have approached the precision and accuracy of established IRMS methods. Laser and FTIR-based analysers usually analyse whole air directly and quantify the concentrations or mole fractions of specific individual isotopologues, while whole-air calibration gases provided by central calibration laboratories are generally specified by their total target gas mole fractions and isotopic δ-values relative to a reference isotopic scale. The conversion between these equivalent descriptions of the trace gas and its isotopic composition is non-trivial, but with the precision and accuracy available from current optical analysers and required for atmospheric research (for example 0.05 ppm for CO_2 total mole fraction and 0.01‰ for $\delta^{13}C$) it is essential that the calcualations be made accurately and precisely without systematic errors or approximations.

Several papers in the last few years have addressed these requirements, with increasing rigour (e.g. Griffith et al., 2012; Wen et al., 2013; Flores et al., 2017; Tans et al., 2017). In this paper I review the requirements for isotopologue-specific calibration of optical analysers and describe a calculation scheme which is rigorously correct to the required accuracy, accounts for all possible isotopologues in the total sample, and is straightforward to apply. It sets out the conversions between isotopologue mole fractions, total mole fraction and δ scales, including the adjustments required to convert between the different isotope reference scales used in the GAW network and the Hitran database commonly used to analyse infrared spectra in optical analysers.

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Calibration strategies for FTIR and other IRIS instruments for accurate $\delta^{13}C$ and $\delta^{18}O$ measurements of CO_2 in air

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This talk will describe calibration strategies in laboratory conditions that can be applied to ensure accurate measurements of the isotopic composition of the CO_2 in air, expressed as $\delta^{13}C$ and $\delta^{18}O$ on the VPDB scale, with either FTIR (in this case a Vertex 70V (Bruker)) or an Isotope Ratio Infrared Spectrometer (IRIS) (in this case a Delta Ray (Thermo Fisher Scientific)). In the case of FTIR, two standards with known CO_2 mole fraction, and isotopic composition, in air are sufficient to make accurate measurements with standard uncertainties of 0.05 ‰ and 0.77 ‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively at a nominal CO_2 mole fraction of 400 µmol/mol in air. In the case of the IRIS system, two pure CO_2 gas isotope standards, diluent air and two standard of CO_2 certified for mole fraction and isotopic composition ($\delta^{13}C$ and $\delta^{18}O$) are sufficient to make accurate measurements of $\delta^{13}C$ and $\delta^{18}O$ with standard uncertainties of 0.29 ‰ and 0.60 ‰ respectively. The calibration strategy was validated using a set of five traceable Primary Reference Standards. The standards, produced with whole air or synthetic air as the matrix over the mole fraction range of 378- 420 µmol mol-1, were prepared and/or certified either by the National Institute of Standards and Technology (NIST) and the National Physical Laboratory (NPL). The standards were prepared in three subsets of different $\delta^{13}C$ values between -35‰ and -1‰ using pure CO_2 obtained from specific sources, namely: combustion; Northern Continental and Southern Oceanic Air and a gas well source. The isotopic composition of all standards was value assigned at the Max Planck Institute for Biogeochemistry Jena (MPI-Jena).

Gaseous reference materials to underpin measurements of amount fraction and isotopic composition of greenhouse gases

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The European Metrology Research Programme HIGHGAS project has led to significant advances in the development of high accuracy, SI traceable, gaseous reference materials of CO_2, CH_4, N_2O and CO. Research has focussed on driving the uncertainty of the reference materials towards the WMO compatibility goals and monitoring their stability. Improvements have been achieved by optimising passivation chemistry used in cylinder treatment, reducing the uncertainty in the gravimetry of the matrix components and making high-accuracy quantification of target impurities in the matrix gas.

In addition a capability to fully characterise the isotopic composition of the CO_2 in the reference materials has been developed to account for measurement biases introduced by instrumentation detecting only certain isotopologues. The data shows that knowledge of the CO_2 composition is crucial for addressing commutability issues from preparing synthetic reference materials but also for assigning the correct atomic weight for the calculation of gravimetrically prepared mixtures, which can change the amount fraction by as much as 4.4 nmol/mol.

This work has provided the framework for new research priorities focussed on developing gaseous reference materials of CO_2 and N_2O for underpinning measurements of stable isotopes to infer their origin in the atmosphere. A new infrastructure is proposed that will deliver international CO_2 reference materials with traceability to the VPDB primary standard, to meet the increasing demand. New international gaseous N_2O reference materials will also be developed with stated uncertainties. The research will develop new field-deployable spectroscopy and initiate SI traceability of the international CO_2 isotope ratio scale by re-measuring the absolute isotope ratios by gas-source isotope ratio mass spectrometry.

Using Isotopic Fingerprints to Trace Nitrous Oxide in the Atmosphere

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Nitrous oxide (N_2O) is a potent greenhouse gas and the strongest ozone-destroying substance emitted this century. Reliable predictions of future emissions, requires knowledge of the responsible N_2O source processes. Isotopic composition of N_2O is a tracer to distinguish between different emission pathways, as well as constraining the stratospheric N_2O sink. The four most abundant N_2O isotopic species are: $^{14}N^{14}N^{16}O$ (99%), $^{14}N^{15}N^{16}O$ (α, 0.4%), $^{15}N^{14}N^{16}O$ (β, 0.4%) and $^{14}N^{14}N^{18}O$ (0.2%). Due to its asymmetric molecular structure, N_2O (α) and N_2O (β) differ only in the position of the ^{15}N atom, and the difference in their abundance – known as site preference (SP) – is a particularly powerful indicator for different N_2O production mechanisms.

Here we illustrate the potential of laser spectroscopy for real-time, high-precision analysis of isotopic composition in ambient N_2O. Furthermore, we present applications, in agricultural as well as suburban environments, illustrating the advantage and necessity of real-time data of trace gas isotope ratios. In an extensive campaign above a managed grassland, nitrifier-denitrification and denitrification were identified as prevalent sources of N_2O and variations in isotopic composition were attributed to alterations in the extent to which N_2O was reduced to N_2 [1]. In an ongoing project, we validate the real-time N_2O isotope data against a process-based biogeochemical soil model (DNDC) with an isotope sub-module (SIMONE), which is based on published isotope effects [2]. At a suburban site, the isotopic composition of atmospheric N_2O was monitored over 18 months to determine the source isotopic composition, which varied significantly compared to chemical and meteorological parameters. FLEXPART-COSMO transport modelling in combination with modified EDGAR inventory emissions was able to capture variability in N_2O mole fraction well, but simulations of isotopic composition showed little agreement with observations, indicating that the range of literature values of isotopic source signatures significantly underestimates the true variability [3].

In summary, we are convinced that real-time analysis of N_2O isotopic composition is an efficient approach to disentangle N_2O source / sink processes in agricultural as well as suburban / industrial environments. Combination of point measurements with modelling approaches provides spatial resolution and enables validation of emission inventories.

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Methane isotopes – clues to the budget changes: and the need for independent isotopic measurement programs.

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Methane is rising, but the causes behind the rise are not clear. One possibility is that methane sources have increased; the other hypothesis is that sinks have decreased. The actual explanation may be between these two end-members. Isotopic measurements provide further constraints: $\delta^{13}C_{CH4}$ is becoming more negative from pole to pole, and the start of this trend coincided with the start of the rise in methane mole fraction. The trend towards lighter $\delta^{13}C_{CH4}$ has been observed by several independent groups.

Had the data all come from one source (i.e. NOAA), it could be argued that the isotopic trend was simply a calibration drift, affecting both standard and trap or target tanks. But on both Ascension and Alert, parallel isotopic time series are being measured by both NOAA and Royal Holloway. The two sets of data are independent, but closely comparable. This gives confidence that the measurements are indeed accurate, and do not hide unrecognised system drift.

Plotted together, the two high-precision (1 s.d ~ 0.05‰) isotopic records are useful in a different way: changes in methane sources can quickly shift regional $\delta^{13}C_{CH4}$ values (e.g. in the remote Arctic or S. Atlantic marine air). In contrast, changes in methane sinks only have a slow impact on $\delta^{13}C_{CH4}$ of remote air masses. The 'bumpiness' and rapid steps in the Alert and Ascension $\delta^{13}C_{CH4}$ data sets thus indicate that increased sources are driving the growth in methane, rather than declining sinks.

Nisbet, E. G., et al. (2016) *Global Biogeochem. Cycles*, 30, doi:10.1002/ 2016GB005406

Integrated urban Greenhouse Gas Information System (IG^{3}IS): Advances in the urban GHG monitoring implementation plan and results of previous and current city-scale studies

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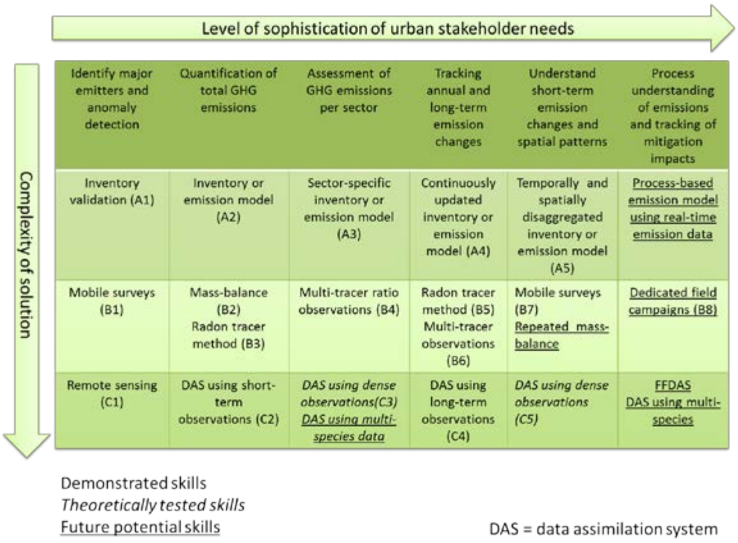
The Lima–Paris Action Agenda of the Paris Agreement has formalized a role for sub-national entities such as cities (large urban source regions) as leaders in greenhouse gas mitigation and climate adaptation. Currently, over half of the world's population lives in metropolitan areas and future population growth is also predicted to occur mostly in these urban centers. Therefore, the implementation plan of the Integrated Global Greenhouse Gas Information System (IG^{3}IS) of WMO/UNEP has identified urban GHG emission as a core action area where scientific information can be expected to respond to stakeholder needs in the near future. The IG^{3}IS activities aim to help create the framework to provide diagnosis of urban emissions at scales relevant to urban decision making and enable identification of low-carbon or carbon mitigation opportunities.



Identify major emitters and anomaly detection	Quantification of total GHG emissions	Assessment of GHG emissions per sector	Tracking annual and long-term emission changes	Understand short-term emission changes and spatial patterns	Process understanding of emissions and tracking of mitigation impacts
Inventory validation (A1)	Inventory or emission model (A2)	Sector-specific inventory or emission model (A3)	Continuously updated inventory or emission model (A4)	Temporally and spatially disaggregated inventory or emission model (A5)	Process-based emission model using real-time emission data
Mobile surveys (B1)	Mass-balance (B2) Radon tracer method (B3)	Multi-tracer ratio observations (B4)	Radon tracer method (B5) Multi-tracer observations (B6)	Mobile surveys (B7) Repeated mass-balance	Dedicated field campaigns (B8)
Remote sensing (C1)	DAS using short-term observations (C2)	*DAS using dense observations(C3)* DAS using multi-species data	DAS using long-term observations (C4)	*DAS using dense observations (C5)*	FFDAS DAS using multi-species

Demonstrated skills
Theoretically tested skills
Future potential skills

DAS = data assimilation system

Here, we present the current status of the IG^{3}IS implementation plan and report on the identified (widely varying) needs of city stakeholders. IG^{3}IS will provide a tiered approach to help address those needs ranging from basic to most detailed emission information. Many research groups have worked on different data-driven, observational and (inverse) modelling techniques for city-scale GHG studies that can become core elements of a future IG^{3}IS framework after a harmonisation of techniques can be achieved. This study will also give a (short) overview of key elements of a potential tiered system and results from test-bed experiments e.g. Indianapolis, Paris, Recife, etc. where novel techniques (total column CO_2, lower-cost sensors, multi-species observations and modelling, etc.) have been tested.

Detection of trends in urban CO_2 emissions: Results from the INFLUX tower network

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The overall objective of the Indianapolis Flux Experiment (INFLUX) is to develop, evaluate and improve methods for measuring greenhouse gas emissions from cities. The atmospheric-based top-down method of determining greenhouse gas emissions is complementary to inventories, allowing an independent assessment of emissions and the ability to quickly detect temporal changes in emissions. Cavity ring-down spectroscopic measurements of CO_2 on a network of towers began in Indianapolis in 2010. A regional atmospheric inversion system uses these data to infer urban emissions. Here we focus on the ability to detect trends in the Indianapolis CO_2 emissions from 2012 to 2015. Over the period, an agreement in the 3-year trend emerged from the comparison of inverse CO_2 emissions to annual estimates from energy use statistics despite differences in the year-to-year variability.

Furthermore, we use CO_2 mole fraction data alone to demonstrate the ability to quantify point source emissions, and their changes. The Harding Street Power Plant in downtown Indianapolis, like many power plants across the country, was recently converted from coal to natural gas, with the conversion being completed in March 2016. The Harding Street Power Plant is in the southwest quadrant of downtown, 6 km to the west of INFLUX Tower 10. Forward modeled CO_2 indicates that prior to the conversion of the power plant from coal to natural gas, 47% of the CO_2 mole fraction enhancement at Tower 10 was attributable to the electricity production sector. Using the standard deviation within the hourly CO_2 measurements as an indicator of plume strength, we detect changes in CO_2 plumes that are correlated with coal use at the Harding Street Power Plant.

The North-East Corridor: Baltimore-Washington DC Urban Greenhouse Gas Network

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Global trends in urbanization have focused carbon cycle community interest on urban emissions, leading to many recent studies on greenhouse gas (GHG) emissions from cities. Many efforts to quantify urban emissions have focused on establishing long-term, relatively dense networks of tower or roof-based continuous in-situ trace gas observations. The North-East Corridor: Baltimore/Washington DC (NEC-BW) project is one such effort, a partnership between the National Institute of Standards and Technology (NIST), Earth Networks, University of Maryland, NOAA, and Arizona State University to estimate and determine trends in CO_2 and CH_4 emissions from the cities of Washington, DC and Baltimore, MD, USA. The project incorporates high-resolution emissions modeling (Hestia), tower-based in-situ and flask-based trace gas observations, aircraft-based observations from periodic intensive campaigns (Fluxes of Atmospheric Greenhouse Gases in Maryland, FLAGG-MD), low-cost sensor testing and deployment, and meteorological and statistical modeling. A goal of the project is to develop new and evaluate existing techniques for flux estimation at the urban scale, with an aim toward documentation and standardization of such methods.

Here we introduce the NEC-BW tower network, with continuous in-situ measurements of CO_2 and CH_4 made using an observing system based on high-precision CRDS analyzers. The network was designed to maximize the effectiveness of the observations in constraining urban emissions in the NEC-BW and characterize incoming air masses. As the network has come online, we have applied quality-control and data processing methods for all the in-situ tower-based observations, and have developed an algorithm for calculating the uncertainty of those observations (Verhulst et al., 2016). We will present the calibration method and uncertainty calculation for the network data, as well as initial analyses of the time series of observations from the established tower network sites. We show seasonal differences in the diurnal cycle in CO_2 and CH_4, and the variability across the rural-urban gradient. Lastly, for some of the longer-running regional sites, we document the seasonal cycle by subtracting the global trends in CO_2 and CH_4.

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Amazon Greenhouse Gas Measurement Program

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With the objective to understand the role of the Amazon in the global carbon balance, poorly constrained component of the carbon cycle, and the climatic variation effect on this balance, we developed a scientific strategy of GHG measures involving different scales, since local until regional scales, using small aircraft to perform vertical profiles, measures in tower, flasks, satellite and FTIR. The LaGEE activities starting in 2003, constructing a replica of NOAA/ESRL/GMD GHG Laboratory and installing in Brazil in 2004. Since this time the places studied and the types of measures taken have grown to reach our goal.

The tropics are a poorly constrained component because until recently there have been very few lower troposphere greenhouse gas measurements that are regionally representative. Amongst the tropical land regions the Amazon is by far the largest and also hosting the largest carbon pools around 200 PgC.

The greenhouse gas (GHG) monitoring activities conducted firstly by IPEN/LQA from 2004 to 2015 (Atmospheric Chemistry Laboratory) and later by INPE/CCST/LaGEE study Amazon Basin and Brazilian coast. The aircraft measurement program was started in 2000 with monthly/biweekly vertical profile sampling at SAN (2.86S 54.95W). From December 2004 to December 2007 we performed vertical profiles at MAN (Dec 2004 / Dec 2007). In 2010, a new step in our program was started. We added three more aircraft sites: TAB (5.96S 70.06W), RBA (9.38S 67.62W) and ALF (8.80S 56.75W). In 2013 TAB site was moved to TEF (3.39S 65.6W) and we add two more aircraft sites with vertical profiles from 300m to 7300 m, at Salinopolis (SAH 0.60S; 47,37W) near the Atlantic coast and RBH at the same place then RBA, in the western Amazon to compare with GOSAT.

In 2016 a new measurements using FTIR (TCCON new site) start to be made with a partnership of BIRA-IASB / IFRO and INPE. The instrument is installed at IFRO campus in Porto Velho, Rondonia (8.74°S, 63.87°W). In 2017 we returned the 4 Amazon sites (RBA, ALF, TEF and SAN) and add a special measurements at coast in a 100m tower at Itarema, Ceará state with weekly flask samples. From 2000 to 2017, we performed 646 vertical profiles. The vertical profiles sampled from 300m to 4400m above sea level, measuring CO2, CH4, N2O, CO and SF6 on WMO mole fraction scales.

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CO2, CH4, and CO with CRDS technique at the Izaña Global GAW station: instrumental tests, developments and first measurement results

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At the end of 2015, a CO2/CH4/CO CRDS was installed at the Izaña Global GAW station (Tenerife, Spain) to improve the Izaña GHG GAW measurement programme. The acquisition of the instrument was largely financed by European FEDER funds through a Spanish R+D infrastructure project.

In this presentation, we firstly detail the results obtained in the initial tests performed to the instrument (precision, repeatability, sensibility to inlet gas pressure, response function…). Secondly, we analyse the results of the calibrations performed every 3-4 weeks since the end of 2015 using Tertiary WMO standards, and provide some details on the numerical processing software developed to evaluate the calibrations. Thirdly, some details of the obtained water vapour correction are provided. Finally, the ambient measurements carried out till now are presented, as well as some details in the numerical processing software developed to obtain the ambient air CRDS measurements from raw data and the calibration results, and compared with those obtained with other Izaña measurement instruments.

Additionally, we very briefly mention some few more novelties in the Izaña GHG measurement programme.

Atmospheric CO2 and other greenhouse gases monitoring in India

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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 Greenhouse gases (GHGs) 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 have already set up :i) an ambient CO2 and other GHGs monitoring site at the surface since year 2009 ii) air sample analysis lab which uses WMO/GAW calibration standards iii) cruise and airborne campaigns and iv) CO2 transport model as well as lagrangian particle dispersion model etc. The present study is an attempt to analyze available CO2 and other GHGs observation and model simulations over India which may help to improve the flux estimates and GHGs budget over this region.

Fractionation of O_2/N_2, Ar/N_2, and CO_2 at Aircraft Sampling Inlets

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For airborne measurements of high relative precision, such as those of $\delta(O_2/N_2)$ or $\delta(Ar/N_2)$, separation of gases as a result of pressure driven diffusive effects has been recognized as a potential challenge (Steinbach, 2010; Bent, 2014). We have conducted airborne in situ measurements of $\delta(O_2/N_2)$ and CO_2 since 2007 and airborne flask sampling for $\delta(O_2/N_2)$, $\delta(Ar/N_2)$, CO_2, and isotopologues of CO_2 since 1999 using a wide range of aircraft and inlet designs. We have used the $\delta(Ar/N_2)$ measurements, expected to be near constant in the troposphere, as well as differences in $\delta(O_2/N_2)$ between *in situ* and flask measurements made using differing inlets and flow rates, to characterize inlet fractionation effects.

Fortuitously, for the combination of inlets and flight envelopes we used from 1999-2015, inlet fractionation was modest at -20 per meg $\delta(Ar/N_2)$ and -5 per meg $\delta(O_2/N_2)$ over the full tropospheric column or less. For the HIPPO1-5 (2009-2011) campaigns on the NSF/NCAR GV aircraft, we used aft facing tubes inside of a cylindrical pylon with expanding diameter, designed to slow the internal air speed. The small fractionation effects we observed were consistent with pressure gradients perpendicular to the streamlines, as suggested by Steinbach (2010), which resulted in more of the lighter molecules making the turn into the inlet tube.

After switching to a new exposed aft facing inlet design for the ORCAS (2016) campaign, in order to mitigate concerns over potential cabin air contamination via the pylon, we found fractionation of up to -40 per meg $\delta(O_2/N_2)$ for our *in situ* analyser between 400 and 200 hPa. Then, moving to the NASA DC-8 aircraft for ATom I (2016) we experienced extreme fractionation effects of up to -200 per meg $\delta(O_2/N_2)$ between 400 and 200 hPa. During this campaign we experimented with 6 different inlet configurations and were successful in eliminating these effects part way through the campaign.

The most extreme fractionation we observed using these experimental configurations was with a side-facing inlet, which performed nominally up to an altitude of 350 hPa then fractionated $\delta(O_2/N_2)$ by approximately -2000 per meg and CO_2 by approximately -3 ppm. The ratio between these effects matches the ratio of O_2 and CO_2 mass differences with N_2, suggesting a pressure gradient effect such as that proposed by Steinbach (2010). This observed fractionation of CO_2 relative to air suggests that even for lower relative precision airborne measurements, careful consideration of inlet sampling artifacts should not be neglected.

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Comparison of interferometric and mass spectrometric measurements of O_2/N_2 by the Scripps O_2 program

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Since 2001, measurements of O_2/N_2 ratio by the Scripps O_2 program have been routinely made using both the interferometric and mass spectrometric methods. At that time, the interferometric analyser system, which had been used since 1990, was augmented by incorporating an ISOPRIME mass spectrometer equipped with eight collectors (m/z = 28, 29, 30, 32, 34, 36, 40, 44). This mass spectrometer was plumbed in parallel with the interferometer, sharing calibration gases and allowing the standard 5L flasks used throughout the Scripps O_2 station network to be analysed for O_2/N_2 ratio on both analysers (Keeling et al., 2004). Since then, the system has been used to analyse more than 10,000 flask samples collected around the world on both analysers. The system has also been used for more than 10,000 simultaneous reference gas analyses, thus providing the most exhaustive comparison to date of two physically independent O_2/N_2 measurement methods. This presentation will discuss the details of this comparison, which provides insights into systematic errors on both systems, such as trace-gas interference, as well as insights into the intrinsic long-term stability of both analysers in relation to the calibration gas suite and the instrument span sensitivities.

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Preparation of high precision standards (with ± 1 ppm) using a gravimetric method for measuring atmospheric oxygen

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About ten years ago, Tohjima et al. developed standards for atmospheric O2 measurements using a gravimetric method, with an uncertainty of O2 amount fraction (mole fraction) of 2.9 ppm (k = 1). In order to make a more accurate measurement of atmospheric O2, we have developed more precise standards using a gravimetric method in accordance with ISO 6142:2001. The uncertainty of O2 mole fraction in the standards developed by Tohjima et al. was caused mainly from the process of determining masses of the source gases, pure N2 and O2, which calculated from the masses of a high pressure cylinder before and after filling it with the source gases. We carefully studied factors of uncertainty for weighing the cylinder using our weighing system, in which a new high-precision balance was recently installed in the system. We confirmed the uncertainty for weighing the cylinders was improved significantly from 2.6 mg to 0.8 mg. We also determined the average atomic masses of nitrogen and oxygen in the source gases by measuring precisely the difference of their isotope ratios from the corresponding atmospheric value using an isotope ratio mass spectrometry. The expanded uncertainties for the standards prepared using the new weighing system and the averaged atomic masses were 1.3−1.6 ppm (k = 2). Residuals from the calibration line for O2 mole fractions in standard gases measured by a paramagnetic O2 analyser were less than ±1 ppm.

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TOWARDS THE UNIFYING OF THE DETECTION SYSTEMS FOR THE MEASUREMENT OF THE MAJOR GREENHOUSE GASES AND RELATED TRACERS

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Atmospheric chemistry laboratories which measure trace gases, in particular greenhouse gases (GHGs), use a variety of methods and equipment for measuring specific species in order to get the best precision. This often requires separate sampling pathways and multiple calibration tanks, which in turn requires more laboratory space and equipment investment.

The Global Atmospheric Sampling LABoratory (GASLAB) at CSIRO is working toward unifying the methods and equipment for measuring such GHGs by using the Pulsed Discharge Helium Ionisation Detector (PDHID) coupled to a gas chromatograph (GC). This presentation is a continuation of the work presented at GGMT-2015 (La Jolla, USA) on the use of PDHID for hydrogen and some GHGs, with a focus on precise measurements of methane and nitrous oxide.

The initial results show that comparable precision for nitrous oxide on a PDHID can be obtained compared to the electron capture detector (ECD) results, where the PDHID shows significantly smaller magnitude in the non-linear response function than the ECD's. Better precision for methane has been obtained on PDHID when compared to the flame ionisation detector (FID) results, but with slightly more non-linear response. Previously we confirmed that PDHID offers superior results (precision and linearity) over the Reduction Gas Analyser (RGA) detectors for molecular hydrogen. While the precision for the direct measurement of carbon dioxide on PDHID is gradually approaching the precision of the well-established GC-FID (after its conversion to methane) in the ongoing research in our laboratory, the work on the precise measurement of carbon monoxide on PDHID is in its initial phase. In summary, major GHGs and related tracers currently measured on three different detectors could in the near future be measured on one single detection platform - PDHID.

Calibration and Field Testing of Cavity Ring-Down Laser Spectrometers Measuring Methane Mole Fraction and Isotopic Ratio Deployed on Towers in the Marcellus Shale Region

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Four in-situ cavity ring-down spectrometers (Picarro, Inc.) measuring methane, carbon dioxide and the isotopic ratio of methane were deployed at towers with heights between 46 and 61 m AGL. The study was focused on the Marcellus Shale natural gas extraction region of Pennsylvania. The leakage rate of methane determines whether natural gas is useful as a bridge fuel, in terms of greenhouse effects compared to coal or oil. In addition to leakage from natural gas extraction, there are other unrelated sources of methane. The isotopic signature of the methane can be used to help distinguish these sources. Heavy isotope ratios are characteristic of thermogenic (e.g., oil and gas) methane sources and light isotope ratios are characteristic of biogenic (e.g., landfills, agriculture) sources.

The calibration of the continuous isotopic methane analyzers used in this study is challenging for several reasons, including the need for both a linear calibration and a mole fraction correction, and cross-interference from ethane. We describe laboratory and field calibration of the analyzers for tower-based applications, and characterize their performance in the field for the period January – December 2016. Prior to deployment, each analyzer was calibrated using high methane mole fraction air bottles with various isotopic ratios, from biogenic to thermogenic source values, diluted in zero air. Furthermore, at each tower location, three field calibration tanks were employed, from ambient to high mole fractions, with various isotopic ratios. By testing various calibration schemes, we determined an optimized field calibration method. A method to correct for cross interference from ethane is also described. Using an independent field tank for evaluation, the standard deviation of 5-day means of the isotopic ratio of methane difference from the known value was found to be within our target compatibility of 0.2‰. Following improvements in the field calibration tank sampling scheme, the standard deviation of 1-day means was within the target compatibility. Round robin style testing using tanks with near ambient isotopic ratios indicated mean errors of –0.33 to 0.24‰ for the tests completed for each analyzer and round-robin tank. Flask to in-situ comparisons indicated mean differences over the year of 0.02 and 0.08‰, for the East and South towers, respectively, where the standard error was 0.06‰ and 0.04‰.

Adaptation of a commercial greenhouse gas analyser for airborne measurements with expanded altitude range and application on the ORCAS and ATom campaigns

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The commercial availability of the Picarro cavity ring down spectrometer (Crosson 2008) has advanced our community's ability to make highly stable and precise measurements of CO_2 and CH_4 mixing ratios in the atmosphere. We have expanded the Picarro's operating altitude range through a software modification to lower its cell pressure set point. This approach for airborne applications eliminates the need for significant engineering of auxiliary systems, such as upstream sample pumping or pressure control. The concept of a flexible cell pressure set point, without significant reductions in pressure control or measurement precision, opens up new possibilities for continuous greenhouse gas measurements on airborne platforms with minimal ancillary engineering and operational requirements.

We evaluate the behavior of a Picarro analyzer with a modified pressure set point through a series of laboratory tests and controlled field tests, and describe its performance on two aircraft campaigns that sampled at altitudes up to 14 km (150 hPa). We compare Picarro measurements on the ORCAS and ATom campaigns to those made by several other measurement systems, including a high-precision laser spectrometer (QCLS, Santoni et al. 2014), a non-dispersive infrared spectrometer (LiCor/AO2, Stephens et al. 2003), and two flask-based systems (Medusa from Scripps and Programmable Flask Packages from NOAA). We present an empirical uncertainty analysis of the Picarro measurements that accounts for short-term measurement precision, stability in the analyzer response during individual flights and for a campaign duration, the analyser-specific empirical water vapor correction that is applied to the undried measurements, and the traceability of reported values to WMO scales. By this methodology total average uncertainty is approximated for 1-second measurements as 0.1 ppm for CO_2 and 0.7 ppb for CH_4 (1-sigma) for these two campaigns.

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A new lightweight active stratospheric air sampler

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High-accuracy stratospheric measurements of greenhouse gas concentrations are useful to validate remote sensing measurements from ground and from space, which has been primarily performed by comparison with collocated aircraft measurements (0.15 km – 13 km), and more recently with AirCore observations (0 – 30 km). AirCore measurements of greenhouse gases are accurate in concentrations, but are less accurate in the vertical altitudes. However, validation of AirCore measurements has been proven to be challenging, as in-situ stratospheric measurements of greenhouse gas concentrations are challenging due to either stringent requirements on the stability of on-board instruments or difficulties in collecting air samples at a low ambient pressure.

We developed a new lightweight, ~2kg, active sampler to fly with small weather balloons. The sampler consists of 4 Multi Layer Foil (MLF) sampling bags, custom-made valves and manifold, and a lightweight pump. Prior to the field test, we performed a series of laboratory storage tests to assess the accuracy of the greenhouse gas measurements using the MLF bags, and evaluated the performance of the lightweight pump under low-pressure environments.

The sampler was flown together with an AirCore in Sodankylä, Finland (67.368N, 26.633E, 179 m.a.s.l) on April 26th 2017. The sampler, sampling during ascent, successfully collected 4 stratospheric air samples. Sample sizes range from 200 mL to 500 mL, with a vertical resolution of 0.5 to 1.3 km between 12 to 22 km altitudes. We analyzed the four air samples for concentrations of CO_2, CH_4 and CO, and will show the comparison between the sample analysis results and weighted averages of the AirCore profile measurements. Furthermore, these air samples provide an excellent opportunity for analysis of isotopic composition measurements to understand and constrain atmospheric chemical and physical processes in the stratosphere.

Low-cost sensors for CO_2 monitoring: calibration, characterization and assessment

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The Swiss project Carbosense proposes a uniquely dense CO_2 low power sensor network combined with atmospheric transport models. It relies on three levels of CO_2 measurements: (i) 300 nodes of battery-powered CO_2 low-cost diffusive NDIR sensors (SenseAir LP8), (ii) 30 temperature stabilized, mains-powered NDIR sensors with active sampling and zero-air connection (SenseAir HPP [1]), and (iii) high-precision laser spectrometers (Picarro G1301/G2401, CRDS) as reference instruments. The sensors will be distributed nationwide, mainly at Swisscom radio transmitter locations and at MeteoSwiss meteorological stations. All LP8 and HPP data is transmitted as 10 minute averages through Swisscom's new Low Power Network (LPN).

Over 300 LP8 CO_2 sensors have been integrated with relative humidity and temperature measurements and with LoRaWAN communication [2]. All sensors were characterized with respect to carbon dioxide (350 – 1000 ppm), temperature (-5 to 50 °C) and pressure (770 – 1010 hPa). A calibration model was developed based on the Beer-Lambert law, and relating the raw signal of the IR detector to the true CO_2 mixing ratio, determined by CRDS, and referenced to the NOAA scale.

The impact of temperature and pressure variations on the IR detector signal is modelled by including polynomial correction terms in the calibration model. Largest IR signal changes are related to temperature variations. Pressure effects are slightly higher than expected for an ideal gas due to factors such as absorption line characteristics and sensor design [3]. Relative humidity becomes a critical issue above ca. 95%, likely because of local condensation.

Before network deployment, all 300 sensors were placed next to a Picarro instrument for several weeks. To account for a wide range of operating conditions, these deployments took place at the rural site Dübendorf (432 m a.s.l.) and the mountain site Rigi (1031 m a.s.l.).

Two HPP sensors were also characterized with respect to pressure (770 to 1010 hPa) and CO_2 (450 to 900 ppm) and operated in the field next to a reference instrument for several months. Pressure, correction was based on measurements of integrated sensors, and zero drift was measured by pumping CO_2 free air into the instrument at regular intervals.

This paper presents findings obtained from the extensive CO_2 sensor data set. These include the accuracy of the LP8 and HPP sensors, variability in performance between sensors, long-term sensor behaviour, power consumption and reliability of the data transmission. Furthermore, we discuss operational aspects such as deployment strategies, quality assurance, model based drift correction and assessment of the long-term data quality.

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Measurements of atmospheric oxygen using a newly built CRDS analyzer and comparison with a paramagnetic cell and an IRMS

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Oxygen is a major and vital component of the Earth's atmosphere which is consumed or produced through biochemical processes such as combustion, respiration, and photosynthesis. Changes in its concentration and isotopic composition can be used to better understand different biogeochemical processes as well as to constrain the global carbon cycle. However, the variations of oxygen in the atmosphere are relatively small, in the order of a few ppm's, posing a technical challenge for accurate measurements since a very high level of precision is required.

Here we present atmospheric oxygen concentrations and isotopic measurements based on a new high-precision gas analyzer that utilizes the technique of Cavity Ring-Down Spectroscopy (Picarro G2207-*i*). The instrument's compact and ruggedness design combined with high precision and long-term stability allows the user to deploy the instrument in the field for continuous monitoring of atmospheric oxygen. Measurements have a 1-σ 5-minute averaging precision of 1-2 ppm for O_2 over a dynamic range of 0-50%. We will present comparative test results of this instrument against the incumbent technologies such as the mass spectrometer and the paramagnetic cell. In addition, we will demonstrate its long-term stability from a field deployment at the Beromünster tall tower and the High-Alpine research site Jungfraujoch in Switzerland.

Microwave sensing column oxygen amounts for surface air pressure and greenhouse gas mixing ratio estimates

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For general meteorology and atmospheric sciences, air pressure is a basic required physical variable in calculations of atmospheric dynamics and is also essential for greenhouse gas (GHG) volume mixing ratio (or mole fraction) estimations. Currently, surface air pressure can only be observed by in-situ sensors in limited ground stations over land and very-sparsely over oceans. There are no global or regional observations of surface air pressure fields. This observational gap in surface air pressure generates significant problems in GHG volume mixing ratio measurements. For example, current GOSAT and OCO-2 satellites and the future ASCENDS space mission can measure column CO2 amounts. However, they need modelled (or assimilated) surface air pressure fields to convert the measured column CO2 amounts to column CO2 volume mixing ratio (XCO2). For this conversion, a critical part of surface air pressure is dry air pressure since wet air part can be observed well by current satellite column water vapor measurement capabilities. Because of large sizes of grid boxes of global models and limited constraints in the models over remote land regions and open seas especially the southern ocean, significant errors in surface air pressure fields could be introduced in the areas of satellite column CO2 measurements, which would lead considerable uncertainties in estimated XCO2.

This effort tries to develop a feasible active microwave sensing approach that measures surface air pressure, especially over open seas, from space using a Differential-absorption BArometric Radar (DiBAR) operating at 50-55 GHz O2 absorption band in order to constrain assimilated dynamic fields of numerical weather Prediction (NWP) models to close to actual conditions and to improve the weather forecasts. Analyses show that with the proposed space radar the errors in instantaneous (averaged) pressure estimates can be as low as ~4mb (~1mb) under all weather conditions. With these surface pressure measurements, uncertainties in satellite estimates of GHG mixing ratios, especially those in XCO2 values, will be significantly improved.

NASA Langley research team has made substantial progresses in advancing the column O2 measurement concept since the DiBAR concept developed about a decade ago. The feasibility assessment clearly shows the potential of surface barometry using existing radar technologies. The team has also developed a DiBAR system design, fabricated a Prototype-DiBAR (P-DiBAR) for proof-of-concept, conducted laboratory, ground and airborne P-DiBAR tests. The flight test results are consistent with the instrumentation goals. The precision and accuracy of radar surface pressure measurements are within the range of the theoretical analysis of the DiBAR concept. Observational system simulation experiments for space DiBAR performance based on the existing DiBAR technology and capability show substantial improvements in surface air pressure predictions. DiBAR measurements will provide us an unprecedented level of the prediction and knowledge on global air mass distributions in improving GHG observations.

The AirCore atmospheric profiler: methods, challenges, applications, and updates

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The AirCore atmospheric profiler is currently the only platform capable of delivering near-complete, finely resolved vertical profiles of atmospheric gases (currently of CO2, CH4, and CO). The 100m-long passivated stainless steel tubing coil works as a sort of atmospheric “tape recorder”—it is launched on a balloon with one end open, allowing the tube to empty as it ascends, and fill back up with an atmospheric profile as it descends.

For CO2, CH4, and CO, the sampled air is analyzed on a Picarro cavity ring down spectrometer in a temperature controlled setting after recovery, and provides dry mole fraction of the three gases from 30 km (~12 mbar) to the surface or >98% of the atmospheric column. Ambient meteorological data and a fluid dynamics model map the resulting core to the pressure altitude at which a given parcel of air was sampled. Here, we present the current NOAA GMD sampling and analysis methodology, discuss challenges relating to repeatability of profiles, and demonstrate the utility of a software package in Python intended to standardize the analysis of AirCore profiles coming from different laboratories.

A UAV-based active AirCore system for accurate measurements of greenhouse gases

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We developed a UAV-based active AirCore and field-tested it for atmospheric concentration measurements of CO_2, CH_4, and CO. The system is based on the AirCore technique invented by NOAA. As opposed to the conventional concept of passively sampling air using the atmospheric pressure gradient during descent, the active AirCore samples atmospheric air using a micropump to pull the air through the tube. This inclusion of the micropump opens up the possibility of sampling atmospheric air in both vertical and horizontal planes. The active AirCore used for this study weighs ~1.2 kg. It consists of a 49.1 m long 1/8” stainless steel tube with a 0.005” wall thickness, a 7.5 cm 1/4” stainless steel tube filled with magnesium perchlorate, a small KNF micropump and a 45 µm orifice working together to form a critical flow of dried atmospheric air through the active AirCore.

Shortly after collection, we analyze the air sample on site using a gas analyzer (Picarro CRDS model G2401) for mole fraction measurements of CO_2, CH_4, CO and H_2O.

We conducted an experiment with a prototype active AirCore mounted on a UAV near Lutjewad, an atmospheric measurement station hosting a 60 m high monitoring tower located next to the Wadden sea dike northwest of the city of Groningen in the Netherlands. Five consecutive flights took place over a five-hour period in the same morning, starting at sunrise to obtain vertical profile measurements during the collapse of the nocturnal boundary layer and the establishment of the mixed layer. We compared measured concentrations to continuous greenhouse gas mole fraction measurements at the nearby atmospheric tower. The results show a good agreement between the active AirCore sample and the continuous measurements obtained from the atmospheric station (N = 121, R^2_{CO2}: 0.97 and R^2_{CH4}: 0.94, and mean differences: Δ_{CO2}: 0.14 ppm; Δ_{CH4}: 5.56 ppb). The nocturnal boundary layer height was clearly observed in two out of three vertical profile measurements, and seen to increase as the boundary layer stabilized as the morning progressed. By flying in a horizontal plane perpendicular to the dike we furthermore detected a CH_4 hotspot in the coastal wetlands, which demonstrates the potential of this new active AirCore method to measure at locations where other platforms have no practical access.

Stratospheric measurements of ozone-depleting substances and greenhouse gases using AirCores

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The use of AirCores (Karion et al., 2010) to collect stratospheric profiles of CO_2 and CH_4 up to 30 km has been increasing in recent years. AirCores are technically simple and inexpensive to build and deploy, providing an alternative to traditional large stratospheric balloons or aircraft measurements. They consist of long coils (up to 200 m) of lightweight stainless steel tubing that is evacuated on a meteorological balloon-powered ascent and filled during the subsequent descent. AirCores collect whole air samples and thus enable crucial satellite validation for a range of trace gas species, including greenhouse gases. Due to the payload restrictions on small balloons sampled air volumes are small, around 200-300 ml of stratospheric air. This makes analysis of less abundant (ppt range) trace greenhouse gases, such as halocarbons, difficult.

The ERC-funded EXC^{3}ITE project (EXploring stratospheric Composition, Chemistry and Circulation with Innovative Techniques) aims to conduct regular – several flights per season – analysis of up to 30 key greenhouse and ozone depleting substances from AirCore samples. Here we present the first stratospheric measurements of more than 10 halocarbons (including SF_6, CFCs, halons and HCFCs) in AirCores obtained using UEA's highly sensitive (detection limits of 0.01-0.1 ppt in 10 ml of air) gas chromatography mass spectrometry system. The analysed air originates from a stratospheric air sub-sampler (Mrozek et al., 2016), which collects AirCore segments after non-destructive CO_2 and CH_4 analysis. Comparisons with previous high altitude aircraft campaigns show good agreement with our AirCore results for some compounds, e.g. SF_6 and Halon-1211, and for other compounds method development is underway to improve the agreement. Both current results and methodological developments will be presented. For some compounds, analytical uncertainties associated with our AirCore data are already within the range of previous high altitude aircraft and balloon samples analysed at UEA: for example SF_6 AirCore uncertainties are around 0.8% compared to 0.5-1.2% for previous campaigns. This highlights the potential for AirCores data to be used in the derivation of 'mean age of air'. Mean age is used to help determine chemical lifetimes and we hope to use AirCore-derived mean ages to provide better constraints on the stratospheric lifetimes, and therefore the global warming potential, of several non-CO_2 greenhouse gases.

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APRECON-TOF-MS: A new state-of-the art instrument for the analysis of halogenated greenhouse gases

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Halogenated organic trace gases are strong greenhouse gases and deplete the stratospheric ozone when containing chlorine and bromine. Measurements of these compounds at atmospheric background sites started in the 1970s by gas chromatography-electron capture detection (GC-ECD) (Lovelock, 1971). These data were used for showing the ubiquitous abundance of halogenated long-lived substances in the global atmosphere and were key to the subsequent detection of the origin of the ozone hole of the Antarctic continent. Subsequently, detection by mass spectrometry became the predominant analysis technique for continuous measurements of these gases. In the global AGAGE network, halocarbons have been measured by the Adsorption Desorption System (ADS, Simmonds et al., 1995) since 1997, which has been followed by measurements from the further developed Medusa system (Miller et al, 2003) in 2003. With the APRECON-TOF-MS we present a newly developed system, which combines a fundamentally redesigned preconcentration unit with a new, powerful detection system for measurements of halogenated trace gases.

At the core of the APRECON (Advanced Preconcentration system) is a copper plate which is cooled to -180 °C by means of a Stirling cooler. Two copper cones are fixed on this copper plate on which the preconcentration traps are mounted on detachable hats (adopted from a design by NOAA/ESRL/GMD). Halocarbons from 2 liters of air are sampled on these traps during the cold phase. For the subsequent heating phase, the hats can be removed from the base plate for desorption of the analytes. This design allows fast switching of the traps between heating and cooling cycles.

First results will be shown of measurements down to the fmol/mol (ppq, 10^{-15}) range, using both an established quadrupole mass spectrometer (QP-MS) and a new time-of flight mass spectrometer (TOF-MS) for detection. The latter is superior because of its ability to detect the exact mass and because it allows the simultaneous analysis of all ions. APRECON-TOF-MS has, therefore, major advantages over earlier systems and may well become the standard measurement technique for atmospheric halogenated organic trace gases.

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Medusa-Aqua System: Development of Analytical Techniques for Novel Halogenated Transient Tracers in the Ocean

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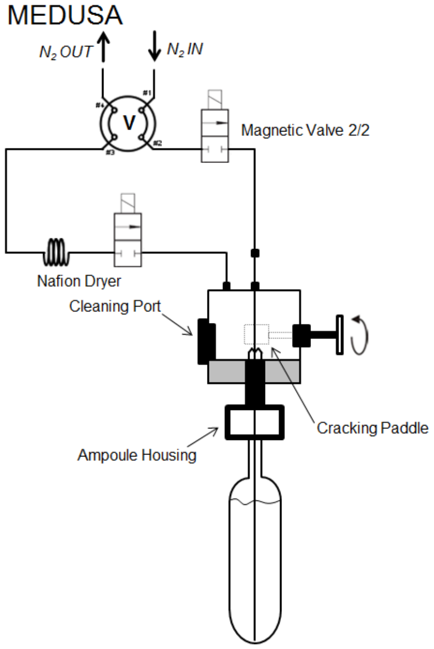
Chlorofluorocarbons (CFCs) and SF_6 are widely used oceanic transient tracers for the determination of oceanic circulation, mixing and for estimating oceanic uptake of anthropogenic CO_2. However, the utility of CFCs is increasingly restricted by their negative atmospheric growth rate. There is a need to explore other transient tracers with positive growth rates. Utilization of multiple transient tracers facilitates empirical determination of the transit time distributions (TTDs) in the ocean, a fundamental property of transport.

A proven analytical technique based on a pre-concentration step followed by GC-MS analysis, the Medusa system [*Miller et al.*, 2008], enables the reliable and fast simultaneous determination of a large number of relevant transient trace gases. The goal of this study is the analysis of ocean waters in order to obtain depth profiles of a suite of potential oceanic transient tracers, such as HCFC-22, HFC-134a, HFC-125, HFC-23, CF_4 and C_2F_6. This will be performed by modification of the “Medusa” analytical system (the Medusa-Aqua system) to be able to measure seawater.

The Medusa-Aqua system consists of a Medusa system and a seawater sample pretreatment system. The Ampoule-Cracker-System (see figure in right-hand side) was developed as the seawater sample pretreatment system to degas the samples from gaseous tracers before injecting into the Medusa. This method is used for off-line seawater samples in 1.1L ampoule that are flame sealed at sea and measured in the lab in Kiel. This method is based on purge-and-trap technology, where the Medusa system serves as the trap unit and chromatographically separates the sample for detection on a mass spectrometer.



The Medusa-Aqua system has measured over 20 seawater samples from two research cruises to the tropical Atlantic Ocean in 2011 and 2016. It can detect over 25 species in seawater samples. Except C_2F_6, HCFC-22, HFC-134a, HFC-125, HFC-23 and CF_4 can all be detected. The purge efficiencies for HCFC-22 reach 98.3±1.2% after purge three times. For other compounds, they can reach 100%.

Here we will show results from seawater measurements and discuss the potential for some compounds as oceanic transient tracer in view of their atmospheric history, feasibility of analysis and stability in sea water.

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Fifteen years of surface water CO_2 measurements from cruise ships in the Caribbean Sea

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Measurement of surface water CO_2 concentrations over time has been the primary means to determine regional and global air-sea CO_2 fluxes, and to determine increases in surface water CO_2 as they contribute to ocean acidification (Takahashi et al. 2014). The data have been largely gathered from ships of opportunity (SOOP-CO2). Currently, observations from approximately thirty ships are obtained in automated fashion using similar accurate and calibrated instrumentation with many of the same design (Pierrot et al., 2009). The multi-investigator data are collated through a community effort, the Surface Ocean Carbon Atlas (SOCAT) (Bakker et al., 2016).

At the inception of the global surface water CO_2 observing program the Caribbean Sea was highlighted as region with a dearth of measurements. Through a partnership with Royal Caribbean Cruise Lines the area now has 15-years of quality data from weekly voyages through the region. The combination of temperature, salinity, marine boundary air and surface water CO_2 measurements has made it possible to determine the uptake of CO_2 by the ocean and the attribution of change. Good correspondence between atmospheric XCO_2 measurements from the ship-based instrument and GLOBALVIEW-CO2 (2013) are observed but improved methods of quality control and flagging are necessary.

The marine boundary and surface water CO_2 measurements show that for much of the region the surface water CO_2 has increased only at about ½ the atmospheric growth rate over the past 15 years. The instrumentation, data delivery and quality control along with scientific highlights of the campaign in the Caribbean Sea, and future improvements will be discussed.

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Towards including atmospheric CO_2 data from the oceanic community into the global high-accuracy atmospheric CO_2 network

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There are currently more than 100 sites making high-accuracy measurements of atmospheric CO_2, and yet oceanic regions remain severely under-sampled. Many of these oceanic regions, however, are relatively densely sampled by underway systems deployed on research vessels and ships of opportunity that typically measure the dry mole fraction of CO_2 of both air equilibrated with surface seawater and the overlying atmosphere. The accuracy of the atmospheric CO_2 data from these ship-based underway CO_2 systems ($uwCO_{2atm\text{-}dry}$) does not typically meet the rigorous standards of the atmospheric community, as set out in the World Meteorological Organization recommendations. Improving and validating the quality of $uwCO_{2atm\text{-}dry}$ data will most likely provide mutual benefits to both the oceanic and atmospheric communities. For example, we find that incorporating $uwCO_{2atm\text{-}dry}$ data into an atmospheric CO_2 inversion in the North Atlantic region leads to a reduction in the posterior CO_2 flux uncertainty when compared to using GLOBALVIEW-CO2 data (https://www.esrl.noaa.gov/gmd/ccgg/globalview/co2/co2_intro.html). Improved $uwCO_{2atm\text{-}dry}$ data quality may also enable the oceanic community to more easily identify offsets/biases between measurements made by different ships that are then combined into global data products, such as the Surface Ocean CO_2 Atlas (http://www.socat.info/).

Here, we quantify the offsets between $uwCO_{2atm\text{-}dry}$ data and high-accuracy CO_2 measurement system data from five ships. We compare these CO_2 offsets to those from the Cucumbers intercomparison programme (http://cucumbers.uea.ac.uk/), to determine whether some $uwCO_{2atm\text{-}dry}$ data can already be reliably included in atmospheric CO_2 inversions. We also show the results of a 'Target Tank' comparison exercise between two systems installed on the Cap San Lorenzo container ship, which indicate that incomplete sample air drying can be the dominant contributor to inaccuracies in $uwCO_{2atm\text{-}dry}$ data. Lastly, we make several recommendations for improving the quality of $uwCO_{2atm\text{-}dry}$ data, which we hope will facilitate more discussion and collaboration between atmospheric and oceanic communities regarding atmospheric CO_2 measurement.

The PGGM measurements of atmospheric carbon dioxide concentrations over the Asia-Pacific and the Asia-Europe commercial shipping routes: The 2009-2017 results

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The Pacific Greenhouse Gases Measurement (PGGM) project has conducted measurements of global greenhouse gases for climate research: started from June 2009 for the ship-based CO2 measurements; and started from June 2011 for the air-based H2O, O3, CO, and cloud particle measurements. The main EU partner for the PGGM air-based measurements is the IAGOS project; while the main partner for the PGGM ship-based measurements is the Cambridge University in the UK. The main industrial partners for the PGGM project are Evergreen Marine Corporation (EMC) for the ship-based measurements and China Airlines (CAL) for the air-based measurements. The ship-based measurements have collected data over the the Pacific Ocean, Indian Ocean, Persian Gulf, Red Sea, Mediterranean Sea, northwestern and northeastern Atlantic Ocean. As a result, we are able to understand CO2 concentrations downwind of the main industrial countries in the world, including East Asia, Japan, Korea, North America (Canada and USA), South America (Peru and Chile), Southeast Asia countries, India, Arabian countries, Mediterranean countries (Italy and countries from north Africa), and European countries (UK, Germany, France, the Netherland, Spain, Portugal, Belgium). The air-based measurements collect data cover regions of East Asia, Japan, Korea, North Pacific upper troposphere, Southeast Asian countries (the Philippine, Vietnam, Indonesia, Malaysia, Singapore), European countries (Germany, the Netherland, Austria), north America (Canada), and upper troposphere over the Euro-Asian continent. The ship-based measurements use 9 biggest and newest global commercial cargo ships (L-type, S-type, and D-type ships) from EMC. We have collected a total of more than 300 cruises of measurements since June 2009. The ship-based measurements are still on going. The ship-based CO2 data shows that CO2 levels close to the industrial regions have surpassed 430 ppmv, while the CO2 levels in the middle of Pacific have also passed 400 ppmv. The CO2 trends are higher than 1.5 ppmv per year from over both industrial regions and remote regions. As a bonus of the industrial collaboration with the EMC, we have also collected data of atmospheric dose rates over the Tokyo Port and the North Pacific Regions from March 2011 (right after the Fukushima nuclear power plant accident) to end of 2015. Our ship-based data and land-based data clearly indicated the immediate impact of nuclear radioactive materials over the Tokyo and the North Pacific regions. These data indicate the importance and add-on values of data collected from routine and scheduled global container cargo ships. The flexibility and agility of a commercial container cargo ship moving around global waters enable us to collect data that are normally difficult to collect by conventional methods.

Atmospheric CO_2, CH_4 and N_2O mixing ratios in the China sea-shelf boundary layer during the spring 2017 campaign

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High-accuracy and continuous ship-based cavity ring-down spectroscopy (CRDS) was used to simultaneously measure mixing ratios of atmospheric CO_2, CH_4 and N_2O in the China sea-shelf boundary layer from 26 March to 15 April, 2017. The CRDS analysers (G2401 and G5101i, Picarro Inc., USA) and CO_2, CH_4 and N_2O high pressure reference gas cylinders (29L, Scott-Marrin, USA) together with two-stage gas regulators (CGA-590, Scott Specialty Gases, USA) were carried by a specially designed marine survey vessel named "Dongfanghong II", which provided an atmospheric observation laboratory and related facilities. The vessel was also equipped with ship-borne meteorological sensors. Air inlet was placed at the front and the highest position near the ship-borne meteorological sensors, ca 15 m above sea surface. Dry air or reference gas flowed through an eight port multi-position valves (Valco Instruments Co. Inc. USA) into the CRDS analysers.

Latitude and longitude data were used for locating the atmospheric mixing ratio data measured by the CRDS system. Meteorological data were used for excluding abnormal data and verifying air mass transport analysed by models. The observed atmospheric CO_2, CH_4 and N_2O data showed latitudinal distributions between 36°N and 25°N. The distribution was not only resulted from air mass transport from the Asian continent and the Pacific Ocean induced by winter monsoon and trade winds, but also by air-sea exchange and atmospheric chemical processes. Moreover, mixing ratios of atmospheric CO_2, CH_4 and N_2O showed temporal and spatial correlation, this was possibly due to the influence of long-range air mass transport and various mixed status. Next ship-based campaign has been scheduled in the autumn 2017.

UPDATED GUIDELINES FOR ATMOSPHERIC TRACE GAS DATA MANAGEMENT

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Measurement programs working to better our understanding of the global carbon cycle incorporate many different strategies for the collection of raw data. Programs may collect both continuous insitu and discrete flask measurements from fixed locations as well as mobile platforms like aircraft, shipboard & vans. Collected data must be stored in a central repository to be processed and analyzed. Details of the collection equipment, analysis instruments and potential issues must be documented. Many different users will interact with the data at various stages to manage logistics and perform quality control. Finally, processed data must be publicly available to the community for comparisons and further analysis.

A thoughtfully implemented data management strategy is essential to the long term success of a trace gas measurement program. Utilizing a well designed database management system will allow multi user access in a secure environment while maintaining accountability, data integrity and flexibility. We will discuss basic concepts, design strategies and implementation details from the CCGG database system.

Introduction of new WDCGG website

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The World Data Centre for Greenhouse Gases (WDCGG) is one of the World Data Centres(WDCs) under the Global Atmosphere Watch(GAW) programme. It serves to gather, archive and provide data on greenhouse gases (CO2, CH4, CFCs, N2O, etc.) and related gases (CO, etc.) mainly in the atmosphere, as measured under GAW and other programmes.

An ongoing reform of the services in the WDCGG (http://ds.data.jma.go.jp/gmd/wdcgg/), in consultation with the data providers and users, is in progress, to be shifted to the new WDCGG website (https://gaw.kishou.go.jp/). This website is open only to the data providers of GHG (including CO) data/metadata for data submission, and will be open to all users after this October when some operation tests concerning security checks will be accomplished.

To serve better as a bridge between data contributors and users, improvement and stabilization of our services such as the new way of data/metadata submission are presented and discussed.

Mobile Laboratory improving the data quality of ICOS atmospheric station network

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ICOS (Integrated Carbon Observation System) is a European-wide research infrastructure consisting of high precision long-term network of stations measuring greenhouse gas concentrations in the atmosphere and greenhouse gas fluxes from ecosystems and oceans. ICOS is designed around central facilities, of which main tasks includes provision of calibration gases, standardized data processing, technical support and training, and quality control. As part of the Atmosphere Thematic Centre (ATC), a mobile laboratory (MobileLab), operated by the Finnish Meteorological Institute (FMI), is responsible for atmospheric station audits and internal quality control. The ICOS Atmospheric Station Specifications –document (https://icos-atc.lsce.ipsl.fr/filebrowser/download/27251), composed in conjunction with the atmospheric scientists and maintained by the ATC, provide the guidelines for the MobileLab audits.

The MobileLab is a fully equipped mobile unit visiting 3-4 atmospheric stations per year. The MobileLab instrument repertoire includes state-of-the-art greenhouse gas analysers; Picarro G2401 (CO_2, CH_4 and CO), Ecotech FTIR (CO_2, CH_4, CO and N_2O), and LGR-EP (CO and N_2O); as well as a set of calibration gases. An audit comprises a multi-day station evaluation visit, a cross-check of the calibration gases, and ambient air intercomparison measurements for one to two months. For the audits, the MobileLab uses travelling standard cylinders (TSs) prepared by FMI and calibrated against the laboratory standards (WMO CCL scale) prepared by WMO Central Calibration Laboratory at NOAA (National Oceanic and Atmospheric Administration, USA). Since the preparation of the MobileLab TSs is separated from the ICOS Central Analytical Laboratory (CAL) that normally provides standard gases for the stations, the MobileLab audits are independent from the ICOS CAL gas standards and thus have a nature of an external audit. The stability of the FMI laboratory standards, however, is ensured with regular cross-checks against the ICOS primary standards maintained by CAL. During the audit visits, all the station infrastructure associated to the ICOS atmospheric measurements, including compliancy of meteorological sensors, and professionality of local personnel will be evaluated.

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. The quality management procedures of the MobileLab have been applied using the ISO 17025 global standard for good laboratory practises and quality management criteria that is also compliant with the ISO 9001 standard, as a guideline. The measurement data from atmospheric stations are centrally processed in the ATC to ensure the data consistency. Data produced by the MobileLab, however, is calculated separately to maintain the independent nature of the MobileLab and at the same time to evaluate the performance of the centralised data processing. During the audit visit, the MobileLab operators monitor the intercomparison measurements and helps the local personnel to improve the measurements. After the audit visit, a report summarising the results and including possible recommendations will be written.

From 2014 onwards, the MobileLab has set up its instrumentation, developed its operating procedures, quality system and reporting, and conducted seven audits. So far, the ICOS atmospheric station network has been under the building stage, but during 2017 the first stations will accomplish the labelling process. Due to the building stage of the atmospheric stations as well of the MobileLab, the frequency of audit visits has remained below the initial plans during these first years of operation. However, the audits performed at the stations with varying level of readiness have proven the high overall level of measurement performance, but also revealed some drawbacks in the chain from measurements to data processing.

5 years of ICOS compliant in situ GHG measurements at OPE: set up, quality control and calibration system

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Andra and LSCE are jointly operating an ICOS observation station at OPE in eastern France. The station is located on top of the surrounding hills at around 400m asl altitude in a rural background area. It has been equipped with a robust and autonomous sampling system that can be remotely controlled. Recent IR spectrometers are used to perform continuous in-situ measurements of CO2, CH4, CO, N2O and H2O at three sampling heights (10m, 50m and 120m) on a tall tower.

After a description of the station set up and the quality control and calibration systems used, the poster will present the results of the station quality control (target gas and weekly flasks sampling comparison) and calibration strategy in the framework of the ICOS specifications.

Optimal dry cylinder sequencing on Picarro G2301 and G2401 CRDS instruments

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This presentation describes experiments undertaken to determine an optimal sequence to analyse dry calibration and sample cylinders on Picarro G2301 & G2401 instruments, and to determine whether extended measurements of very dry air eventually degrades the measurement precision for CO_2 and/or CH_4 in an instrument and software designed to also fit a water vapour transition line.

All our standard and calibration cylinders are dried at the point of filling. A Rix SA3 oil-free compressor is used to fill cylinders, with magnesium perchlorate used to strip water out of the gas before it enters the cylinder. This method typically results in water vapour concentrations of less than 30 ppb within our tanks. The cylinders are filled under baseline conditions at Cape Schanck on the southern coast of Australia. Any spikes required are prepared using high purity dry gases in the laboratory and inserted during the filling process.

Numerous sequences were run over a 6 month period on a single Picarro instrument. Some sequences sampled ambient undried air within the sequence, other sequences sampled only dry cylinder gas for extended periods. The sequences varied in length between 5 and 18 hours and the number of times the cylinder was accessed ranged between 3 and 16 occasions. Sample cylinders were accessed between 10 and 30 minutes each time, while the ambient air was run for 10 minute to 2 hour periods within the sequences.

Subsequent experiments ran select sequences on additional Picarro instruments, both in the laboratory and in the field.

The experiments indicate that Picarro instruments are robust regarding extended dried air sequences.

Quality control of flask sample data using Ar/N_2 measurements

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Long-term atmospheric observations of greenhouse gases provide key information for the understanding of their budgets. Since spatiotemporal background concentration gradients of these long-lived trace gases are very small, measurements have to be made with high accuracy. One component in maintaining the accuracy of observation networks has been flask sampling programs where the air samples are then analysed in laboratories. This also allows the measurement of additional parameters of these samples.

The MPI-BGC operates flask sampling programs at 11 stations. Pressurized samples are generally collected in triplicate. At some of the stations logistic challenges have repeatedly caused big delays in shipment of samples to the laboratory. The length of storage times prior to analysis can affect the sample's integrity due to micro leaks in the container seals, causing individual samples to exhibit large deviations in their composition from their siblings. The underlying process is described as Knudsen diffusion that results in a mass fractionation of the escaping relative to the remaining gas. This is manifested in an enriched Ar/N_2 ratio that generally has very little atmospheric variability. The correlation of the effect on different trace gases relative to the bias in the Ar/N_2 ratio can be theoretically derived based on Graham's Law. We compare this theoretical relationship with the observed patterns of flask samples that have been affected by leaks.

The results show a very good correlation of O_2/N_2 deviation relative to Ar/N_2 that allows correcting O_2/N_2 measurements for fractionation effects with concurrent Ar/N_2 measurements, assuming a station-specific time invariant Ar/N_2 ratio. The correlation of the deviations of most of the species analysed relative to the Ar/N_2 deviation also reveals the theoretically expected relationship (CO_2, CH_4, N_2O), yet with too much scatter to be used for a correction. Nevertheless, bounds on the permissible Ar/N_2 ratio can be defined within which the introduced fractionation error for the corresponding other species remains within the WMO accuracy target. This Ar/N_2 ratio indicator then can be used to flag invalid or suspicious data to avoid a systematic bias of the trace gas mixing ratios.

Comparison of Picarro and Los Gatos analysers for CO and N_2O at Hohenpeissenberg

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Since 2015 greenhouse gas measurements have been performed at the global GAW and ICOS station Hohenpeissenberg in rural Southern Germany. At present, a four channel Picarro (CO2/CO/CH4/H2O - G2401) is used for the standard ICOS observations whilst two Los Gatos Analysers (LGR N2O/CO/H2O - 913-0015 (EP)) have been run in parallel for several months providing independent measurements of CO as well as adding the new component N2O to the measurement program. At Hohenpeissenberg the sample line at three different heights (50m, 93m, 131m) is operated under low pressure (0.5 bar) in order to prevent condensation as no external drying of the sample air is implemented. The data from ambient air as well as from the target and calibration measurements are analysed and intercompared demonstrating the performance of the three instruments under those conditions.

Update of 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. To ensure the comparability of observations from the atmospheric stations within the network and to networks of the WMO/GAW a central facility for the ICOS research infrastructure, the Flask and Calibration Laboratory (FCL) in Jena (Germany) was established since 2013. Inter alia FCL covers the provision of 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 an oil-free compressor, absorbers and a spiking system for the production of user-defined reference air mixtures is available.

Within our contribution we will present the actual performance of operations and various quality control activities to ensure accuracy of observational data.

QA/SAC Switzerland – Activities and Achievements

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The GAW Quality Assurance/Scientific Activity Centre (QA/SAC Switzerland) was established at Empa in 2000. It is co-funded by MeteoSwiss and Empa, and closely linked to the World Calibration Centre (WCC-Empa) for surface ozone, carbon monoxide, methane and carbon dioxide. QA/SAC Switzerland mainly supports measurements of the same gases but with much wider scope, providing worldwide technical and scientific support.

This paper will give a comprehensive overview of the main tasks of QA/SAC Switzerland, which are

- training, twinning, and capacity building, i.e. technical support of GAW stations, advice for adequate instrument selection, instrument operation and calibration strategies, assistance with data quality and data submission issues, and regular teaching activities within GAWTEC;

- research activities promoting technical progress and scientific data analysis, e.g. evaluation of novel measurement techniques, assessment of their applicability for long-term monitoring purposes, dissemination of know-how to the GAW community through publications and presentations, and supporting GAW investigators in data exploitation and publications;

- contribution to GAW outreach, e.g. by being actively involved in writing GAW reports, in particular measurement guidelines and standard operation procedures, as well as contributing GAW results to other reports and publications;

- networking / cooperation with other programmes / projects in line with the GAW strategy, e.g. by sharing expert knowledge to establish close links to GAW, to foster synergies between GAW and other programmes, projects and initiatives, and to ensure accordance with GAW measurement guidelines.

Methane in Hong Kong: isotopic characterisation of local and regional methane sources

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Greenhouse gas measurements have recently commenced at the Swire Marine Institute at Cape d'Aguilar, on the southern tip of Hong Kong Island (22.21°N, 114.26°E). Air samples have been collected from the station twice a week since April 2015 for methane mole fraction and δ^{13}C analysis at RHUL. Methane and carbon dioxide mole fractions are now also measured in situ by cavity ringdown spectroscopy. This station receives air from important source regions: southerly marine air from the South China Sea in summer and northerly continental air in winter. These measurements together with back trajectory analysis will allow an integrated assessment of emissions from the region.

In addition to the regular sampling, RHUL has carried out field campaigns to map out and isotopically characterise local methane sources. Hong Kong has a wide variety of natural and anthropogenic sources of methane within a small densely populated area. Methane mole fraction was mapped out across Hong Kong during a field campaign in July 2016 using a cavity ringdown spectrometer installed in a car. Methane is mostly emitted from large point sources, with highest concentrations measured close to active landfill sites, sewage works and a gas processing plant. Air samples were collected close to sources and analysed by mass spectrometry with Keeling plot analysis used to determine the δ^{13}C isotopic signatures which ranged from -70 ‰ (cows) to -37 ‰ (gas processing).

European atmospheric $^{14}CO_2$ activities within the ICOS-RI network

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Radiocarbon in atmospheric CO_2 has successfully proven to be a very powerful tracer for carbon cycle studies and for quantifying CO_2 originating from the combustion of fossil fuels. The European research infrastructure ICOS (ICOS-RI.eu) has thus selected $^{14}CO_2$ as one of the key-species to be sampled at all atmospheric ICOS class 1 stations and to be analysed at the ICOS Central Radiocarbon Laboratory. ICOS follows a two-pronged sampling strategy for $^{14}CO_2$. On the one hand, flask samples will be collected during predefined meteorological conditions; on the other hand continuous, two-weekly integrated samples will be collected to estimate long-term trends of fossil fuel CO_2 at the sites.

We present the first results of ICOS integrated $^{14}CO_2$ samples from 10 European stations, starting in 2015. These measurements provide an overview of the current $^{14}CO_2$ levels at predominantly background stations and illustrate the influence from regional fossil fuel sources at individual stations.

Simultaneous field-scale in-situ measurements of the four most abundant N_2O isotopocules

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Understanding and quantifying the biogeochemical cycle of N_2O is essential to develop effective N_2O emission mitigation strategies. We present a novel, fully-automated measurement technique that allows simultaneous, high-precision quantification of the four main N_2O isotopocules ($^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{14}N^{14}N^{18}O$) in ambient air. The instrumentation consists of a trace gas extractor (TREX) coupled to a quantum cascade laser absorption spectrometer (QCLAS), designed for autonomous operation at remote measurement sites. All system components have been integrated into a standardized instrument rack to improve portability and accessibility for maintenance. With an average sampling frequency of approximately 1 hr^{-1}, this instrumentation achieves a repeatability of 0.09, 0.13, 0.17 and 0.12 ‰ for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ and site preference of N_2O in ambient air, respectively. The repeatability for N_2O mole fraction measurements is better than 1 ppb (parts per billion, 10^{-9} moles per mole of dry air).

This TREX-QCLAS technique was deployed in the framework of the ScaleX campaign 2016 at the TERENO site Fendt, Germany. Isotopic signatures of the emitted N_2O were interpreted in relation to management events and meteorological conditions to shed light into different N_2O source processes. Next, N_2O isotopic information will be evaluated in conjunction with $\delta^{15}N$ values of nitrogen precursors (NH_4^+, NO_3^-), and additional soil parameters. Finally, results will be discussed in relation to a biogeochemical soil model (L-DNDC) with an isotope sub-module (SIMONE) developed at IMK-IFU, and a ^{15}N tracer approach applied by Thünen Institute.

High precision spectroscopic measurement of N_2O clumped isotopic species

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Nitrous oxide (N_2O) is a major greenhouse gas and the most important ozone destruction species. Understanding formation mechanisms and clarifying its disperse and highly variable sources and sinks is important for mitigating the emissions. Measuring the doubly substituted “clumped” isotopocules of N_2O can add new and unique opportunities to fingerprint and constrain the N_2O biogeochemical cycle. A similar strategy has recently been applied for other atmospheric constituents such as CO_2, CH_4, and O_2.[1-4]

Within this project, we are developing an analytical technique for the selective and precise analysis of the most abundant clumped N_2O isotopic species: $^{15}N^{14}N^{18}O$, $^{14}N^{15}N^{18}O$, and $^{15}N^{15}N^{16}O$. The measurement setup is based on a dual quantum cascade laser absorption spectrometer (QCLAS) with an astigmatic Herriott multi-pass absorption cell.

We will present the measurement concept, in particular the selection of wavelength regions for maximum sensitivity for the clumped species as well as for simultaneous analysis of singly substituted isotopologues, required for referencing the measurements. The absorption lines of singly substituted and clumped N_2O isotopocules are verified in terms of their frequency and line-strengths by standard addition experiments. Clumped N_2O gases for this verification were prepared by thermal decomposition of chemically synthesized double labeled ammonium nitrate. Their isotopic purity was determined by quadrupole MS. Finally, measurement conditions such as pressure and concentration of N_2O as well as instrumental parameters including tuning of the laser source and settings of the spectroscopic software were optimized with respect to overall analytical precision and drift.

We demonstrate that this novel analytical technique is a very promising alternative to the currently emerging high-resolution mass spectrometric approaches[5] in terms of ease-of-use, field deployability, sample throughput, precision, and most importantly, its inherent selectivity for the clumped isotopomers $^{15}N^{14}N^{18}O$ and $^{14}N^{15}N^{18}O$. The performance of the novel QCLAS technique with respect to clumped N_2O isotopes can offer a broad range of prospective applications.

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Development of new N_2O reference materials for $\delta^{15}N$, $\delta^{18}O$ and ^{15}N site preference within the EMPIR project SIRS

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In recent years, research on nitrous oxide (N_2O) stable isotopes has significantly advanced, addressing an increasing number of research questions in biogeochemical and atmospheric sciences [1]. An important milestone was the development of optical isotope ratio spectroscopy (OIRS), which is inherently specific for structural isomers ($^{15}N^{14}N^{16}O$ vs. $^{14}N^{15}N^{16}O$) and capable to collect real-time data with high temporal resolution, complementary to the well-established isotope-ratio mass-spectrometry (IRMS) method.

The compatibility between different IRMS and OIRS laboratories, however, was shown to be limited, in particular for ^{15}N site preference, i.e. the difference between ^{15}N abundance in central (N*NO) and end (*NNO) position [2]. This was attributed to two reasons, first no WMO-GAW Central Calibration Laboratory (CCL) for N_2O stable isotopes currently exists and second no international reference material in the form of gaseous N_2O with stated uncertainty is available. In addition, the accuracy of the NH_4NO_3 decomposition reaction, which provides the link between ^{15}N site preference and the international $^{15}N/^{14}N$ scale, was recently found to be limited by non-quantitative NH_4NO_3 decomposition in combination with substantially different isotope enrichment factors for both nitrogen atoms [3].

The above tasks will be addressed in the upcoming European Metrology Programme for Innovation and Research (EMPIR) project “Metrology for Stable Isotope Reference Standards (SIRS)” 2017-2020. With respect to N_2O reference materials the SIRS project will focus on the following subjects:

1) Develop improved techniques to characterise N_2O gases for $\delta^{15}N$, $\delta^{18}O$ and the ^{15}N site preference with reference to the respective international isotope ratio scales including an uncertainty assessment.
2) Develop at least three new international gaseous N_2O reference materials for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N$ and $\delta^{18}O$, available both as pure substance and diluted in whole air.

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$^{14}CO_2$ measurements from Baring Head, New Zealand

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Measurements of $^{14}CO_2$ have been made in Wellington, New Zealand, since December 1954, making this the longest $^{14}CO_2$ record of tropospheric air in the world. Cape Grim in Tasmania, Australia, is at a similar latitude to Baring Head and independent measurements of $^{14}CO_2$ have been made since 1987 by Heidelberg University. The sample collections at both locations are by the sodium hydroxide absorption method, integrating samples over a two-week period. Comparisons of these two datasets show that they agree well for the most part, but there are a few distinct periods where the records differ. Careful examination of the Baring Head data has been undertaken to identify possible reasons for these periods of difference and many samples have been extracted and measured again, where possible.

In order to identify and quantify the effect of any instrumental, systematic or procedural influences, a direct comparison between the two sites has begun. A Baring Head-style sampler has been installed at Cape Grim and sample collections using the static caustic soda method began in late January 2017. At Cape Grim the NIWA-method collections are co-ordinated with collections of the samples by the Heidelberg University method, allowing both methods to be directly compared through co-located sampling.

Performance of radiocarbon analysis using NIES-CAMS and initial results for air samples obtained in Indonesia.

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Radiocarbon (^{14}C) measurements are useful to estimate fossil carbon contribution on atmospheric carbon dioxide (CO_2) concentrations. In 2014, compact carbon AMS (CAMS, NEC 1.5SDH) were introduced into NIES. NIES-CAMS system is based on a 0.5MV tandem pelletron accelerator. The NIES-CAMS is specialized to analyze $^{14}CO_2$ in the atmosphere, and then to provide information on fossil carbon contribution in the variations of CO_2, which are measured by various methods and platforms, including satellite (e.g. GOSAT).

It is said that CO_2 flux in Asian region gives considerably large impacts to global CO_2 budget. Therefor atmospheric $^{14}CO_2$ monitoring over Asian region is important to reduce uncertainties in carbon budget, however, there are few data on Asian region. NIES have corrected air samples from the western Pacific and two monitoring stations in Japan (Cape Ochi-ishi and Hateruma Island) for many years. Recently we added air sampling sites on Malaysia, Indonesia, and Tokyo megacity. We extract CO_2 gas from whole air samples into grass ampoules and have archived them for $^{14}CO_2$ analysis.

In this study, we show the performance of atmospheric $^{14}CO_2$ analysis using NIES-CAMS and initial results of CO_2 isotope ratio observed at Bogor, Indonesia. We have tried to find best condition of beam quantity, stripper gas pressure, and measurement sequence of NIES-CAMS then the stability and accuracy of measurement was improved. Measurement error in $\Delta^{14}C$ of modern samples might be 2.4 permil in average. We prepared two reference cylinders and simultaneously measured air samples with two references to check the wheel-to-wheel variations. Furthermore, we newly developed volume-adjusted system in the graphitization line. It made equalize amount of graphite produced from CO_2 gas sample. We expect these will help high precision ^{14}C measurements.

Towards SI traceability for CO_2 isotope ratios: Identifying sources of error in optical spectroscopy measurements

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In order to properly characterise the increasing greenhouse gas concentrations in the atmosphere, there is a clear need to distinguish between anthropogenic and natural contributions. A valuable discriminant for such determination is stable isotope analysis, which can provide information on the origin of a gas species. Through technological advances, it is possible to make such measurements with field-capable optical spectrometers. However, with numerous monitoring stations around the world, and with different instrumentation often employed, it becomes crucial to establish a traceability chain to allow accurate comparisons between measurements, both in time and between different monitoring locations.

European metrology research projects, such as the recently completed Metrology for High Impact Greenhouse Gases (HIGHGAS), and the newly commenced Metrology for Stable Isotope Reference Standards (SIRS), have moved to address the need for metrological impact on optical isotope ratio spectroscopy. The goals of these projects cover a range of topics, including the development of static and dynamic reference materials for CO_2 in air, the development of validation routines to provide recommendations on the best practice for monitoring networks, and the development of traceable field-deployable spectrometers which can meet the WMO compatibility goals. To achieve these goals requires the development of significantly stable instrumentation, as well as extremely careful instrument characterisation.

Preliminary work on the development of a metrologically characterised optical spectrometer for the determination of $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 will be presented. Issues related to measurement uncertainty, such as temperature, pressure and matrix effects, and their resulting effects on $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 values, will be covered.

Measurement of nitrous oxide isotopomers in air

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Nitrous oxide (N_2O) is a long lived greenhouse gas that has been accumulating in the atmosphere due to increased anthropogenic usage of N fertilisers to support global food production. The main removal mechanism is chemical destruction in the stratosphere. The global budget is relatively well known but processes that control individual source contributions and the relative importance of several microbial pathways that lead to N_2O emission from soils and the oceans are poorly understood.

N_2O isotopomers provide a method to improve knowledge of N_2O formation processes. The 4 most abundant isotopic variants are $^{14}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$, $^{14}N^{15}N^{16}O(\alpha)$ and $^{15}N^{14}N^{16}O(\beta)$. The site preference variable ($\delta^{15}N\alpha$- $\delta^{15}N\beta$) is thought to be independent of the substrate isotopic composition and depends only on the reaction(s) forming and destroying N_2O – and so provides a possible tool to differentiate between nitrification and denitrification production pathways including the distinct impact of several microbial communities.

A new generation of quantum cascade laser spectrometers has potential to make rapid measurement of isotopomer variants. We show our preliminary experiments using a Los Gatos Research N2O1A-23e-EP analyser, coupled to a custom-made instrument for cryogenic N_2O pre-concentration. Pre-concentration of N_2O is required to increase the signal-to-noise ratio in order to resolve variations of N_2O-isotopomers in air. It is intended to use the new technique in soil chamber and emission experiments to provide new insights into N_2O formation processes.

Stable isotope and mixing ratio measurement of atmospheric CO2 over India

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India has ratified the Paris Agreement with a target to reduce emission intensity. To achieve this target it is of utmost priority to quantitatively understand the processes behind the CO2 emissions over India. This can be achieved through simultaneous measurement of mixing ratio and stable isotope ratio of atmospheric CO2. Few efforts have been taken in India to observe CO2 mixing ratio, but efforts towards monitoring of stable isotope ratio of atmospheric CO2 is very rare. Bhattacharya et al., 2009 and Tiwari et al, 2011 have discussed about Cape Rama India observations and revealed direct impact of the large-scale monsoon circulation, characterized by biannual reversal in surface-level winds on the variability of CO2 mixing ratio over Indian subcontinent. Tania et al., 2010; 2015, discussed about stable isotope observations at Bangalore India. They have calibrated the experiment using IAEA standards, and JRAS air reference mixtures (Tania et al., 2013). Weekly (Cape Rama; CRI) and bi-weekly (Bangalore; BLR) samples were collected at both of these two sites and were analyzed in laboratory (CRI at CSIRO, BLR at IISc). Using stable isotope observations Tania et al., 2015 have identified that fossil fuel, biomass burning, and cements industry emission are the prominent sources at BLR station. Their differential contribution was found to drive the CO2 variability over the station. Single site monitoring can lead to a spatial limitation of data and dependencies of the features of the particular site. In addition, large spatial-temporal heterogeneity of sources in India and local emissions may produces large uncertainty in source estimation based on single site measurement. Thus multiple monitoring stations within a well defined network are in immediate need to develop in India. In comparison to weekly/bi-weekly measurement, continuous monitoring will further provide data-coverage with higher temporal resolution going from annual-seasonal-monthly to daily-hourly-minute scale and will improve the measurement statistics. In summary Indian monsoon dynamic and the enhancement in investing in renewable technology will have a prominent effect on the future per capita emission of CO2 from India. In order to design strategies for emission reduction, possible source identification as well as quantitative estimation of their contribution to CO2 variability are primary important. This highlights the immediate requirement of establishing a monitoring network of multiple stations where high-precision, high-frequency measurement mixing ratio and stable isotope ratio of atmospheric CO2 as well as other GHGs will be conducted.

Pilot study measuring N_2O mole fraction, $\delta^{15}N^{bulk}$-N_2O, $\delta^{15}N^{\alpha}$-N_2O, and $\delta^{15}N^{\beta}$-N_2O using Picarro G-5101i instrument reveals analytical challenges

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Nitrous oxide (N_2O) continues to increase in the atmosphere and ranks the 3rd in long-lived greenhouse gas in radiative forcing (behind CH_4 and CO_2). It is also the dominant ozone-depleting substance emitted in the 21st century. While there are many challenges to understanding N_2O in the free troposphere, the NOAA global flask network offers insights. For example, variations in the N_2O mole fraction measured at NOAA sites are thought to be influenced in part by heightened microbial production from fertilized agricultural systems. Detrended monthly data display large interannual variability, which at some sites challenges the concept of a "mean" seasonal cycle. But soil microorganism processes are spatiotemporally heterogeneous, limiting our ability to constrain the anthropogenic influence on N_2O production at a global scale. The intramolecular position of ^{15}N (β position $^{15}N^{14}N^{16}O$ versus α position $^{14}N^{15}N^{16}O$) in addition to $\delta^{15}N^{bulk}$-N_2O can aid in our understanding of both the biological controls and stratospheric influence of tropospheric N_2O.

Laser based mid-infrared instruments are now available that can measure position specific isotopes of N_2O. The INSTAAR Stable Isotope Lab is testing the capability of the Picarro G-5101i instrument to measure potential small changes in position specific N_2O isotopes at a subset of the NOAA flask network sites. Simultaneous and continuous measurement of N_2O mole fraction, $\delta^{15}N^{bulk}$-N_2O, $\delta^{15}N^{\alpha}$-N_2O, and $\delta^{15}N^{\beta}$-N_2O is performed using the Picarro G5101-*i* wavelength-scanned cavity ring-down spectrometer. The work builds upon that of Steiker (2014) and now incorporates an automated flask manifold along with a water trap and scrubbers for both carbon monoxide and carbon dioxide to eliminate spectroscopic influence. Preliminary results suggest that instrument stability is critical for making measurements that are precise enough to constrain interannual variability at the NOAA baseline sides, specifically to resolve site preference differences. It is still unclear whether or not tropospheric $\delta^{15}N^{bulk}$ or SP exhibits a season cycle, but if the technique can be perfected, monitoring these isotopomers over a longer decadal time scale could provide answers to questions concerning large scale shifts in source emissions, or help to quantify the stratospheric influence of seasonal N_2O variability, which is essential in order to refine the global N_2O budget.

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Measurement of N_2O isotopes at the high-altitude station Jungfraujoch

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Nitrous oxide (N_2O) is a strong greenhouse gas and the strongest ozone-depleting substance emitted in the 21st century. The substantial increase in atmospheric N_2O mixing ratio since the preindustrial era has raised worldwide concern. This increase has largely been attributed to increased nitrogen (N) fertilizer use in agriculture. However, due to the long life time of N_2O (~ 120 years) in the atmosphere, spatial and temporal gradients are small, which makes it difficult to distinguish sources and plan mitigation strategies. In addition, the factors governing seasonal and interannual variabilities in N_2O concentration and growth rate remain poorly constrained. Recently, modelling of the N_2O cycle combined with atmospheric isotope measurements has been proven as an effective approach for decoding the atmospheric N_2O budget. However, long-term data with high precision is still limited.

In this study, we present N_2O mole fractions and isotopic compositions in background air monitored at the high-altitude Jungfraujoch (JFJ) research station, from 2014 to now. N_2O mole fractions were determined *in situ* by GC-ECD (2005-2015) and OA-ICOS (since January 2015), while air samples for isotopic analysis were collected weekly/bi-weekly and analysed subsequently by quantum cascade laser absorption spectroscopy at Empa with a repeatability below 0.1‰ [1]. $\delta^{15}N^{bulk}$ of N_2O significantly decreased over the past years, likely due to ^{15}N-depleted anthropogenic sources. In contrast, no statistically significant trend was observed for $\delta^{15}N$-site preference (SP) and $\delta^{18}O$ of N_2O, however a distinct seasonal variability was detected. The observed changes might reflect the seasonal variation in N_2O production processes or stratospheric destruction. For example, N_2O site preference was generally lowest in the summer months (July to September) and highest in winter (January), which can be explained by a larger contribution of N_2O produced by heterotrophic denitrification, with low SP, as compared to nitrification in warm, humid summers. In addition, the seasonal pattern of N_2O-SP may be partly attributed to stratosphere-troposphere exchange coupled with stratosphere N_2O sink. To further enhance our understanding of the global N_2O cycle, a box modelling approach will be applied and the temporal and spatial coverage will be extended by including N_2O isotope measurements from the Cape Grim Air Archive on the Southern Hemisphere.

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Evaluation of methane sources by isotopic analysis in central London

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Identifying urban methane sources in urban environments such as London and estimating their relative importance is necessary to accomplish methane reduction targets, but still an unresolved issue. High precision stable isotope analysis of atmospheric methane has been used to provide a better understanding of urban sources and demonstrate how relative proportions by source type of methane emissions, given by national inventories (NAEI), are not well constrained (Zazzeri et al., 2017).

A Picarro G2301 analyser was installed on the roof of King's College London (KCL), located in the city centre, and connected to an air inlet located 7 metres above roof height. An auto-sampler was connected to the same air inlet and launched remotely when a high nocturnal build up was expected, allowing up to twenty air bags to be collected for methane isotopic analysis over a 24 hour period.

High precision isotopic measurements enabled assessment of the isotopic signal of the source mix in central London (Zazzeri et al., 2017). However, a continuous isotopic record would definitely provide insight into the interpretation of methane emissions and their seasonal trend. A Picarro G2201 analyser for CH_4 and CO_2 mole fractions and isotopic ratios measurements, has been installed at the Physics Department of Imperial College London, with an air inlet located on the departmental roof at ~24 metres height.

The isotopic signature of the source mix measured at KCL was -45.7 ±0.5 ‰, a value that confirmed the primacy of fossil methane emissions in the overall methane budget in central London. The new measurements carried out at Imperial College will be compared with the KCL record, allowing further investigation of urban methane sources.

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Inter-comparison study of European atmospheric ^{222}Rn and ^{222}Rn progeny monitors

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The noble gas radon (^{222}Rn) is widely used as tracer to study different research topics related with atmospheric transport and mixing processes within the planetary boundary layer, experimental estimation of fluxes of greenhouse gases (GHGs), etc. High-quality ^{222}Rn activity concentrations observations are needed with high spatial resolution. Worldwide monitoring networks of GHGs are already performing atmospheric ^{222}Rn measurements at different heights from the ground and using different measurement principles. These data should be harmonized before being used for regional-to-global applications, as suggested by the International Atomic Energy Agency, because calibration issues could introduce significant biases and therefore limit the data utility.

An inter-comparison study, lasting 3 months, was carried out in Gif sur Yvette (France) in fall 2016 using ^{222}Rn/^{222}Rn progeny monitors based on different measurement techniques. Two single-filter ^{222}Rn progeny monitors (a **H**eidelberg **R**adon **M**onitor (**HRM**) and a **K**azan **M**onitor (**KM**)); two two-filters ^{222}Rn monitors by the **A**ustralian **N**uclear **S**cience and **T**echnology **O**rganisation, (**ANSTO)** and an electrodeposition **A**tmospheric **R**adon **MON**itor (**ARMON**) were simultaneously running and sampling air at 5 m and at 100 m above ground level (a.g.l.). The ARMON requires dry sampled air (< 2000 ppmv). The HRM and KM utilize the disequilibrium factor (F) between ^{222}Rn and its progeny. The aim of this study was to evaluate: i) possible biases and associated correction factors between monitors; ii) the dependence of the monitors response in relation to the sampling height, the meteorological and aerosol conditions; iii) the portability and maintenance of each monitor.

The linear regressions between monitors hourly data were calculated using the HRM as reference instrument following past studies. At 5 m a.g.l. results show slopes between 0.760 and 1.44 and biases ranging between -0.310 and 0.996 Bq m^{-3}. Results at 100 m a.g.l. show slopes between 1.06 and 1.16 with offsets being between 0.13 and 0.21 Bq m^{-3}. Correction factors, including calibration and disequilibrium contributions, ranged between 0.42 and 0.62. Changes of F were observed in relation to the sampling height, under rainy and/or clean atmospheric aerosol concentrations (< 500 particles cm^{-3}) events. These last influences should be further investigated for a complete harmonization of the data.

Evaluation of an OA-ICOS (Off-axis Integrated Cavity Output Spectrometer) for N2O measurements at Schauinsland station

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High precision atmospheric N2O measurements in different networks and at in-situ stations were measured in the last decades by gas chromatography (GC) but since a few years, new analysers have been developed based on spectroscopic technologies. The concentration gradients over the continent or between maritime and continental air are small and need to be measured very precisely which is challenging for both GC and optical analyzers.

At the UBA station Schauinsland (German Environmental Agency) an OA-ICOS analyser developed by Los Gatos Research is running since January 2015 in comparison to a GC system. Within this study we characterize the short-term and long-term repeatability, drift, temperature dependence, linearity and cross interferences with water vapour. The analyser shows standard deviation better than 0.1 ppb for the 5 min averages. The water vapour correction algorithms applied by LGR is not sufficient for high-precision atmospheric measurements and even the small differences in water vapour content of calibration gases and ambient air dried with a cryogenic cooler need to be corrected. The calibration procedure was optimized taking the non linearity, the analysers drift and the gas consumption into account. Here we present a calibration strategy using a drift standard which is injected every 6 hours. Comparison with GC measurements yield still a difference between (-0.07 and 0.33) ppb in 2017 which we could not explain with cross analysis of calibration gases and inlet line tests

Estimation of BG CO2 concentration from CRDS measurements at AMY site in South Korea using Quality Assurance Flagging Codes

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Since November 2011, KMA has been operating the CRDS (Cavity Ring Down Spectrometer) instrument, manufactured by Picarro inc., USA, at Anmyeondo (AMY) site for measuring background carbon-dioxide. The AMY site was designated as a regional WMO GAW site in 1998, and has the longest history of atmosphere watch elements in Korea. As for the CO2, the AMY site started its measurement using NDIR instrument in 1999 at first, then replacing it with the CRDS in 2011.

Beginning this year, the AMY site makes it routine to record the operational status for every measurement instruments in operation using flagging codes in an effort to ensure the activities in quality assurance and quality check of the measured raw data. The flagging codes for the CRDS are consisted of following 7 categories: flag 0 for well mixed air sample and good operating conditions, flag 1 for influence of local high concentration source but good operating conditions, flag 2 for possible influence from dehumidifier, flag 3 for suspected instrument malfunction and data quality, flag 4 for raw data loss from instrument malfunction, flag 5 for instrument correction, and flag 6 for data loss from other causes other than the instrument malfunction. Figure 1a illustrates probability densities for each of the 7 codes for the CRDS raw data from 2012 through 2016.

In a retrospective way the past 5-year CRDS raw data, from 2012 through 2016, were flagged with above-mentioned codes on purpose to assess and make comparison of the existing methodology to estimate background CO2 concentration in Korea. Here, we assume that the CRDS raw data flagged with the flag 0 are representative of well mixed background air conditions, while those with the flag 1 representing the local pollutant air. Those annual and monthly mean concentrations for each of the past 5 years were obtained from the simple arithmetic average using only those raw data with flag 0. Figure 1b shows the annual mean concentrations, making comparison among the 5 years.

In the upcoming meeting the detailed feature of the results will be presented, making comparison of the above simple arithmetic average with those of statistical signal processing method that has been used at KMA.

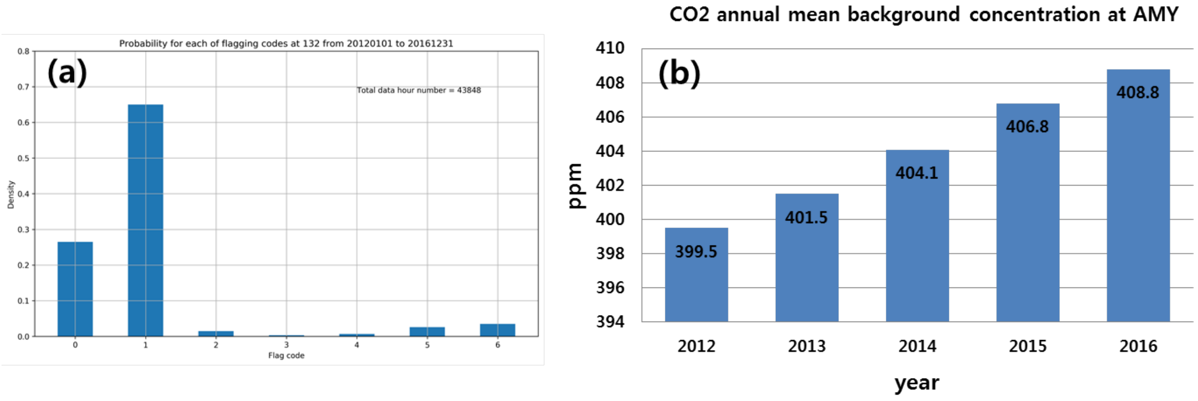

Fig. 1. (a) Probability density for each of flagging codes of the CRDS raw data from 2012 through 2016, (b) Annual mean CO2 background concentrations at AMY site obtained from simple arithmetic average of those raw data with flag code 0 only.

Synthesis and evaluation of near real air CO_2 reference gas

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Laser-based instruments are the widely-used analyzers for measuring atmospheric CO_2 and trace gas mole fractions because of its high precision as well as easiness of operation. However, these measurements are affected by both the isotopic composition of CO_2 (Lee et al., 2006, Tohjima et al., 2009) and by the $O_2/N_2/Ar$ composition of Air (Chen et al., 2010, Nara et al., 2012). Several kinds of “near real air” gas mixtures were synthesized, measured and evaluated using several analyzers.

Gas mixtures of pure CO_2 with adjusted isotope ratios in balance air were used as “near real air” samples: compressed dry natural air gas was used as the “real air” sample. The isotope ratio of pure CO_2 gas was adjusted to $\delta^{13}C = -8.0$ ‰ (VPDB) and $\delta^{18}O = +11.9$ ‰ (VPDB) by mixing CO_2 gases which had different isotope ratios by Air Liquide. Gas mixtures of containing the pure isotopically adjusted CO_2 and purified natural air (Grade 1, Japan Fine Products) were filled in 10L Luxfer aluminum cylinders at NIES. Gas mixtures of the adjusted isotopically pure CO_2 and CO_2-free natural air (Alphagaz Natural Air, Air Liquide) were also filled in 10L Luxfer aluminum cylinders at NIES. Dry natural air gases were filled in aluminum cylinders by NIES at Tsukuba, Japan (CO_2 ~ 410 ppm, H_2O < 3 ppm) and by Air Liquide in Spain (Alphagaz Natural Air, Air Liquide). In these experiments, gas mixtures of CO_2 with fossil fuel combustion origin and purified natural air were used as reference gases. Both the sample gases and reference gases were calibrated using NDIR (LI-6252, Li-COR) against NIES 09 CO_2 scale. Mole fractions of sample gases were corrected for biases due to different CO_2 isotopes ratios between the sample gases and the secondary reference gases because the secondary reference gases were mixtures of fossil fuel combustion CO_2 ($\delta^{13}C = -32.5$ to -25.3 ‰ (VPDB), $\delta^{18}O = -29.4$ to -22.7 ‰ (VPDB)) and purified natural air (Tohjima et al., 2009). To evaluate these samples, they were measured with CRDS (G2401, Picarro and G2101i, Picarro) based on the reference gases.

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Replacement of CH_4 calibration system for WCC-JMA

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The Japan Meteorological Agency (JMA) serves as the World Calibration Centre (WCC) for methane (CH_4) 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).

Since the WCC-JMA was established in 2001, the methane calibration system using a gas chromatograph equipped with a flame ionization detector (GC/FID) has been used for analysis of CH_4 mole fractions of standard gases. In consideration of the recent advances in measurement techniques and the widespread use of instruments based on laser spectroscopic techniques at many measurement stations, the WCC-JMA plans to replace the current GC/FID with a wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) analyzer which has some clear advantages concerning sensitivity, precision, linearity, time response and the measurement setup.

In order to assess the consistency in the continuity of the CH_4 calibration, we examined the standard gases and atmospheric CH_4 mole fractions calibrated/measured by both the GC/FID and WS-CRDS analyzers. We report our new calibration system and the results of comparative measurements between the old and new calibration systems.

Stability and Material Testing Results of Aluminum Cylinders and Regulator Comparisons

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With so many standards and regulator types being used within the WMO/GAW community, we undertook several tests of commonly used materials as they relate to analyte stability. Aluminum (Luxfer) cylinders used under 5 l · min-1 delivery (high flow) exhibited CO2 drift which increased after cylinder pressure decreased below 25 bar while lower flow (0.3 l · min-) exhibited stability to a lower pressure. Luxfer Superior Gas StabilityTM (SGS) cylinders behaved no different than untreated bare aluminum cylinders for CO2 although there is suggestion of increased drift of the CO concentration. Stability after storage or use of small carbon wrapped aluminum Luxfer cylinders show measureable drifts in CO2. Airgas Kel-FTM tipped CGA590 fittings were compared to brass fittings of the same type and were found to give stable delivery of CO2. Testing has expanded to include CH4 and CO. Flushing cycles, conditioning and delivery stability of one preferred specific model each of Airliquide, Matheson, and Tescom regulators are compared.

Causes of Instability in the Relative Abundance of the Major Constituents of Reference Air in High-Pressure Tanks

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Long-term measurements of $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ made with an isotope ratio mass spectrometer (IRMS) on a single working tank against a reference tank show variability over time scales ranging from hours to months, creating significant artifacts at the per meg level that impact the overall measurement quality of the system. While some of this variability is a result of instrument performance and drift, the majority of it is due to gas handling issues that cause fractionation of oxygen and argon relative to nitrogen, and to real changes in the relative composition of reference air within the tanks. Previous work has shown that measures such as storing tanks horizontally, keeping them thermally insulated, or equipping them with a diptube reduces the amount of fractionation substantially, though not completely. As part of an ongoing effort to understand the causes of instability in reference tanks, a suite of experiments were conducted to systematically isolate the factors contributing to this instability. These experiments included the use of a thermally-isolated "Y" to direct air from a single tank to two different regulators, the comparison of single- and dual-stage regulators, and different approaches to mechanically mix the air within the tank itself.

Investigation of adsorption / desorption behavior of high pressure small volume cylinders and its relevance to atmospheric trace gas analysis

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A critical issue for the long term monitoring of atmospheric trace gases is precision and accuracy of the measurement systems employed. In order to achieve a globally integrated and well established greenhouse gas observation network, the World Meteorological Organization (WMO) has recommended compatibility goals for measurements of trace gases within its Global Atmosphere Watch (GAW) programme [1]. These challenging limits can only be achieved by regular calibration with standard gases of known composition. However, standard gases may not be stable throughout a measurement period due to diffusion, leakage, regulator effects, gravimetric fractionation and surface processes [2, 3]. The latter, which encompasses adsorption / desorption, is also dependent on temperature, pressure and surface properties. Currently there exists only limited data and a few attempts to quantify these surface processes [4, 5].

For this study, high pressure small volume measurement chambers were produced which enable to investigate trace gases and their affinity for adsorption / desorption on various surfaces over a set of temperature and pressure ranges. The presented experiments are designed to investigate the filling pressure dependency up until 40 bars, and temperature dependency up until 50°C for these prototype cylinders of steel and aluminum. Here, we focus on measurements of CO_2, CH_4, CO and H_2O using a cavity ring down spectroscopy analyzer. Moreover, a theoretical adsorption isotherm is used to explain the changes in the measured concentrations for both pressure and temperature variations.

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11-year statistics for in-situ CO_2 data obtained in airliner project of CONTRAIL

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Since 2005, we have conducted an observation program using the passenger aircraft of the Japan Airlines named Comprehensive Observation Network for TRace gases by AIrLiner (CONTRAIL). We report change history of measurement conditions, quality control processes and spatiotemporal distributions of the Continuous CO_2 Measuring Equipment (CME) data in the past 11 years. CME has obtained about 8-million in-situ CO_2 data from more than 14000 flights between Japan and Europe, Australia, North America, or Asia. The initial CME operations had several problems such as pump stops during the flights, shortage of standard gases, and insufficient performance of dehumidification. To deal with these operation problems, we have optimized the pump operation conditions, the calibration intervals of standard gases, and use of perma pure dryer, as well as modification of the additional observational aircraft. Accordingly, more stable in-flight observations have been achieved without decreased accuracy of the measurements; number of measurement flights with valid CO_2 data was dramatically increased from only 29 and 572 in 2005 and 2006, respectively, to more than 1000 flights in each year since 2010. Geographical coverage of the CME data has been also changed depending on operation of the aircraft. For example, we have many observations along the flights to/from Europe from 2006 to March 2014 but less since April 2014, and ample flights over India in 2010, 2011, and 2014 but sparse in other years. We need to consider such non-uniform data distributions in time in analyzing seasonal or inter-annual changes of CO_2.

A Nafion-based air sample dryer for atmospheric flask sampling allowing accurate measurements of CO_2 and its stable isotopes in humid air

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Atmospheric flask samples are either collected at atmospheric pressure by simply opening a valve of a pre-evacuated flask or pressurized up to a few bar above ambient providing more air for analysis. Under humid conditions, there is a risk that water vapor in the sample leads to condensation on the walls of the flask notably at higher than ambient sampling pressures. Liquid water in sample flasks is known to affect CO2 mixing ratios and more importantly, alters the isotopic composition of oxygen (17O and 18O) in CO2 (referred to as isotopic fractionation). Hence, to be able to accurately detect CO2 and its stable isotopes it is vital to dry the air samples before they are pressurized in the flasks to a sufficiently low dew point, thus avoiding condensation (dew point < 5 °C at 2.8 Bar (40 psi)). Here we present a simple air sample dryer to provide dry air samples to be collected over the Amazon up to about 6 km altitude as part of the “Airborne Stable Isotopes of Carbon from the Amazon” (ASICA) project. A major objective of the ASICA project is to provide high-precision measurements of 13C, 17O, and 18O in CO2 from more than 5000 flasks to be collected over the Amazon at 4 different sites over a period of 5 years to improve our understanding of the carbon balance of the Amazon rain forest (http://www.asica.eu).

The air sampling system onboard the aircrafts used for the ASICA project consists of a “Programmable Compressor Package” (PCP) and a “Programmable Flask Package” (PFP) containing twelve 700cc flasks both designed by NOAA’s Carbon Cycle Group. The design of the “ASICA air dryer” presented here consists of 2 Perma Pure PD-Series gas dryers containing 200 Nafion strains in a stainless steel tube shell (PD-200T-24MSS) placed in series. A dry purge gas within the shell that flows countercurrent to the feed removes moisture from the sample air stream permeating the tubing. The dry purge air is provided by feeding the exhaust flow of the PFP through a 350 g of dry Molecular sieve (type 3A) cartridge.

Here we present first results of extensive experiments to test the stability and potential interference of the dryer on CO2 and its stable isotopes. Our results indicate that the dryer is effectively drying a humid air stream up to ~12 L/min at 80% RH and 32 °C without any impact on the CO2 mixing ratios. Isotopic measurements of a sample air stream fed through the drier was performed using a new Tunable Infrared Laser Direct Absorption Spectrometer (TILDAS, Aerodyne Research, Inc.), specially designed for the measurements of δ13C, δ17O, and δ18O. Under moderate ambient conditions (60% RH at 22 °C), the TILDAS measurements show that the Nafion based drying system has negligible impact on the CO2 isotope measurements. The resulting measurement precisions obtained with the TILDAS are as specified by the manufacturer (<0.02‰ for δ17O and δ18O). Finally, we present first results of tests with a prototype ASICA dryer set up with a PCP and PFP done at NOAA-ESRL and the University of Colorado.

Potential bias in the NOAA manometric measurement system

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Offsets between CO_2 datasets from different measurement locations can lead to mis-appropriation of carbon sources and sinks. To avoid such offsets, CO_2 measurements should be calibrated on a common scale such as the WMO CO_2 X2007 scale, which is recommended by the WMO (World Meteorological Organization). NOAA maintains the WMO CO_2 calibration scale using 15 aluminum high-pressure cylinders (primary standards), which are measured regularly with a manometric system. One advantage of the manometric method is that it provides traceability to the SI while also allowing for periodic measurement over time to assess drift. To measure CO_2 with the manometric system, an aliquot of gas from a primary standard is introduced into a precisely known large volume and together with the measured pressure and temperature the number of moles in the large volume can be calculated. Then the gas is pumped through a cold trap, where the CO_2 of the sample is frozen out and the other constituents are evacuated. The trapped CO_2 is transferred to a smaller volume by using liquid nitrogen. After thawing, temperature and pressure of the small volume are measured. The pressure and temperature measurements of the two volumes in combination with the known ratio of the small to the large volume can be used to calculate the CO_2 mole fraction of the gas sample. However, there is the possibility of small CO_2 losses in the manometric system due to e.g. adsorption by the glass and steel walls, diffusion through O-rings of the valves, which adds to the uncertainty of the CO_2 measurement of the primary standards. By identifying and quantifying potential losses, improvements in manometric CO_2 measurement might be achieved, which could reduce uncertainties and improve drift detection.

Comparison of in situ N_2O and CO measurements using gas chromatography, reduction gas analysis and off-axis integrated cavity output spectroscopy.

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Atmospheric N_2O and CO mole fraction measurements have been made within the UK Deriving Emissions linked to Climate Change (DECC) network since it first started in 2012. These measurements have been used to better understand regional pollution events, calculate UK emissions of trace gases in conjunction with inverse models and verify UK emission inventories for the Kyoto basket gases (Ganesan et al., 2015; Manning et al., 2011). Historically N_2O and CO measurements have been made using gas chromatography coupled with electron capture detectors (GC-ECD) and reduction gas analysers (RGA) within the network. These older measurement techniques have provided high frequency, good quality data; however they no longer meet the World Meteorological Organization Global Atmosphere Watch (WMO/GAW) recommended N_2O inter-laboratory comparability goal of ±0.1 ppb (Lebegue et al., 2016). In addition, N_2O pollution events are often sporadic and may not be captured by the temporally limited (10-minute) sampling frequency of the GC-ECD and RGA.

A number of new optical instruments have become commercially available over the past few years, which are more precise and collect data at a higher frequency than previous systems. Lebegue et al. (2016) has previously compared N_2O measurements made with optical instruments within a laboratory setting. However, sampling and environmental conditions (e.g. temperature stability and pressure fluctuations) at field locations are often different to those within a laboratory; therefore, comparisons of in situ measurements are needed.

In September 2016, an off axis-integrated cavity output spectrometer (OA-ICOS; Los Gatos Research EP30 N_2O/CO analyser with Scripps Institute of Oceanography modifications) was installed at one of the UK DECC network stations (Tacolneston tall tower, Norfolk, UK; GAW ID: TAC), where it has been running alongside a GC-ECD and RGA system. A comparison of in situ N_2O and CO mole fractions made using GC-ECD, RGA, and OA-ICOS will be presented. OA-ICOS precision up until 1st May 2017 was enhanced compared to the older system for N_2O (c.f. 0.08 and 0.2 ppb for the OA-ICOS and GC-ECD, respectively) and CO (c.f. 0.19 and 0.53 ppb for the OA-ICOS and RGA) based on repeat injections of a calibrated standard gas. A mean bias of -0.42 ppb N_2O and -2.84 ppb CO (GC-ECD/RGA – OA-ICOS) was observed in air samples (minute means and discrete samples used for OA-ICOS and GC-ECD/RGA) between 1st September 2016 and 30th April 2017. The exact mechanism driving the bias between instruments is not yet clear.

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Quantifying Nafion cross-membrane CO_2 and CH_4 gas leakage and it's dependence on sample mole fraction and water content

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The UK DECC (Deriving Emissions linked to Climate Change) tall tower sites were established in 2012 with the aim of quantifying key greenhouse gases including halocarbons, sulphur hexafluoride, nitrous oxide, methane and carbon dioxide. As Nafion water-permeable membranes have a history of successful use in drying air samples of halocarbons, N_2O and SF_6 (e.g. Foulger and Simmonds (1979)) the approach was implemented at DECC and later GAUGE (Greenhouse gAs Uk and Global Emissions) tall tower sites coupled with Picarro Cavity Ring-Down Spectrometers (CRDS). Unfortunately, this drying method is not suitable for CO_2 and CH_4 as these gases can pass across the Nafion membrane (Chiou and Paul 1988). Once the issue was identified, the drying systems were removed; however, a quantity of possibly contaminated data remained.

Welp et al. (2013) have previously considered the issue of gases passing through the Nafion membrane. However, the drying approach they used was not directly comparable to that of the DECC/GAUGE sites. Also, that study was limited to only two sample H_2O saturations, dry (0% H_2O) or wet (2% H_2O), and did not conduct wet experiments with samples of above ambient (~393 ppm CO_2 & ~1874 ppb CH_4) mole fractions. Considering the importance of water in gas transport across the membrane (Naudy et al. 2014) and the elevated range of water content (>3% H_2O), and CO_2 and CH_4 mole fractions (>500 ppm CO_2 & >2500 ppb CH_4) observed in the DECC/GAUGE network, further investigation of this issue was required.

As such, a series of laboratory experiments were designed to investigate the effect of sample water content (0 to 3.5%v) and sample mole fraction (370 to 510 ppm CO_2 and 1780 to 2600 ppb CH_4) on Nafion cross-membrane leakage, with the aim of deriving an empirical correction that could be applied to the effected tall tower data. These experiments showed CO_2 and CH_4 leakage, with losses greater than 0.2 ppm CO_2 and 5 ppb CH_4 observed at high sample mole fractions and elevated water content. Interestingly CH_4 leakage was found to increase linearly with water content while CO_2 leakage peaked at ~2%v H_2O and then decreased. The exact mechanism driving these results and the possible impact of the CRDS water correction is not yet clear.

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Optimisation of the Spectronus FTIR instrument for tall tower greenhouse gas observations

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The Spectronus FTIR-instrument of Ecotech has been modified to increase the performance. These modifications includes cell-temperature control and a gold-plated cell (as presentated on GGMT 2015 by Alex Vermeulen et al.). After final lab testing the instrument was installed at Cabauw tower in The Netherlands in December 2014, measuring CO_2, CH_4, N_2O and CO at four measurements heights (20, 60, 120, and 200 m).

In order to improve time-integration for the different measurements heights mixing volumes with a volume of 20 L were installed, kept at 1700 mbar sample pressure. Due to the large air volume used by the Spectronus for the measurements the calibration scheme was modified to ensure sufficient lifetimes of the calibration flasks. The time series of the spectronus measurements thus far will be presented.

The CO_2 and CH_4 measurements of the Spectronus instrument are compared to those measured by the Cabauw Picarro G2301. From August 2015 onward the Picarro is measuring from the same mixing volumes as the Spectronus. After significant effort a compromise has been found between required gas volume per measurements cycle, length of the cycle and precision and accuracy of both ambient and calibration gas cycles.

Developing a lower-cost medium precision urban GHG monitoring system using commercial NDIR sensors

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Abstract:

Atmospheric pollution due to anthropogenic activities from cities is a major issue for air quality and for climate change by causing an increase in the atmospheric concentrations of GHG. It is also clear that accurate estimates of the magnitude of anthropogenic emissions are needed to assess their influence on the regional and global carbon balance.

A reliable dense ground-based GHG monitoring in cities (here Paris) combined with an atmospheric inversion framework would have the potential allow retrieving sector specific GHG emission estimates (Wu et al. 2016). One major barrier for denser observation networks can be the high cost of high precision instruments or high calibration cost of cheaper and unstable instruments. Within a climate KIC project, LSCE and SenseAir AB have worked on novel inexpensive NDIR sensors for CO_2 measurements (so-called HPP platform). The aim of the project is to obtain a prototype which delivers measurements that are accurate within 1 ppm for hourly means but only requiring monthly calibration. We conducted extensive laboratory tests (short and long-term repeatability, cross-sensitivities, etc.) on a series of prototypes and the final versions were also tested in a climatic chamber. On four final HPP prototypes the sensitivity to pressure and temperature were precisely quantified and correction&calibration strategies developed. Furthermore, we fully integrated these HPP sensors in a Raspberry PI platform containing the CO_2 sensor and additional sensors (pressure, temperature and humidity sensors), gas supply pump and a fully automated data acquisition unit. This platform was deployed in parallel to Picarro G2401 instruments in the peri-urban site Saclay, near Paris, France. These measurements were conducted over several months in order to characterize the long-term drift of our HPP instruments and the ability of the correction and calibration scheme to provide bias free observations.

From the lessons learned in the laboratory tests and field measurements, we developed a specific correction and calibration strategy for our NDIR sensors. Latest results and calibration strategies will be shown.

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High-resolution Mobile Measurements of Methane Concentrations and Fluxes Using High-Speed Open-Path Technology on Cars, Ships, Airplanes, Helicopters and Drones

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The major sources of methane include agricultural and natural production, landfill emissions, oil and gas development sites, and natural gas distribution networks in rural and urban environments. The majority of agricultural and natural methane production occurs in areas with little infrastructure or easily available grid power (e.g., rice fields, arctic and boreal wetlands, tropical mangroves, etc.). The majority of oil and gas and urban methane emission occurs via variable-rate point sources or diffused spots in topographically challenging terrains (e.g., street tunnels, elevated locations at water treatment plants, vents, etc.). Landfill methane emissions traditionally assessed at monthly or longer time intervals are subject to large uncertainties because of the snapshot nature of the measurements and the barometric pumping phenomenon. Locating and measuring such methane emissions is challenging when using traditional micrometeorological techniques, and requires development of novel approaches.

A lightweight, high-speed, high-resolution, open-path technology was recently developed for eddy covariance measurements of methane flux, with power consumption 30-150 times below other available technologies [1, 2]. It was designed to run on solar panels and be placed in the middle of the methane-producing ecosystem without a need for grid power [1].

Lately, this instrumentation has been utilized increasingly more frequently outside of the traditional use on stationary flux towers [3]. These novel approaches include measurements from various moving platforms, such as cars, aircraft, and ships. Projects included mapping of concentrations and vertical profiles, leak detection and quantification, mobile emission detection from natural gas-powered cars, soil methane flux surveys, etc.

This presentation will describe the latest state of the key projects utilizing the novel lightweight low-power high-resolution open-path technology, and will highlight several novel approaches where such instrumentation was used in mobile deployments in urban, agricultural and natural environments by academic institutions, regulatory agencies and industry.

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The automated air sampler for the ICOS network

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An important aspect of the quality control for the in-situ measurements in the ICOS network is the comparison with results from discrete grab air samples taken at the stations analyzed at the central flask laboratory (ICOS-FCL). The analytical facilities at the central ICOS laboratories enable furthermore to make supplementary measurements (e.g. of O_2/N_2, $\delta^{13}C$ and $\Delta^{14}C$ of CO_2) in these flask samples that can provide supplementary information on the sample origin or sources of the greenhouse gases. To reach these different goals of flask sampling various sampling strategies for collecting flask samples can be appropriate.

An automated flask sampler has been designed for ICOS monitoring stations that offers various sampling modes under highly standardized conditions. The diverse options for sampling triggers and schemes cover a broad range of possible applications. All sampling and sensor data is automatically stored. The poster will give an overview of the sampler and its capabilities.

Measurement of greenhouse gases from novel ground-based remote sensing instruments; the FRM4GHG campaign at the Sodankylä TCCON site, N. Finland.

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Ground-based infrared remote sensing greenhouse gas (GHG) observations are extensively used for the validation of GHG measurements from satellites such as SCIAMACHY, GOSAT and OCO-2, as well as for model studies. The current standard network providing reference ground-based total column GHG data for satellite and model validation is the Total Carbon Column Observing Network (TCCON). TCCON is a network of about 23 stations distributed globally and measuring precise and accurate total column abundances of GHGs (scaled to WMO standards) using a Fourier-transform infrared solar absorption spectrometer (Bruker IFS 125HR). TCCON has some deficiencies in terms of the gaps in coverage, especially in remote locations and locations with high or low albedo. Setting up a TCCON station is expensive, requires special operational conditions with trained personnel for operation and maintenance, and it is not easy to move the station to a new location. This makes it very costly if further expansion of the network is desired.

Several new portable, low cost, easy to operate and maintain spectrometers have recently been developed that have the potential to ameliorate those deficiencies and complement the TCCON network. However, the performances of these instruments have not been fully characterized. The ongoing ESA funded campaign “Fiducial Reference Measurements for Ground-Based Infrared Greenhouse Gas Observations (FRM4GHG)” at the Sodankylä TCCON site in northern Finland aims at characterizing several of these low cost portable spectrometers performing TCCON type measurements simultaneously under different atmospheric conditions in comparison with a co-located TCCON instrument. Regular AirCore launches will also be performed from the site and will provide in-situ reference profiles of the target gases, which will be useful to verify the instruments’ calibrations and biases.

The campaign organized between March – October 2017 will provide a dataset of CO_2, CH_4 and CO measurements which can be used for validation purpose during the Sentinel 5 – precursor (S5P) commissioning phase, as well as by other satellites and model validation teams. Furthermore, it will provide a comparative characterization of the participating instruments with respect to the standard TCCON in terms of the precision, accuracy, stability, portability and ease of deployment, cost factor, etc. The outcome of the campaign will then be a guideline for the further development of new observation sites to complement the TCCON network and better support for the validation of existing and future satellite missions and models. This poster will focus on the objectives of the campaign and the first results of the measurements performed since the start of the campaign in March 2017.

Technical challenges of using high precision atmospheric O_2 measurements as a tracer for determining carbon fluxes in terrestrial ecosystems

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Atmospheric oxygen (O_2) measurements are a very useful tool for studying carbon cycle processes at the global scale, and have previously been used, for example, to separate the land and ocean sinks for carbon dioxide (CO_2) (e.g. Keeling and Manning, 2014). Until now, the potential of O_2 measurements at ecosystem level has not been exploited, largely owing to the significant technical challenges faced in measuring atmospheric O_2 to an accuracy and precision of a few ppm or less against a background mole fraction of 21%.

We introduce the “OXYFLUX” project (“Oxygen flux measurements as a new tracer for the carbon and nitrogen cycles in terrestrial ecosystems”), funded by the European Research Council and led by the University of Göttingen, Germany. OXYFLUX aims to develop high precision O_2 flux measurements as a new ecosystem-scale tool for understanding carbon and nitrogen cycle processes in the terrestrial biosphere. Using a network of soil and branch chambers in conjunction with a commercially available “Oxzilla” fuel cell O_2 analyser (Sable Systems Inc.) and a Li-820 CO_2 analyser (LiCor Biosciences), we will measure O_2 and CO_2 fluxes, and quantify oxidative ratios from different ecosystem components and processes at two sites in Germany: a beech forest site and an agricultural site. In addition, we will employ a state-of-the-art prototype laser-based O_2, CO_2 and H_2O instrument (Aerodyne Inc.) with a high flow-rate and fast measurement frequency to measure O_2 fluxes at the whole ecosystem level using the eddy covariance technique.

Our initial tests of several chamber system materials typically used by the CO_2 flux community reveal extremely large O_2 artefacts (biases ranging from 100 per meg to over 1000 per meg), and highlight the technical challenges that we face.

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Continuous observation of atmospheric oxygen concentration onboard a cargo ship sailing between Japan and North America

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In-situ observation of atmospheric oxygen (O_2) and carbon dioxide (CO_2) mixing ratios have been conducted in the North Pacific by using a cargo ship, New Century 2 (NC2), sailing between Japan and United State since December 2015. A fuel-cell type analyzer (Oxzilla-II) and a non-dispersive infrared analyzer (LI-840) are used for the measurements of the O_2 and CO_2, respectively. To detect their variations in the atmosphere, the flow rates of the air samples introduced into the analyzers and the outlet pressure are precisely controlled. We adopted the relatively low flow rates of the air samples of 10 cm^3 min^{-1}, which sacrifice the precision and time resolution, mainly to reduce the consumption rate of the reference gases stored in high-pressure cylinders. The final precisions of the O_2 and CO_2 measurements when the system is set in the laboratory is 1 ppm for O_2 (4 per meg for O_2/N_2 ratio) and 0.1 ppm for CO_2. After the in-situ observation started onboard NC2, we found that the ship movement caused false wavy variations of O_2 signal with the amplitude of more than several tens ppm and the period of about 20 seconds. Although we have not solved the problem at this stage, hourly averaging considerably suppressed the errors associated with the ship movement; comparison between the in-situ observation and flask sampling of air samples onboard NC2 shows that the averaged differences are −2.1±9.2 per meg and −0.02±0.33 ppm, respectively. The one-year data clearly show seasonal variations in the extensive North Pacific region.

Japan Meteorological Agency's ship-based observations for carbonate parameters in the surface and interior ocean

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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 CO_2 in surface seawater (pCO_2^{sea}) and in overlying air (pCO_2^{air}) 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 pCO_2, we have been using a non-dispersive infrared (NDIR) gas analyzer, a showerhead-type equilibrator and a set of CO_2 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. We have been using a coulometric DIC analyzer and using a spectrophotometric measurement for TA and pH. We have been using the certified reference materials provided by the Scripps Institution of Oceanography.

We are providing various information regarding ocean carbon cycle. The trend of pCO_2^{sea} increase has been observed along 137°E and 165°E repeat lines together with the increase of pCO_2^{air}. The growth rates of pCO_2^{sea} and pCO_2^{air} are 1.2~3.4 and 1.7~2.1 µatm/year, respectively. The rate of pH decrease in surface seawater was about 0.02 per decade in most regions. The accumulation rates of oceanic anthropogenic CO_2 inventory along 137°E and 165°E are approximately 4~12 and 3~13 $tC \cdot km^{-2} \cdot y^{-1}$, respectively. The rates of pH decrease in the ocean interior are 0.003~0.036 per decade (http://www.data.jma.go.jp/gmd/kaiyou/english/oceanic_carbon_cycle_index.html).

The CO_2 data we obtained are publicly available from the WMO's World Data Centre for Greenhouse Gases (WDCGG) operated by JMA and from SOCAT database (http://ds.data.jma.go.jp/gmd/wdcgg/wdcgg.html) (http://www.socat.info/).

Long-term monitoring of atmospheric greenhouse gases and data validation in NIES-VOS program

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The National Institute for Environmental Studies (NIES) has performed atmospheric monitoring of greenhouse gases and other climatically important gases and aerosols over the Pacific Ocean under NIES Volunteer Observing Ship (VOS) program, which has been operated by the Centre for Global Environmental Research of the NIES since 1992. The gas monitoring in the NIES-VOS program was made along three constant routes: North Pacific (Japan-USA) and Oceania (Japan-Australia/New Zealand) routes for background atmospheric monitoring and Southeast Asia (Japan-Southeast Asian countries) route for anthropogenically polluted atmospheric monitoring (e.g., Nara et al., 2011).

On board the VOS ships, we have performed measurements of CO_2, CH_4, CO and O_3 along with flask sampling observation followed by laboratory analysis of CO_2, CH_4, N_2O, CO, H_2, SF_6, O_2/N_2. For CO_2, we have distributed the onboard measurement data on the web (http://soop.jp/ or http://www.socat.info/) for the use in the ocean CO_2 research community. We now go ahead with rigorous validation work for the atmospheric CO_2 measurement data through the comparison with that from flask sampling analysis to fulfill the WMO recommended inter-laboratory compatibility for the use in the atmospheric research community, together with those for CH_4 and CO.

We will describe detailed our quality assurance and quality control system for the NIES-VOS data and will present results from the validation work for CO_2, CH_4, and CO.

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CarboSense: a low-cost low-power CO_2 network for the city of Zurich and Switzerland

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The project CarboSense establishes a dense network of 300 sensors distributed over Switzerland, with a denser cluster of 40 sensors in the urban area of Zurich. It uses the unique opportunity of combining newly available wireless low-power communication through LoRaWAN (long-range wide-area network) with low-cost sensor devices. The 300 CO_2 nodes are deployed at strategic locations in Switzerland and Zurich, including operational air quality monitoring stations, weather measurement sites, telecommunication towers and ad hoc sites such as lamp poles for the dense deployment in Zurich. Such a dense network will help documenting the spatial and temporal gradients of CO_2 atmospheric concentrations at the regional and smaller scales. The final objective is to constrain CO_2 surface fluxes from both anthropogenic and biogenic sources, including fossil fuel emissions and vegetation uptake. For the city of Zurich, the specific objective is to monitor the temporal evolution of the anthropogenic CO_2 emissions, to attribute these emissions to different sectors, and to evaluate the success of the measures taken by the political authorities in the context of various initiatives to reduce the energy demand and carbon footprint of the city. For this purpose, the sensor measurements are combined with building-resolving simulations of the CO_2 dispersion within the entire city.

Here we will present first measurements from the city network as well as first CO_2 simulations and emphasize the challenges in properly accounting for all CO_2 sources and sinks within the city including human respiration and vegetation uptake.

Continuous Near-IR and Mid-IR CRDS Measurements of Atmospheric CO_2, CH_4, N_2O, and CO in the Megacities Los Angeles Network: Design Criteria

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Greenhouse gas (GHG) measurements in urban areas are an important component in quantifying the global emissions of anthropogenic GHGs. Measurements in these environments share some of the same limitations of background measurements. Station accessibility is often not ideal and requires a high level of autonomous operation, as well as efficient use of resources, including calibration gases and infrequent maintenance visits. The wide ranges of concentrations measured in the urban environment also pose calibration challenges that differ significantly from those at background stations. Previously, Welp et al. (2013) demonstrated a configuration for calibration of a single Picarro cavity ring-down spectrometer (CRDS) infrared (IR) analyser (either model G2301 or G2401), using a temperature-controlled “calibration box” containing a pressure-stabilized Nafion drier and an automated calibration gas switching system. This configuration has been deployed throughout the Los Angeles Megacities network (Verhulst et al., 2017). Here we show that this calibration box can also be employed with two Picarro analyzers (G2301 & G5301) plumbed in parallel downstream, allowing for simultaneous measurements of CO_2, CH_4, N_2O, and CO with calibration gases shared for all four measurements. To use calibration gases efficiently, the flow rates for each instrument have been reduced significantly. Instrument control and data logging is done using the GCWerks software package configured especially for dual-instrument applications. We present details of the configuration design, including results of Allan variance and other tests performed on both Picarro instruments. We also show comparisons between the Picarro G5310 and the Los Gatos Research N_2O/CO Analyzer (Enhanced Performance model with customizations) instruments for mid-IR measurements of N_2O and CO, as well as for CO in the near-IR by the Picarro model G2401. Data from the deployment of the combined Picarro G2301 and G5310 instrument configuration at sites in the Los Angeles Megacities network will also be shown.

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New monitoring project of GHGs and air pollutants around Jakarta, Indonesia

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We have conducted a monitoring project of greenhouse gases (GHGs) and related air pollutants around Jakarta urban area (Jabodetabek) in Indonesia since 2015 to observe those anthropogenic emissions from the largest megacity in tropical Asia.

For this purpose, we developed a ground-based comprehensive monitoring system of GHGs and air pollutants which consists of instruments for continuous measurements of CO_2, CH_4 (G2301, Picarro), CO (CO-30r, Los Gatos Research), NO_x (Model 42i-TL, Thermo), SO_2 (Model 43i-TLE, Thermo), O_3 (OA-787, Kimoto Electric), aerosol concentrations ($PM_{2.5}$, PM_{coarse}, BC) and chemical components (ACSA-14, Kimoto Electric), and for flask sampling of air (Koshin-RS). This system allows us to monitor/control all instruments remotely as well as peripheral devices (e.g., pumps, valves). Also, it is important feature that the monitoring system can operate automatically for electric power failure because not only lightning activity is very high, but also electric power supply is sometimes unstable in Indonesia. After the operating test of the system at National Institute for Environmental Studies, we delivered and installed it at 3 sites in Indonesia: Bogor (centre of Bogor city) in March and May 2016, Serpong (Jakarta suburb) in August and September 2016, and Cibeureum (mountainous area, background-like site) in March and May 2017.

The concentrations of CO_2, CH_4, and CO observed at Bogor from June 2016 to March 2017 show urban characteristics with hourly average values ranging from 389 to 502 ppm for CO_2, from 1818 to 3067 ppb for CH_4, and from 88 to 3733 ppb for CO. While we need to obtain more data set for a long time to understand seasonal and annual variability, we found that those concentrations exhibit low values during December 2016–January 2017 compared with the other months.

We will report the temporal variability of the GHGs concentration observed at the 3 monitoring sites in Indonesia.

Start of greenhouse gases and related tracer measurements at Tokyo Megacity

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Anthropogenic emissions of carbon dioxide (CO_2) are treated as a true value for estimations of natural source and sink. Thus uncertainties in these inventories are concerned for quantification of global carbon budget. To reduce the uncertainties in the inventories, high-precision measurements of atmospheric concentrations of CO_2 and tracers for detecting fossil fuel burnings such as carbon isotopes and oxygen are required in urban area as well as in background sites.

We built atmospheric observation facilities at Tokyo Skytree (TST), broadcasting tower located in the center of Tokyo, to monitor the greenhouse gases (GHGs) emissions from the most populous metropolitan in the world. At first, we started continuous in-situ measurement of CO_2 concentrations using Licor Li-840A in March 2016. The Li-840A was replaced by PICARRO G2401 for continuous in-situ measurements of CO_2, CH_4, and CO concentrations in January 2017. We also started continuous in-situ measurements of oxygen concentrations using Oxizilla in February 2017. Air samplings using 2.5L glass flasks have been preformed since July 2016. The air samples were analyzed in NIES for concentrations of CO_2 (using NDIR), CH_4 and CO (GC-FID), N_2O and SF_6 (GC-ECD), $^{13}CO_2$ (MAT-252 and 253), and $^{14}CO_2$ (NIES-CAMS). Furthermore, we have a plan to install a radon analyzer at TST.

In this presentation we show the initial results obtained from the TST observations, including time series of CO_2, CH_4, CO, and O_2 concentrations and analysis of carbon isotopes and oxygen for partitioning of CO_2 emitted from biosphere and fossil fuel burnings.

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Trace gas mixing ratios, carbon, water, and energy exchanges measurements at ARM facilities

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The LBNL-led Carbon project and its associated suite of instruments first deployed in 2001 are in the process of becoming a part of the ARM Baseline. One of these instrument, AOSGHG, if part of the ARM standard collection of instruments and component of the Aerosol Observing system (AOS). We report on the status of ground-based measurements of atmospheric greenhouse gases from continuous analyzers and flask samplers, carbon, water and energy fluxes at Atmospheric Radiation Measurement Program Climate Research Facilities in the US Southern Great Plains (SGP), the Eastern north Atlantic (ENA), North Slope of Alaska (NSA), and ARM mobile facility deployed at Oliktok Point (AMF3).

Greenhouse Gases: Background Concentrations in Brazilian coast.

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In Tropical areas, and specifically in the Atlantic Ocean, there are not enough measures on greenhouse gases (GHG), and Amazon Basin represent around 50% of the world's rainforest [1]. Understand the characteristic GHG concentrations in Tropical Global range on Atlantic Ocean is an important task for many studies to determine GHG balances. The motivation of this study was understanding better the typical background for Amazon Basin from the air masses that arrived on North and Northeast Brazilian coast, come from the Atlantic Ocean in the period 2006 to 2016. We started to collect air samples on the Brazilian coast: Arembepe/BA (ABP: 12º45’46.79”S; 38º10’08.39”W – from 2006 to 2010, 15 meters above sea-level), Salinopolis/PA (SAL: 00º36’15.03”S; 47º22’25.02”W – from 2010 to 2017, 10 m a.s.l.), Natal/RN (NAT: 05º29’22.05”S; 35º15’39.64”W 15 m a.s.l – since 2010 to December 2015, then the site moved to 05º47’42.77”S; 35º11’07.10”W, 87 m a.s.l.), Camocim/CE (CAM: 02º51’47.00”S; 40º51’36.70”W – since 2014, 21.5 m a.s.l.), and in December 2016 it was started a special place at Itarema/CE (ITA: 02º55’57.11”S; 39º50’38.49”W, 96.5 m a.s.l.), where the inlet was installed in the top of a 100 m tower in the beach. In each site, the air samples, with variable height were collected weekly by using a pair of glass flasks (2.5L) and a portable sampler. The air samples were analysed on the Greenhouse Gas Laboratory (LaGEE) at IPEN (until April 2015) and later at INPE/CCST. It was quantified the respective gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), sulphur hexafluoride (SF_6) and carbon monoxide (CO). Results showed that each site presents seasonality when compared to Ascension Island (ASC: 07º96'67.00"S; 14º0'00.00"W, South Atlantic Ocean) and Ragged Point Barbados (RPB: 13º16'50.00"N, 59º43'20.00"W, North Atlantic Ocean) global stations. Simulations of backward trajectories by HYSPLIT model (using 240 hours) [2], allowed observing how each study site is influenced by global circulation and process like Intertropical Convergence Zone [3]. Between Jan-May, the ITCZ is below SAL and CAM latitude, influencing the air masses that arrived at sites in this period. At SAL and CAM the air masses came from both North and South Atlantic Ocean, depending on time of the year, and at NAT and ABP the air masses came from only South Atlantic Ocean. The GHG concentrations showed seasonality and sometimes periods with high concentrations. Overall, all Brazilian coast sites, showed the same increase on the GHG concentrations than global mean.

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Observations and modelling combine to inform network developments.

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The New Zealand monitoring network has developed over four decades from a single observation station at Baring Head (41.41°S, 174.87°E), (Brailsford etal, 2012) monitoring CO_2 in baseline conditions, to three active in situ stations that now provide continuous observations of atmospheric CO_2. The additional observation stations have been in the Central Otago region of the South Island at Lauder (45.034°S, 169.68°E), and the Central North Island at Maunga Kākaramea (38.33°S, 176.38°E). With time the use of CO_2 data has changed, from understanding the southern hemisphere seasonal cycle of CO_2, to informing on longer term trends. In recent years the National Institute of Water and Atmosphere (NIWA) have developed a regional inverse modelling capability (Steinkamp etal, 2017). Initial assessments utilised two observation stations and revealed differences between the current bottom up national inventory and the top down approach from observation and inverse modelling.

Following this study an assessment was undertaken to develop an enhanced observation network for CO_2 that would provide a greater national coverage in the observations and therefore increased input for the inverse modelling. This study revealed three main geographic regions that currently lack strong visibility. Consideration of three key national CO_2 source/sink processes, forests, pasture and urban, ensure that the placement of stations add significant value to the National Inventory Reporting. We present the process of determining the site locations, through back trajectory analysis, topography and meteorology and source region studies. The enhanced network would provide a high degree of coverage nationally, and include the addition of 2 to 6 new observing stations in the three regions identified.

The sites would be based in Southland with contributions from Fiordland, a large mature forest area that is uninhabited, which appears to be a significant carbon sink. Monitoring in Canterbury will have exposure to farmlands that are a mixture of cropping and livestock farms. The largest city in New Zealand, Auckland will be the focus of the urban study with a series of stations located across the urban area to identify carbon processes in this urban environment.

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“CASLab”: The United Kingdom’s Clean Air Sector Laboratory at Halley Research Station, coastal Antarctica

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In 2003, a new laboratory (“CASLab”) was commissioned at the Halley Research Station in coastal Antarctica (75.61°S, 26.21°W), dedicated to studies of the clean background atmosphere and air/ice exchange processes with the snow. With its position near the edge of the Weddell Sea, the CASLab is well placed to capture air masses with a variety of origins, including from the Antarctic continent, over the sea ice zone and over the open ocean. Since its inception, the laboratory has been run in a dual mode, with specific measurement campaigns operating alongside long-term observations such as greenhouse gases.

Here we introduce the laboratory and the instrument suite, and present the type of measurements that we are now able to make. While operated by the British Antarctic Survey, we also support measurements and instruments from several UK and overseas collaborators, including NOAA, USA, University of Groningen, The Netherlands, and UEA, UK.

Of particular relevance to GGMT, we present our greenhouse gas-related in-situ instruments, namely a Picarro CO_2/CH_4 analyser, a Los Gatos Research N_2O/CO analyser, and a custom-built O_2/CO_2 system that incorporates a Sable Systems “Oxzilla” O_2 analyser and a Siemens “Ultramat 6E” CO_2 analyser.

The Franco-Belgian greenhouse gases monitoring program at La Réunion Island

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The location of Reunion Island (21°S, 55°E) presents a great interest for the monitoring of greenhouse gases concentrations due to the low density of the measurement network in the tropics and particularly in the southern hemisphere. Atmospheric measurements have been initiated in 1994 at the coastal site of Saint Denis mostly for the survey of tropospheric and stratospheric ozone and related key species as part of the NDSC/NDACC (Network for the Detection of Stratospheric/Atmospheric Composition Change). In 2012, a new observatory was inaugurated at Maïdo at 2200 m above sea level. The two sites are currently equipped with instruments dedicated to both surface and total column measurements of CO2 and CH4. The column measurements are solar absorption measurements performed with Fourier-transform Infrared (FTIR) spectrometers in the framework of TCCON (Total Carbon Column Observing Network); they started at St Denis in September 2011 and at Maido in March 2013. High precision measurements of the surface CO2 and CH4 mole fractions have been installed in compliance with the technical requirements and specifications of ICOS, in August 2010 at Saint Denis, and in December 2014 at Maido. The latter will be proposed for an ICOS-ERIC labelling in the coming months.

We will present a summary of the surface and total columns time series, with characterization of the diurnal and seasonal cycles as observed at the coastal and mountain sites. The differences between the two sites will also be discussed. Influence of long-range transport and possible contributions of African and South American biomass burning will be evaluated. Finally, comparison of the observations with Copernicus Atmospheric Monitoring Service (CAMS)-IFS model analyses, performed as part of the CAMS-84 project, will be discussed.

Long Term Nitrous Oxide Measurements Over Amazon Basin Using Small Aircraft

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The Nitrous Oxide (N_2O) is the third most important natural greenhouse gas on Earth (WMO, 2016). Globally, the main sources are nitrification and denitrification promoted by microorganisms and it can be natural (~60%) or anthropogenic (~40%) (IPCC, 2007). Approximately two thirds of soil emissions are provided from tropical areas and ~20% of this are from rainforests ecosystems as the region we have studied (Van Haren et al., 2005; Melillo *et al.* 2001). In Brazil 87% of N_2O anthropogenic emissions are from agricultural activities. In this study, natural air was sampled in glass flasks using small aircraft over four sites in the brazilian Amazon Basin in order to have a great quadrant to better understand the whole area: Alta Floresta (ALF; 8.80ºS, 56.75ºW), Rio Branco (RBA; 9.38ºS, 67.62ºW), Santarém (SAN; 2.86ºS, 54.95ºW) and Tabatinga (TAB; 5.96ºS, 70.06ºW), ALF, RBA and TAB sites started in 2010 and we still perform sampling in these sites, the last one changed to Tefé (TEF; 3.39°S, 65.6°W) in 2013 due to technical problems. The measurements in SAN started in 2000 and the quantification was done by NOAA until 2003, after this year the analysis started to being done by our laboratory. The mixing ratios in all the studied stations have presented an increase along the years, varying from ~316ppm in 2000 in to ~330ppm in the present days, *i.e*. a mean growth rate of ~0.82ppm yr^{-1}, which is consistent with global data where the growth rate for the past 10 years is around 0.89 ppm yr^{-1}(WMO, 2016).

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Continuous observations of CO_2, CH_4 and O_3 in the boundary layer of the central Mediterranean basin

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Southern Europe and the Mediterranean basin are recognized as hotspot regions both in terms of climate change and air quality, also representing a major crossroads of different air mass transport processes. In particular, large amounts of anthropogenic pollutants emitted in continental Europe are transported towards the basin. Meteorological conditions such as frequent clear sky and high solar radiation in summer enhance the formation of photochemical ozone (O_3) due to the availability of natural and anthropogenic precursors. In particular, large amounts of anthropogenic pollutants emitted in continental Europe are transported towards the basin where intense photochemical O_3 production occurs. Ricaud et al. (2014) have shown that the meteorology in the Mediterranean basin favors a western basin enriched for instance in methane (CH4) compared to the eastern basin. Widespread open biomass burning further exacerbate air quality and the impact of anthropogenic emissions on the regional climate.

In this work, we will compare and discuss continuous $CO_{2,}$ CH_4 and O_3 observations carried out in the boundary layer of the central Mediterranean basin at Lampedusa and Capo Granitola (Italy), where two WMO/GAW regional stations are located. Lampedusa (LMP: 35.5182°N, 12.6305°E, 45 m a.s.l.) is a small island located in the hearth of the central Mediterranean Sea. Here CO_2 and CH_4 continuous measurements are carried out together with flask monitoring programmes since 1992 and 1994, respectively. Near-surface O_3 is measured since 2015.Capo Granitola (CGR, 37.66670°N 12.65000°E; 5 m a.s.l.) is located at the southern Sicily coastline facing the Strait of Sicily, at Torretta Granitola (12 km from Mazara del Vallo, 52,000 inhabitants). At this station CO_2 and CH_4 observations are carried out since 2015. Both the measurement sites are equipped with CRDS instrumentation for CO_2 and CH_4 measurements (Picarro G2401), while near-surface O_3 is measured by UV-absorption technique. All the measurements are referred to WMO calibration scales.

The main aim of this work is to compare the variability and average levels of these greenhouse gases over the period for which simultaneous measurements are available. Moreover, we will investigate special events as well as measurement periods representative of the atmospheric background to identify and quantify processes affecting $CO_{2,}$ CH_4 and O_3 variability in the central Mediterranean basin.

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Carbon Monoxide Measurements as a Biomass Burning Tracer at the Amazon Basin

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The tropical rainforests have an amount of carbon stored into its plants and soil comparable to half of the amount of atmospheric carbon contained at the atmosphere before the start of industrialization at the 18th century. Among the tropical regions, the Amazon forest covers the largest area and also hosts the largest carbon pool (~200 PgC), corresponding for 50% of its biome globally (1) . Considering the capability of rapid release and the amount of storage carbon, there are surprisingly few studies of emission ratios (2) and, in order to elucidate the actual contribution and the carbon emission from biomass burning in the Amazon Basin, measurements of carbon monoxide are an important tool.

We will report results of a pan-Amazon low troposphere program used small airplanes, in 7 study sites from 2000 to 2016. The aircraft measurement program was started in 2000 with monthly/biweekly vertical profile sampling at SAN (2.86S 54.95W). From December 2004 to December 2007 we performed vertical profiles at MAN (Dec 2004 / Dec 2007). In 2010, a new step in our program was started. We added three more aircraft sites: TAB (5.96S 70.06W), RBA (9.38S 67.62W) and ALF (8.80S 56.75W). In 2013 TAB site was moved to TEF (3.39S 65.6W) and we add two more aircraft sites with vertical profiles from 300m to 7300 m, at Salinópolis (SAH 0.60S; 47,37W) near the Atlantic coast and RBH at the same place then RBA, in the western Amazon.

The Amazon Basin biomass burning carbon emissions have been determined by applying a mass balance technique to carbon monoxide (CO) measured from vertical profiles in sites over the Amazon Basin, which is compared with carbon dioxide (CO2) emission when it is a clear biomass-burning plume in the vertical profile (3).

We will present these CO results that is related to biomass burning and compare the carbon monoxide emissions with those from carbon dioxide, resulting in a ratio of carbon biomass burning emission which we will analyse with respect to climate, deforestation and number of fire hot spots.

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Amazon Basin and Brazilian Coast SF_6 Study in a 15 Years Time Series

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The sulphur hexafluoride (SF_6) is known as a potent Long Lived Greenhouse Gases and it is a synthetic gas with a millennia lifetime, about 3200 years, and has a Global Warm Potential 23000 time higher than the Carbon Dioxide (CO_2). Levin et al. (2010)[1] showed that SF6 emissions decreased after 1995, most likely because of emissions reductions in developed countries, but then increased after 1998. It is produced by the chemical industry, mainly as an electrical insulator in power distribution equipment[2]. Due its very long lifetime, SF_6 emissions are accumulating in the atmosphere. Its global mole fraction increased nearly linearly in recent decades and in 2014 is about twice the level observed in the mid-1990s[3]. Its concentration was 4.2 parts per trillion (ppt) in 1998 (TAR) and has continued to increase linearly over the past decade, implying that emissions are approximately constant. Because of these characteristics, the SF_6 has been as an essentially inert tracer to study atmospheric and oceanic transport processes[3].

The Amazon Basin is an ecosystem that has a growing interest by researchers around the world because of its role at the Climate Change. The emissions of SF_6 in the Amazon Basin are considered non existents and, a time series of 15 years has the potential to show the behaviour of this gas in a large area.

Until now, our mainly interest in SF_6 concentrations is to use this gas as a transport tracer to calculate the BKG to Amazon and determinate the CO_2, CH_4 and N_2O fluxes over the Amazon Basin. SF_6 atmospheric measurements were started with vertical profiles using small aircrafts, since 2000 in Santarém (SAN; 2.86ºS; 54.95ºW), 2009 in Rio Branco (RBA; 9.38ºS, 67.62ºW), 2010 in Alta Floresta (ALF; 8.80ºS, 56.75ºW)and Tabatinga (TAB; 5.96ºS, 70.06ºW), all these sites located in Brazilian Amazon Basin. Since 2010, we started flasks 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) and later in 2014 at Camocim (CAM; 2.86°S, 40.08°W) and in 2016 at Itarema in a 100m tower (ITA; 2.93°S, 39.84°W).

This work will present analyse of 15 years SF_6 measurements at the Amazon Basin and Brazilian coast show the trends, comparing the years and the behaviour among the sites regions which is expect to change mainly by the differences of the air masses origin.

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Atmospheric molecular hydrogen (H2) at the WMO/GAW stations in China

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Atmospheric molecular hydrogen (H_2) mole fractions have been measured at the two WMO/GAW stations in China, which are Mt.Waliguan (WLG) global station and Shangdianzi (SDZ) regional station. The samples at WLG were collected and analysed at the Earth System Research Laboratory of National Oceanic and Atmospheric Administration (NOAA). The H_2 at SDZ were in-situ measured by a GC-HePDD system. In the study, we present the atmospheric H_2 time series from May 1991 to May 2014 at WLG and from 2015 to 2016 at SDZ, and investigate the seasonal and inter-annual variations.

The results at WLG indicate the influence of terrestrial ecosystem, corresponding to the midlatitude to high-latitude Northern Hemisphere. Annual mean background H_2 mole fractions at WLG vary from a minimum of 496±7 ppb (parts per billion, 10^{-9} dry air mole fraction) in 1997 and 2004 to a maximum of 515±3 ppb in 1998, with a mean (± standard deviation) of 503±2 ppb during the observation period. The atmospheric H_2 show decreasing trend with an average growth rate of –0.8±0.6 ppb y-1. The highest background H_2 mole fraction is observed in March, while the lowest is observed in October. Peak-to-trough amplitude in the seasonal cycle is 23±7 ppb.

Atmospheric H2 mole fractions at SDZ vary from a minimum of 381 ppb (parts per billion, 10-9 dry air mole fraction) to a maximum of 1535 ppb, with a median of 510 ppb and a mean (± standard deviation) of 555±113 ppb during the observation period. The highest regional representative H2 mole fraction is observed in July, while the lowest is observed in October, which is different with the WLG. Peak-to-trough amplitude in the seasonal cycle is 63±3 ppb. H2 mole fractions show night time depletion in all seasons, and the atmospheric H_2 mole fractions are also influenced by local surface wind direction at SDZ.

Japanese observation programs of atmospheric greenhouse gases in polar regions

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The National Institute of Polar Research (NIPR) and Tohoku University (TU) have maintained systematic observation programs of atmospheric greenhouse gases at Syowa station, Antarctica (69.00°S, 39.58°E; Morimoto et al., 2003) and Ny-Ålesund, Svalbard (78.92°N, 11.93°E; Yamanouchi et al., 1996) since 1984 and 1991, respectively. The National Institute of Advanced Industrial Science and Technology (AIST) also joined the programs at Ny-Ålesund and Syowa station in 2013 and 2016, respectively.

At Syowa station, we initiated continuous measurements of the atmospheric CO_2 concentration in 1984, and then expanded in-situ continuous measurements to CH_4, CO and O_2 concentrations in the framework of the Japanese Antarctic Research Program. In addition to these measurements, systematic air sampling with subsequent laboratory analysis has been carried out for the CO_2, CH_4, CO, N_2O, SF_6, O_2 and Ar concentrations and the isotopic ratios of CO_2 and CH_4. We also have cooperated with the air sampling program of the National Oceanic and Atmospheric Administration (NOAA) at the station.

At Ny-Ålesund, we have maintained weekly air sampling since 1991 with aid of the Norwegian Polar Institute to measure the atmospheric CO_2 and CH_4 concentrations and carbon isotopic ratio of CO_2. Currently, the concentrations of CH_4, CO, N_2O, SF_6 and O_2 and the isotopic ratios of CH_4 are also measured. In addition, we started in-situ continuous measurements of the atmospheric CO_2 and O_2 concentrations using a NDIR/fuel-cell oxygen analyzer system in 2012 (Goto et al., 2017), as well as of the atmospheric CO_2, CH_4 and CO concentrations using a cavity ring-down spectrometer system in 2013.

In this presentation, we report our observation activities of atmospheric greenhouse gases at Syowa station and Ny-Ålesund, including observational results.

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First results of tall tower surface-atmosphere N_2O flux measurements over a mixed agricultural region in Central Europe

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In summer 2015 an eddy covariance (EC) system was put into operation at the Hungarian WMO GAW tall tower greenhouse gas monitoring site (Hegyhátsál - 46°57'N, 16°39'E, 248 m asl) to monitor the vertical flux of nitrous oxide (N_2O). The site is located in rural environment, as far from direct pollution sources as it is possible in Central Europe. The N_2O EC system is co-located with a previously installed EC system that monitors the surface/atmosphere exchange of CO_2 at 82 m above the ground. The high-elevation, large-footprint EC systems are primarily intended for the monitoring of the net fluxes of the mixed agricultural fields surrounding the tower and characteristic for an extended region. Monitoring of the greenhouse gas exchange of a typical mixture of different agricultural fields might better support the estimation of the regional/national level emission than that of specific ecosystems. The measurements also contribute to the development and validation of ecosystem models. Both EC systems are precisely calibrated and also suitable for the long term monitoring of the atmospheric concentrations. The poster focuses on the first results of the N_2O flux measurement system describing the setup, presenting the temporal variations in both the concentration and the vertical flux, as well as the upgraded version of Biome-BGCMuSo process oriented biogeochemical model (Hidy et al., 2016) extended for the simulation of the full nitrogen budget of the ecosystems. This biogeochemical model has proved to be suitable for filling the data gaps in the direct surface-atmosphere N_2O flux measurements. According to the preliminary data the annual N_2O emission for year 2016 was ~200 mg N/m^2. The development of the quality assurance and uncertainty estimation methods are in progress. The concentration data series between May, 2015, and December, 2016, indicate a 0.95 ppb/year upward trend, which is closed to the global tendency. Early 2017 several regional scale pollution episodes, elevated CO_2, CH_4 and N_2O concentrations were observed at the monitoring site. These episodes will be further studied.

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Recent updates from the Cape Point long-term data records

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The Cape Point (CPT) long-term trace gas data records have matured well and have become valuable sources of information for climate change and related observations. Carbon dioxide (CO_2), for which measurements started in 1993, is showing an unabated upward trend, with growth rates ranging between 2.20 – 2.40 ppm/yr for the 2014 -15 season. On a per-month basis, the background mean values have increased 21.14 ppm for the past decade. The much awaited 400 ppm average monthly background mean barrier has also been breached during the first quarter of 2016.

Atmospheric methane (CH_4), having a 35 year measurement record at CPT, has recently displayed a sharp increase in its growth rate, doubling from around 5.5 ppb/yr in 2013 to well over 11 ppb/yr in the 2015 season. The observation from CPT follows a similar trend to what has been observed globally.

Contrasting the observed increases in greenhouse gas atmospheric mixing ratios, our carbon monoxide (CO) records on the other hand, has displayed a small, but significant decreasing trend over the past 8+ years starting around 2005. Cape Point's 33 year old surface ozone record has also displayed a downward trend of -0.4 ppb/yr for the smoothed growth rates of 2014 – 2015, ranging from -0.1 to -0.8 ppb/yr during that same period.

The CPT Gaseous Elemental Mercury (GEM) data set, now spanning 20 years, has shown a downward trend over the first decade of measurements, but has reversed sign and is now showing an upward trend during the most recent decade with the flex point occurring sometime during 2004 – 2007 measurement period.

Whilst radon measurements at CPT are primarily applied to identify and aid with air-mass selection, its own mixing ratios in the atmosphere has shown some very interesting features over time. The frequency of CPT long-term Rn^{222} observations have shown a decrease in the upper percentile values, specifically those occurring within certain seasons and sectors. This is most likely as a result of shifting air-mass patterns within a specific wind sector due to climate change enhancements.

From a CPT regional activity perspective, our two decade old Dobson data measurements at Springbok and Irene are maturing into a fine data set with both showing an upward trend for column ozone respectively.

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Atmospheric CO_2/CH_4/CO measurements at the Amazon Tall Tower Observatory (ATTO, Brazil)

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At the Amazon Tall Tower Observatory site (ATTO, Brazil; 2°08'S, 59°00'W), we run since March 2012 continuous, high-precision measurements at the 80 m walk-up tower with two CRDS analyzers (G1301 and G1302; Picarro Inc., USA) calibrated against the NOAA-2004, WMOX2007, and WMO X2004 scales for CH_4, CO_2, and CO, respectively. Sample air inlets are installed at five levels (79, 53, 38, 24, and 4 m a.g.l.). In order to bridge the switch-over time between the different inlet heights, the atmospheric signal is integrated by using 8 liter buffer volumes that are continuously flushed with sample air, which is then passed in parallel through both analyzers. While the sampled air is not dried for the CO_2/CH_4 measurement (G1301), a Nafion drier is used for the CO/CO_2 measurement (G1302).

The 325 m-tall tower at ATTO is currently being equipped with scientific measurement instrumentation. Since February 2017, pilot CO_2/CH_4/CO measurements using a G2401 analyzer (Picarro Inc., USA) are done from the top, 321 m a.g.l. level. The installation of the remaining inlet heights will take place until end of 2017.

We present here a summary of the performed tests on our installations, available data from the 80 m walk-up tower, and preliminary data from the 325 m tower.

Our work was performed within the frame of the German-Brazilian project ATTO and supported by the federal government agencies BMBF and MCT (BMBF grant number 01LB1001A and FKR 01LK1602A). We acknowledge the fundamental support by the Max Planck Society, INPA and UEA. Special thanks go to the Amazonas State SDS/CEUC-RDS Uatumã.

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Combined balloon, aircraft, and surface greenhouse gas measurements at Traînou supersite, France

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The Traînou supersite, located approximately 100 km south of Paris, is the only site in Europe where both ICOS and TCCON networks are operated: this supersite benefits from a tall tower setup for in-situ greenhouse gas (GHG) measurements at 5, 50, 100 and 180 m height, and is equipped with a ground-based FTIR (TCCON-Orléans) for total column measurements. In addition, an aircraft measurement program allows monthly flights to measure GHGs between 100 and 3000 m above the tall tower.

Recent developments of AirCores carried by weather balloons make now possible to derive GHG vertical profiles up to 30 km above the mean sea level (amsl) for moderate costs and logistics. These innovative systems are based on passive sampling of ambient air in a long tube while descending from high altitude. Analysis of trace gas mixing ratios in the sampled air core provides information on the vertical distribution of these trace gases from 30 km down the surface. Initially invented at NOAA, different versions have been developed with success in several research institutes.

Since October 2016, LSCE and LMD have developed their own AirCore system and initiated several intensive field campaigns at Traînou supersite. The aim of these campaigns is to demonstrate the scientific interest for combining surface, airborne, balloon-based and remote sensing measurements of CO_2 and CH_4 mole fractions. During the campaigns, several lightweight AirCores specifically designed for weather balloons were flown and successfully analyzed for GHGs retrieval. In parallel, aircraft measurements were performed. Moreover both a LIDAR and a second compact FTIR (EM27) were implemented during the last campaign (April 2017) at the bottom of the tall tower. In addition to the Traînou tower, we have benefited from the measurements of both the Saclay ICOS station (~80 km north of Traînou) and the Qualair plateform (in Paris downtown) where a second ground-based FTIR (TCCON-Paris) sampled the urban atmospheric column. The instrumental synergy used during the campaigns leads us to be in a unique and innovative position for analyzing spatiotemporal coherence between various measurement technics dedicated to the GHG survey.

Our poster describes in details the AirCore measurement technique developed at LSCE and LMD. We also present the dataset acquired from the different campaigns that merge observations from surface, aircraft, and AirCore measurements at the Traînou supersite, at the Saclay station and at the Qualair platform.

Atmospheric nitrous oxide observations at Mount Waliguan station in China, from 1995 to 2014

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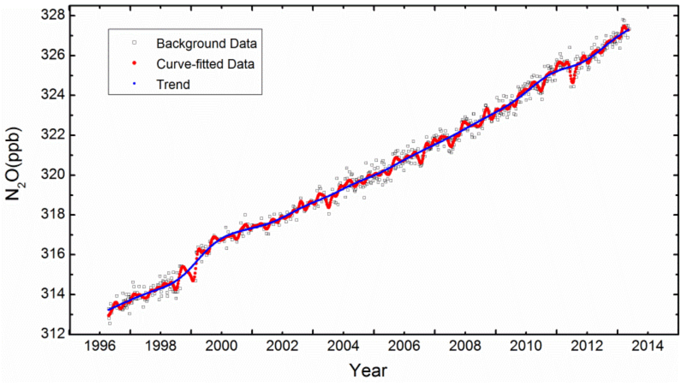
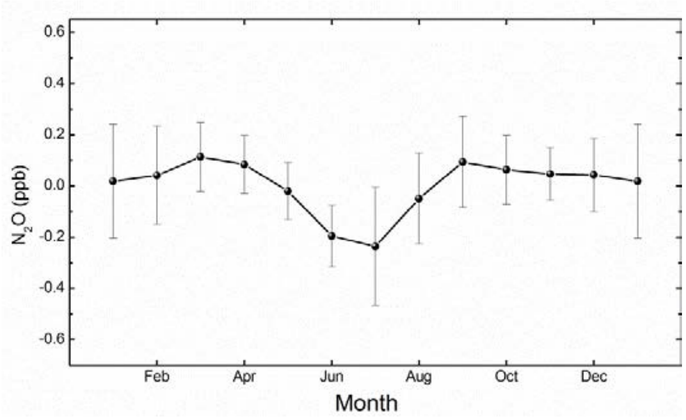
N_2O data obtained from discrete flask air sampling during 1995-2014 at Waliguan (WLG) station (36˚17N, 100˚54E, 3816 m asl) is presented for the first time, with a description of data quality. WLG station is the only global background station of WMO/GAW in central Eurasia. Characteristics of the mole fractions, growth rates, seasonal cycles, as well as influence of long-distance transport were investigated from selected background data. Observed time series suggests that atmospheric background N_2O possess long-term trends of increase and a statistically significant seasonal cycle. N_2O annual means vary from 313.5±0.1 ppb to 327.2±0.2 ppb, With an mean annual growth rate of 0.8±0.1ppb yr^{-1}, which is close to the global mean annual growth rate.

Averaged seasonal cycle shows minimum value of -0.24 ppb in July and two peaks with maximum value of 0.1 ppb in March and smaller value of 0.09 ppb in September. The amplitude of the seasonal cycle is 0.34 ppb, which is in consist with results of previous researches about other monitoring stations located in the Northern Hemisphere. The negative values in summer are mainly the result of maximum stratospheric-troposphere exchange (STE). The positive values in winter and early spring are possibly due to thawing of the frozen soil under the cold plateau climate which induce the increase in N_2O emission.

Evaluation of the influence of transport on N_2O variability has been carried out using backward air-mass trajectory analysis and highlights the effect of the regional distribution of sources. The widely use of fertilizer in agricultural practices in northeastern China strongly contribute to the continuous increase in N_2O mole fractions at WLG station. The results from this study can provide atmospheric N_2O characteristics in Asian inland regions, and be used in other studies to improve the understanding of N_2O source and sink distributions.





The Australian Greenhouse Gas Observation Network – where we are and where we are heading

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This poster will provide an overview of the Australian Greenhouse Gas Observation Network (AGGON). CSIRO runs AGGON in collaboration with the Bureau of Meteorology and the Australian Antarctic Division, providing continuous in situ measurements of CO_2 and CH_4 to the World Meteorological Organisation (WMO) Global Atmosphere Watch (GAW) program via the World Data Centre for Greenhouse Gases (WDCGG).

We will describe the calibration strategies that link these data to the internationally recognised calibration scales, providing comparability with similar international datasets available through the WDCGG as hourly means.

The quality control and data processing protocols used in AGGON will be described, and we will present representative data from each site and consider issues such as the impact of moving from minutely to hourly data, the effect of the number of minutes contributing to the hourly mean and the usefulness of the minutely standard deviation information to better understand the dataset. From these examples, we hope to point to some ‘smart’ data selection tools for utilising the data that can help validate Australian terrestrial carbon cycle models.

Finally, we speculate on how we would ideally expand AGGON to provide an optimal dataset for carbon cycle model validation and to provide high quality, low uncertainty top-down estimates of greenhouse gas emissions on a regional to continental scale in support of de-carbonisation initiatives and the Paris agreement.

Atmospheric CH_4 and N_2O measurements at Suva, Fiji

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The researchers from the University of the South Pacific developed the in-house capacity to measure CH_4 and N_2O using GC-FID and GC-ECD respectively. A series of clean air samples were collected from a coastal site near Suva, Fiji (18°08'S, 178°26'E). The precision for CH_4 measurements is 4 ppbv and for N_2O measurements is approximately 2 ppbv. The seasonal cycles of both greenhouse gases observed are similar with a seasonal amplitude of approximately 30 ppbv. However some variability is observed during the summer months in the methane dataset which demands further investigation. Unfortunately the N_20 data set is very recent and does not extend back to the previous summer months. The datasets obtained at this site will be compared to other sites such as South Pole and Samoa. The dataset looks very appreciable although it needs to be verified through inter-laboratory comparisons. This site is quite interesting due to complex tropical meteorology in the region affecting transport of methane from the Northern into Southern Hemisphere.

MOYA and *Equianos*: UK methane measurement and GHG monitoring

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Project MOYA (Methane Observations and Yearly Assessments) is a multi-partner UK consortium supported from 2016-2020 by the Natural Environment Research Council. The project is global in scope and includes measurement, field campaigns, and modelling work: http://moya.blogs.bris.ac.uk/project-moya-nercs-study-of-the-global-methane-budget/ . At the core of MOYA is a network of *in situ* observations. Planned continuous CO_2 and CH_4 measurement (Picarro or Los Gatos analysers) are on Ascension Is., E. Falkland Is. , Halley Bay, Antarctica, and the Atlanticcrossing ships RRS JC Ross and Cap San Lorenzo. Flask or bag sampling will be carried out for CF-GC-IRMS analysis of ^{13}C in CH_4 from the island locations. The data archive will be located in the Centre of Environmental Data Analysis (CEDA) at STFC (Science and Technology Facilities Council). Data will be stored online and accessible to users as per the conditions of use stated above. Data will be curated and backed up according to current data centre practices. NetCDF will be adopted for all the processed data generated by the programme. *Equianos* (Equator-Inter-Atlantic-North-South) is an informal Atlantic network with partners including the MOYA consortium, Norwegian Inst. for Atmospheric Research (NILU), Finnish Meteorological Inst. (FMI) -Finland, and the S. African weather service. http://equianos.com/.

Atmospheric greenhouse gas concentrations for five years over a tropical forest in Borneo Island.

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We collected the air samples once a week at the top of the tower of 100 m at GAW station at Danum valley (DMV) (4.98°_N, 117.84°_E, 426 m a.s.l) in the tropical forest of Bornel Island, Malaysia since 2010 by using an automatic flask sampling unit and then we shipped the samples to our institute for analysis for CO_2, CH_4, CO, H_2, N_2O and SF_6 concentration, and isotopic ratios ($\delta^{13}C$ and $\delta^{18}O$) of CO_2. We also collected the air samples using Volunteer Observing Ships (VOSs) over South China Sea (SCS) (2-9°_N, 110°-117_E) and Western Pacific Ocean (WPO) (2-9°_N, 144-151°_E) at 3 or 4-week intervals, and analysed the same component as DMV. In this study, we compared the data of DMV with the data of SCS and WPO to show the characteristics of the greenhouse gas concentrations in the tropical forest in Borneo Island.

CO_2 at DMV and SCS in winter were approximately 3 ppm higher than that at WPO because DMV and SCS were received the air mass of high CO_2 concentration from Asian continent. While CO_2 at DMV in summer was approximately 3 ppm lower than those at SCS and WPO even though the air of DMV was collected at night (10 pm). It was suggested that the CO_2 concentration of air mass of DMV region that pass through over Borneo Island was decreased due to CO_2 absorption by the photosynthesis of the forest. Seasonal variation and long-term trend of $\delta^{13}C$ showed opposite to those of CO_2. $\delta^{18}O$ at DMV and WPO showed a tendency to become heavier in recent years.

CH_4 at DMV, SCS and WPO showed a seasonal variation that it was same as a representative variation in the northern hemisphere. However, CH_4 at DMV was always 10-30 and 30-60 ppb higher than that at SCS and WPO, respectively. It is considered that DMV region has large CH_4 source.

CO at DMV and SCS were 20-100 ppb higher than the data at WPO. CO at DMV and SCS also had two peaks in a year. The peaks in Mar and Oct were occurred due to the transportation of the air mass of high CO concentration from Asian continent, and the influence of the forest fire in Indonesia, respectively. H_2 at DMV also showed two peaks in Mar and Oct, and almost same as those at SCS and WPO except for Oct when the severe forest fire in 2015 occurred.

N_2O and SF_6 at DMV had a seasonal variation that the concentration increased from Nov to Mar, and decreased from Jun to Oct because DMV was received air mass with high concentration from Asian continent in winter, and air mass with low concentration from Southern Hemisphere in summer. The values of N_2O and SF_6 at DMV was almost same as those at SCS and WPO. But the variation of measured values at DMV and SCS were larger than that at WPO.

Thus, it was clearly found that Borneo Island has CO_2 sink, and strong CH_4 and CO source.

Monitoring of Greenhouse Gases with in situ FTIR in East Anglia, UK, as part of a regional sampling network

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The main greenhouse gases (GHG) emitted by human activities in the UK are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Understanding and quantifying their emissions is essential to monitor and guide emission reduction measures. The GAUGE (Greenhouse gAs Uk and Global Emissions) project funded by the UK Natural Environment Research Council (NERC) aims to improve the knowledge of the UK GHG budget by an extensive measurement program.

As part of the GAUGE project, a regional sampling network in East Anglia had been established, focusing on emissions from agriculture as a main source of GHG by encircling a large area to capture the in and out flow of this area. We deployed an in situ FTIR analyser (Spectronus by Ecotech) for simultaneous measurements of CO_2, CH_4, N_2O and CO in Glatton, the most western station of the East Anglia sampling network, between October 2014 and April 2016. Air was sampled continuously from a church tower and measured on a minute time scale. The site is mainly influenced by south westerly winds. A clear diurnal cycle is observed in summer for CO_2, CH_4 and N_2O, which is less pronounced in the winter months.

In this presentation, we show first results from the measurements of CO_2, CH_4, N_2O and CO and describe the applied calibration and correction procedures. Monthly measurements of two primary standards, calibrated in reference to the WMO scale, and daily drift gas measurements were conducted to improve accuracy and monitor drifts in the instrument, respectively. Results from a cylinder intercomparison program (ICP) are shown as well.

Implementation of New Greenhouse Gas Measurements in Cholpon Ata, Kyrgyz Republic

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The provision of reliable scientific data to characterize the atmosphere's chemical composition 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 publicly accessible. Despite the ongoing considerable improvement in spatial data coverage and the large number of GAW stations measuring greenhouse gases around the globe, there are still regions of the world with sparse data coverage.

The project Capacity Building and Twinning for Climate Observing Systems (CATCOS), aimed at establishing and resuming systematic observations of greenhouse gases and other atmospheric and terrestrial Essential Climate Variables in developing and emerging countries where the availability of observations is currently insufficient. It was funded by the Swiss Agency for Development and Cooperation and coordinated by the Federal Office of Meteorology and Climatology MeteoSwiss.

Within CATCOS, Empa established sustainable and high-quality greenhouse gas (carbon dioxide, methane, carbon monoxide and surface ozone) observation in the Kyrgyz Republic. Measurements started in August 2016 at the Cholpon Ata Lake Observatory (42.64 degN, 77.07 degE, 1613 m asl) operated by Kyrgyzhydromet. The observatory is located at the Northern shore of the Issyk Kul lake, a water surface of 180 times 60 km in size. To its north, a mountain range extends up to an altitude of 4300 m. In spring and autumn, clean air is predominantly measured when local activity in the region is low. During summer, touristic activity in the region is prevalent leading to increased traffic. In winter, residential heating in the nearby villages can occasionally lead to elevated greenhouse gas concentrations.

Thus, the station can serve several purposes as it allows observations of background signals representative for a large spatial area, and to assess the impact of local activities on the air quality in the rural Kyrgyz Republic. Repeated training of the Kyrgyzhydromet staff and maintenance visits ensure a sustainable operation which is reflected by a data coverage of more than 94 % during the first 10 months of operation.

ICOS ATC near real time greenhouse gases data: from collection to model validation on the importance of proper water correction and primary scale propagation

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ICOS is the European based 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 including a network of about 40 operational atmospheric stations (measuring atmospheric composition in greenhouse gases and other core parameters). This network is coordinated by the Atmospheric Thematic Center (ATC) that has two main functions: operates the atmospheric data processing chains, which includes data transmission from stations to the routine delivery of near real time quality checked data-stream and carry out regular measurement technology survey, analysis and enable development of new sensors and their testing prior to field deployment within ICOS. The presentation will describe recent advances in GHG measurement and data processing with special focuses on:

- correctly and precisely accounting for water vapor when greenhouse gases measurements are performed in humid air,
- propagating GHG reference scale changes, ensuring traceability.

We will also show the use of this NRT processed data to validate GHG atmospheric transport models e.g. Copernicus

Data Services for Carbon Cycle Science at the ICOS Carbon Portal

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The ICOS Carbon Portal (CP) is the data platform of ICOS but has also the role to coordinate, facilitate and ensure production of elaborated products based on ICOS data in direct collaboration with the modelling community. Global as well as regional flux and emission datasets are collected and will be analysed and displayed at the CP.

A prototype synthesis of European CO_2 surface flux estimates is presented at the CP, based on the inverse model results from three European research groups that also contributed to Global Carbon Project. CP is ready to integrate more contributed flux maps from inverse as well as process-based flux modelling as they become available.

In order to facilitate a coordinated generation of elaborated products, e.g. in inverse modelling intercomparisons, the CP provides access to a variety of datasets that can be used as prior and ancillary information in models, but also to measurement data, like of course the ICOS observations, for example in the form of the ObsPack CO_2 product GLOBALVIEWplus, for which CP collects and processes the contributions from the European laboratories.

As a further service, the CP provides an online tool to analyse potential contributions of natural fluxes and anthropogenic emissions to the atmospheric CO_2 concentrations at currently existing and planned ICOS sites. The tool is based on model simulations of the up-stream influences on the observation location, the so-called footprints, which are coupled to surface flux maps to derive tracer concentration changes at the station. The tool can also generate footprint for any custom location in the model domain.

The model framework currently consists of the Lagrangian transport model STILT together with emission-sector and fueltype specific emissions from the EDGARv4.3 inventory and biospheric fluxes from the diagnostic biosphere model VPRM, but can in general use any model footprint data. Both, footprints and concentration time series, are displayed on the webpage, providing a very simplified approach for the evaluation of measurement strategies.

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Greenhouse gas measurement at Mt Kenya Global Atmosphere Watch station, Kenya

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The Kenya Meteorological Department, KMD, operates the Mt Kenya Global Atmosphere Watch station MKN, (37.22 E, 0.03 S), Kenya. The station was established in 1999 with funding support from the Global Environment Facility of World Bank, World Meteorological Organization and the Kenya Government. Through cooperate support from NOAA, air flask sampling was commenced in 2001 to 2010. Close cooperation with Empa allowed starting continuous surface O_3 measurements in 2000 and in-situ CO_2 and CH_4 measurements using a Cavity Ringdown Spectrometer (Picarro G1301) in 2010, though with data gaps. Instrument audits are performed periodical by Empa personnel. Staff training of station operators has also been undertaken by support from MeteoSwiss, Empa, WMO and GAWTEC. Surface O_3 shows two seasonal maxima peaks in March and in September. These peaks are associated with biomass burning in the vicinity to clear farms for planting in March and long range transport from Southern Africa in September. Transboundary layer exchange also contributes to these peaks. Minimum O_3 values were observed in October, December season due to dominant NE trade winds bringing, clean air from the Arabian ridge to the sampling site. Diurnally, minimum value is attained at 7.00pm local time. This coincides with the time of change from upslope wind to downslope wind. The annual and diurnal variability of CO_2 at MKN is rather small and does not show consistent patterns. This indicates a negligible local and regional influence of the observations (e.g. due to biospheric uptake and respiration) and thus, reveals the excellent location of MKN for undisturbed background monitoring close to the equator, i.e. in a region with very sparse observations.

CH_4 showed maxima in December and January while minimum values are recorded in April. The annual range is also small and indicative of background measurements where variability is mainly governed by long range transport.