WMO GAW GGMT-2022

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Greenhouse Gas Measurement Techniques

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1 Carbon Cycle Research activities by setting up GHG concentration and flux observation network in India

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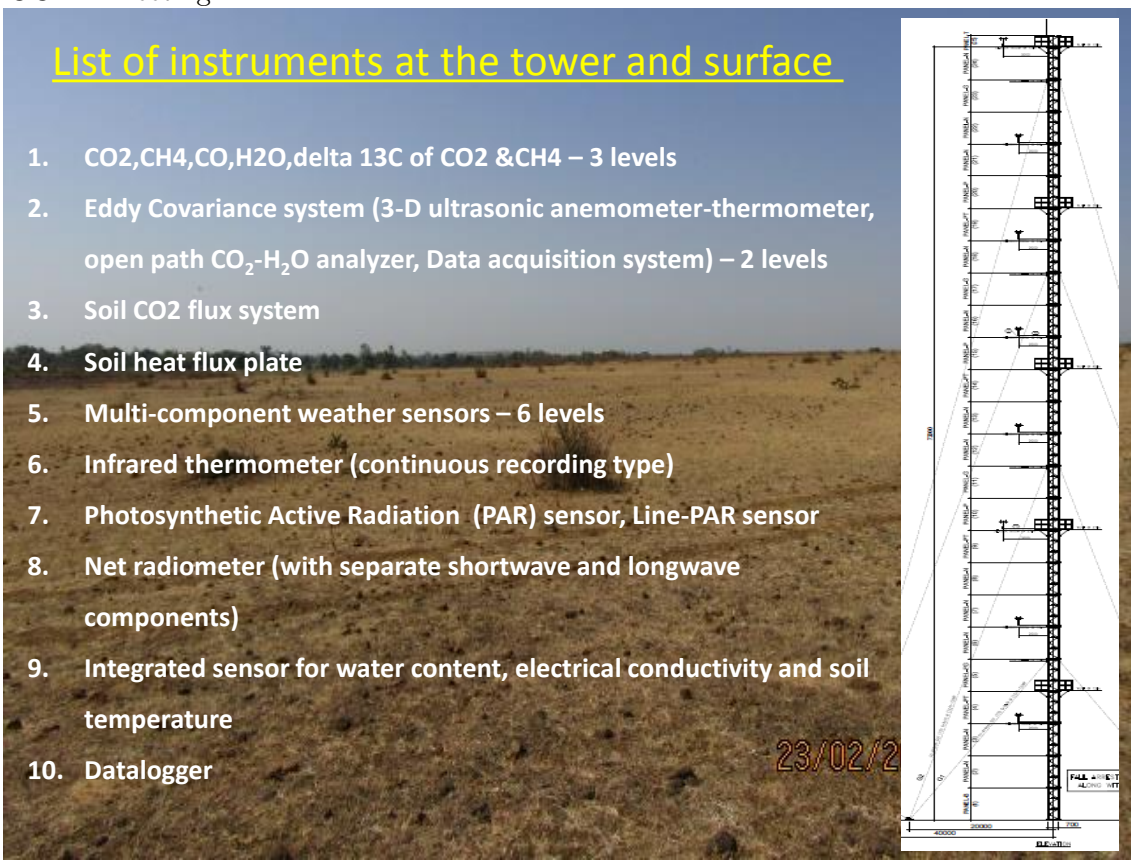
We have initiated various Greenhouse gases/carbon flux monitoring and modeling programs in India. We established a discrete air sample analysis lab and weekly sample collection started in 2009. We also set up an in-situ monitoring site using Picarro instruments in 2014 (GHG and its isotopes). A 72-meter tall tower is already installed and operational in central India. At this tower, we monitor GHG & its isotope, CO_2 flux, Soil CO_2, Weather parameters, etc. Also, We have installed India's carbon flux measurement neatwork (Indo MET-Flux project), where we have monitored carbon fluxes at different ecosystems in India since 2016. For upper atmospheric GHGs monitoring, we used airplane campaigns in 2014, 2015, and 2018 and observed horizontal and vertical GHG profiles in different parts of India. Additionally, We have initiated a GHG transport modeling framework at the IITM Pune to estimate GHGs sources and sink over the Indian sub-continent and adjoining regions.

This study will present observation and modeling efforts and discuss its outputs during the GGMT meeting.



2 Laser dispersion spectroscopy for next generation emissions monitoring

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As scientists from academia and industry seek to improve their understanding and characterisation of greenhouse gas emissions, a suite of measurement technologies has emerged. This tool kit of technologies ranges from satellite retrievals looking at regional and continental flux estimates, to small handheld devices measuring emissions at component level. As understanding of greenhouse gas budgets and inventories has developed, it has become clear that there is a pressing need to improve the characterisation of temporal and spatial resolution of emissions at the facility level.

Mirico has developed an instrument which can continuously and autonomously monitor greenhouse gases such as CH_4 and CO_2 with an unprecedented level of precision and accuracy, providing facility operators, regulators and environmental scientists with the detailed insight required to act promptly and effectively to mitigate unplanned emissions. The open path system, which can cover a facility such as a landfill, wetland, or a gas processing site, can monitor an area of approximately 1 km^2 using a single instrument.

The instrument is able to deliver these remarkable benefits by utilising the novel Laser Dispersion Spectroscopy (LDS), a completely new approach to optical gas sensing. Whereas traditional optical sensing systems rely on measuring the optical power of transmitted light, or the intensity change of light, LDS uses the differential phase change induced by molecules, or the frequency change of the light, meaning the instrument is insensitive to weather conditions such as rain, snow, fog and dust.

We will present data from greenhouse gas measurement campaigns exemplifying the use of the technology in adverse weather conditions with no reduction in performance, where the use of the LDS technique allowed the instrument output to remain accurate, precise and reliable, even in rain, snow, or fog delivering continuous measurements throughout the day and night.

3 Gas reference materials for underpinning measurements of δ^{13}C-CO_2 and δ^{18}O-CO_2 with traceability to the VPDB scale

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To support governments verifying emissions and demonstrating national reduction targets, it is necessary to discriminate between the natural and various man-made sources of greenhouse gases. This requires accurate measurements of baseline concentrations and contributions resulting from emission events. Separating manmade emissions from measured carbon dioxide amount fractions is challenging and requires information on the isotopic composition.

Currently there is no infrastructure to meet the demand for carbon dioxide gas reference materials with the required uncertainties to underpin global observations, compromising the comparability of measurement data. It is therefore necessary to address the existing traceability gap in the measurement of isotopes of carbon dioxide by developing gas reference materials, calibration methods and dissemination mechanisms, which are traceable to existing scales (e.g. VPDB - Vienna Pee Dee Belemnite).

We have developed pure carbon dioxide reference materials at two difference isotopic compositions for underpinning atmospheric observations of δ^{13}C-CO_2 and δ^{18}O-CO_2 using commercial spectroscopy. The first composition is nominally -42 ‰δ^{13}C-CO_2, -36 ‰δ^{18}O-CO_2 and the second is nominally 1 ‰δ^{13}C-CO_2, -8 ‰δ^{18}O-CO_2. A third pure carbon dioxide reference material with the nominal composition -20 ‰δ^{13}C-CO_2, -22 ‰δ^{18}O-CO_2 has been prepared from a blend of the first two. All three reference materials are traceable to the VPDB scale from direct comparisons to NBS19 and are stable for at least 1 year. The pure reference materials have been diluted in air to prepare reference materials at the same isotopic compositions at ambient amount fractions (400 umol mol^{-1}). Differences of 0.03 and 0.13 ‰to the parent mixtures have been observed for δ^{13}C-CO_2 and δ^{18}O-CO_2 respectively. A capability to tune the isotopic composition of δ^{18}O-CO_2 using evaporated, demineralized water to atmospheric composition is also demonstrated, for when it cannot be achieved from blending pure commercial source gases.

4 Development of fluorinated greenhouse gases and ozone depletion substances (ODSs)measurement system and application in Chinese observation network

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Most fluorinated greenhouse gases (F-gas) and ozone depleting substances (ODSs), including CFCs, Halons, HCFCs, HFCs, PFCs, SF_6, NF_3, CCl_4, CH_3CCl_3,CH_3Br, etc, are strong greenhouse gases with high global warming potential (GWP). Gaps were found for several F-gas and ODSs emissions in a global scale between the results from top-down and bottom-up methods. The observation in major source regions could explain or narrow the gap. However, the lack of commercial instrument limits the expansion of the observation network of F-gas and ODSs.

With the support of Chinese National Key R&D Project, ODS5-pro, a cryogen-free preconcentration-GCMS system was developed and commercialized for ambient measurement of F-gas and ODSs. The detection limits were around 0.1 ppt and the precisions were 0.5-5% at ambient levels (1-500 ppt), which could be used for high precision measurement at background conditions. The system were compared with Medusa-GC/MS which developed by Advanced Global Atmospheric Gases Experiment (AGAGE) at Shangdianzi Background Station (SDZ) from October 2020 to September 2021. The result obtained from the two systems generally agreed well and the deviation of data observed within 70 minutes by two systems was basically within ±5% except for a few pollution events.

ODS5-Pro has already been applied for in-situ measurements at background stations as well as for central labs analysis for SS flask samples. In addition, baseline conditions were distinguished from pollution events at SDZ and the polluted data combined with a ratio method were used to firstly estimate the emissions of four groups for F-gas in China using HCFC-22 as tracer. The national total CO_2- equivalent emission for F-gas was 371.6 Mt/yr. Among all substances, SF_6 had the highest proportion of CO_2-equivalent emission (24.9%) due to its high GWP_{100yr} value, followed by HFC-23 (23.4%), HFC-125 (16.4%), HFC-134a (13.4%), NF_3 (8.7%), CF_4 (5.7%), HFC-143a (4.0%), HFC-32 (3.2%) and HFC-152a (0.2%). The Chinese emissions of CF_4, NF_3, SF_6, HFC-23, HFC-32, HFC-125, HFC-134a, HFC-143a and HFC-152a, accounting for 23%, 74%, 45%, 42%, 27%, 20%, 15%, 10% and 8% of global emissions, respectively.

5 Long-term changes in CH_4 emission: Comparing $\Delta CH_4/\Delta CO_2$ ratios between observation and proved model in East Asia (2010–2020)

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To understand the changes in CH_4 emissions in East Asia, mainly in China, we analyzed the synoptic scale variability (SSV) of CO_2 and CH_4 mole fractions at Anmyeondo (AMY; 36.53°N, 126.32°E, 46 m above sea level) in South Korea using near-surface in-situ observation and an atmospheric transport model (ACTM) to investigate the role of prescribed surface fluxes on SSV. The SSV of the tracers at AMY was mainly caused by emission variations from eastern and northeastern China during the winters in 2010–2020, as indicated by the simulated concentration footprints at AMY observed using the WRF-STILT model. The estimated SSV of $\Delta CH_4/\Delta CO_2$ mole fraction ratios from the observations was 4.2–6.2 ppb ppm-1, with a mean of 5.7 ± 0.93 ppb ppm-1 during the winters in 2010 to 2020. We also calculated the CH_4/CO_2emission ratio from China's total annual fossil-fuel emissions, excluding seasonal sources estimated from the Emission Database for Global Atmospheric Research. We found that the ratio was overestimated by ˜98.1% compared to observations, which was likely driven either due to the overestimation of CH_4 or underestimation of CO_2. We discerned that the model-simulated SSV of the $\Delta CH_4/\Delta CO_2$ ratios generally reproduced the observations when the CH_4 FixCoal simulation case was used. This implies that CH_4 from coal was a major contributor to the observed variations in the winter period $\Delta CH_4/\Delta CO_2$ ratios. However, the model did not reproduce the observed ratio in 2012—this discrepancy requires further study. The trend of $\Delta CH_4/\Delta CO_2$ was a slight decrease over time, which was attributed to the earlier onset of CH_4 emissions relative to fossil-fuel CO_2, predominantly due to the reduction of CH_4 emissions from coal. In 2013, a relatively low tracer ratio was noted, which was caused by the large contribution of CO_2 from biomass burning. Overall, the observed AMY $\Delta CH_4/\Delta CO_2$ ratios provide an efficient approach for validating the existing estimates of East Asian sectoral emissions of CH_4.

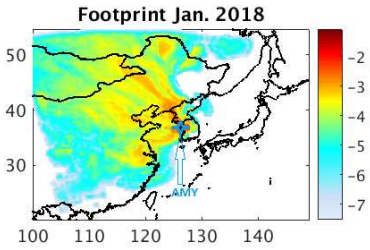

Figure 1. WRF-STILT simulated concentration footprints Anmyeondo (AMY; 36.53°N, 126.32°E, 46 m above sea level) in South Korea (indicated by blue star) during January 2018. Unit for footprint is $\log_{10}$(ppm/μmol m^{-2} s^{-1}).

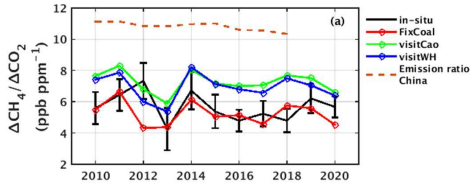

Figure 2. The time series of the synoptic scale variability (SSV) of $\Delta CH_4/\Delta CO_2$ at AMY during winter periods (December, January, February) in 2010–2020. The black line denotes the in-situ observations, and the remaining colors indicate the ACTM model simulation with different CH_4 emissions shown in the legend. Dashed lines denote time series of CH_4/CO_2 emission ratios of annual Chinese total fossil fuel emissions (excluding rice cultivation, enteric fermentation, and manure managements) based on EDGAR v6.0 through 2010 to 2018.

6 Assimilation of methane plume data with grid-scale emissions maps from atmospheric inversions.

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Emissions maps resolved at spatial scales and sectors are needed for the effective implementation of methane monitoring and reduction strategies. While atmospheric inversions of satellite or in-situ data provide a reasonably accurate estimate of emissions aggregated over large spatio-temporal domains, they cannot resolve emissions at high spatial resolutions because of the errors in coarse resolution observations and transport models. Methane emissions from super-emitters are regularly observed and quantified as distinct plumes in high-resolution aircraft and satellite observations (PRISMA GHGSat, Sentinel-2). Recent studies have shown that super-emitters are often responsible for a large fraction of the total regional emissions. This provides a golden opportunity for climate change mitigation. The precise location and sector of a plume emitter is easily determined as plumes are observed close to the source in the high-resolution satellite data. The information content of a plume dataset can be used to improve the spatial and sectoral allocation in a grid-scale emissions map. Here, we present a method for assimilating methane plume datasets with the posterior emissions of a grid-scale atmospheric inversion using a Bayesian approach. We demonstrate the method by combining the plume dataset from a 2019 aircraft campaign and a TROPOMI inversion over the Permian basin. Our method uses the additional information in the plume dataset to improve the spatial allocation and magnitude of grid-scale emissions, while keeping the total regional emissions consistent with the TROPOMI inversion.

7 Identifying bulk regional methane isotopic signatures using long-term records from UK sites

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Long-term records are vital for understanding how our environment is changing. A significant rise in atmospheric methane began in 2007 and has accelerated after that, particularly since 2014. This trend was observed globally and was coupled with a sustained isotopic shift to values more depleted in ^{13}C (more positive $\delta^{13}C\text{-}CH_4$). Currently, there is no consensus as to why these observations have occurred. However, long-term methane isotopic measurements can explain changes in this crucial greenhouse gas source mix. Here, long-term records of CH_4 mole fraction and $\delta^{13}C\text{-}CH_4$ from 5 sites across the UK are presented. The data show an increase in CH_4 and a shift to more negative values of $\delta^{13}C\text{-}CH_4$ on the regional-local scale, similar to those recorded globally. The approximately weekly in-situ measurements offer an insight into the emissions of both suburban and background regions of the UK.

A method for isotopic discrimination from longer-term atmospheric measurements of CO_2 and $\delta^{13}C\text{-}CH_4$, as outlined by *Miller and Tans* (2003), is utilised in this work. Miller-Tans analysis allows for the explicit specification of background values, which is vital when dealing with long-term records due to seasonal, local, regional and global background variations in atmospheric CH_4 and $\delta^{13}C\text{-}CH_4$.

When applying the Miller-Tans method to the long-term data from UK sites, as expected, the heaviest $\delta^{13}C\text{-}CH_4$ source signatures, which are associated with industrial sources such as gas leaks, are observed for the suburban sites, and biogenic, lighter, sources for the background sites. The methane source distribution is compared to results from mobile measurements at Royal Holloway, University of London and the UK National Atmospheric Emissions Inventory (NAEI).

From the initial results, there seems to be a more significant proportion of thermogenic/pyrogenic emissions in this data compared to the NAEI inventory or an overestimation of agricultural sources in the NAEI. At all sites, there has been an increase in CH_4 mole fraction. Using the Miller Tans method, it is possible to calculate bulk regional source signatures, which highlight a distinction between rural and suburban emissions.

8 Mapping urban emissions of CO_2

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A dense (~2km grid) network of CO_2 and AQ (CO, NO, NO_2, O_3 and particles) sensors is being deployed in several cities. San Francisco (50 locations), Los Angeles (12 locations), Providence, RI (25 locations), Glasgow, Scotland (20 locations) are collaborating cities http://beacon.berkeley.edu/about/. Examples of analyses of the network observations using simple models and sophisticated inversions will be described. These will include constraints on annual trends in vehicle fuel efficiency, the dependence of CO_2 emissions on vehicle speed, and maps of emissions with 1 km spatial resolution allowing attribution by sector. The potential for joint inverse modeling of CO and CO_2observations will be discussed.

9 VERTICAL PROFILE OF GREENHOUSE GASES (CO_2, CH_4, CO, N_2O, H_2O) FROM SURFACE UP TO 35 KM WITH AIRCORE: LONG TERM MONITORING PROGRAM AT TRAINOU, FRANCE.

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The AirCore technique consists of using a long custom-made tubing under a stratospheric balloon which enables the passive sampling of atmospheric air from up to 35 km altitude down to the surface (Karion *et al.* 2010, Membrive *et al.* 2017). After AirCore recovery, the air sample is pushed into gas analyzers enabling precise measurement with low volume of air.

The measurement program has started at the Trainou ICOS tall tower in France, in October 2016, and since November 2020, two analyzers (Picarro G2401 (CO_2, CH_4, CO, H_2O) and Picarro G5301 (N_2O, CO, H_2O)) are coupled to measure N_2O in addition to CO_2, CH_4, H_2O and CO, which makes Trainou the unique site in Europe with monthly profiles of those 5 species. More than 90 vertical profiles have been performed since 2016, and 30 of them since the coupling of the two analyzers.

This poster will focus on the mounting of these two instruments in parallel and will also present some results of vertical profiles and comparisons. We will present an evaluation of the measurement uncertainties by comparing the pairs of AirCores launched simultaneously. One AirCore is measured through the two instruments and one is measured through the G24 only. The comparison of CO_2, CH_4 and CO gives good agreement between the two mountings: between 1 and 15 km high, for the coupled instruments, the mean difference is 0.1 $\pm$0.1 ppm, 1.2 $\pm$1 ppb and 1.1 $\pm$1 ppb for CO_2, CH_4 and CO respectively.

A comparison of the observed vertical profiles with the CAMS analysis will be also presented, as an illustration of the interest of such measurements to validate atmospheric transport models.

10 Updated assessment of $\Delta^{14}CO_2$ measurement intercomparability using atmospheric records and standard materials

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GGMT recommends that $\Delta^{14}CO_2$ measurements should deviate no more than 0.5‰between laboratories. Such precision is important for the use of $\Delta^{14}CO_2$ data from multiple research groups in carbon cycle studies, and will provide confidence that differences between sites are due to environmental features rather than systematic measurement bias. While working towards the GGMT goal of 0.5‰intercomparability, a robust method of determining and correcting for such biases while they exist is critical.

Several $\Delta^{14}CO_2$ intercomparison exercises have been performed in recent years. We use these as the basis for an intercomparison of four laboratories reporting $\Delta^{14}CO_2$ data and systematic biases between them. We also discuss the viability of a new method used to correct for offsets between two non-stationary time series. The institutes compared in this study are GNS Science, Scripps Institute of Oceanography and Lawrence Livermore National Laboratory (SIO/LLNL), the Institute of Arctic and Alpine Research and UC Irvine (INSTAAR/UCI), and University of Heidelberg (UH). GNS and UH intercomparability is determined using long-term atmospheric $\Delta^{14}CO_2$ records from sites of similar latitude (Baring Head, New Zealand, and Cape Grim, Australia). For these records, offsets are determined using a curve fitting method from the NOAA Global Monitoring Laboratory (CCGCRV), and errors approximated using a Monte Carlo simulation. Between GNS, SIO/LLNL, and INSTAAR/UCI, intercomparability is assessed using Niwot Ridge tank standard materials (NWT3 and NWT4).

From the relatively sparse intercomparison data available, we find that significant interlaboratory offsets exist, and vary through time. Time-variability in systematic measurement bias highlights the need for continued intercomparisons of $\Delta^{14}CO_2$ to optimize our interpretation of this parameter in carbon cycle studies.

11 What can we learn from over 100 audits in 25 years regarding accurate measurements of greenhouse gases?

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Empa operates the World Calibration Centre for Carbon Monoxide, Methane, Carbon Dioxide and Surface Ozone (WCC-Empa) since 1996 as a Swiss contribution to the Global Atmosphere Watch (GAW) programme. We further collaborated with the World Calibration Centre for Nitrous Oxide (WCC-N_2O) to increase the number of N_2O audits at GAW stations. WCC-Empa plays a central role in sustaining and improving the data quality and data availability required for climate and environmental research.

One of the main tasks of WCC-Empa is the quality control of GAW stations through on-site system- and performance audits. Audits include a station visit by WCC-Empa, comparison of travelling standards, and parallel measurements during one to three months. As of today, we have conducted more than 100 audits as independent checks of the measurement's traceability to the accepted standards of the WMO/GAW programme, which are hosted and distributed by Central Calibration Laboratories (CCLs). The audits further include operator training and capacity building to increase the data availability and data quality, especially in less developed regions.

Our presentation will give an overview of audit results of the last 25 years for all parameters within the scope of WCC-Empa. We observed that more advanced measurement techniques and quality control procedures resulted in a significant improvement of the accuracy of the measurements made at GAW stations. Furthermore, WCC-Empa reanalyzed the reference standards obtained from the CCL for CO_2, CH_4, CO, and N_2O over the past 25 years with respect to internal consistency and drift. We found that the recent revision of the carbon dioxide calibration scale by the CCL resulted in an improved internal consistency. However, the long-term stability of gas mixtures in high-pressure cylinders is dependent on the respective gas, and the drift of calibration standards remains one of the most pressing issues, especially for carbon monoxide. The presentation will discuss potential solutions to overcome this issue by using standards with a higher amount fraction in combination with zero air, and taking advantage of the current performance of spectroscopic techniques.

12 Estimation of CO2, CH4, CO and gaseous elemental mercury fluxes over southern Africa using the radon tracer method

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In an effort to better quantify the emission of greenhouse gases (GHG) and gaseous elemental mercury (GEM) of southern Africa, the Radon tracer method (RTM) as presented in Gaudry et al., 1990 was applied to a dataset of CO_2, CO, CH_4 , Radon 222 and GEM atmospheric abundances recorded at Amsterdam Island (AMS; 37.7983°S, 77.5378°E) between 1981 and 2021. The overall contribution of southern Africa regarding GHG and GEM emission was found to be positive. Emissions fluxes of CO_2 over southern Africa was estimated to 95.2 ±89.2 $gCO_2.m^{-2}.month^{-1}$. CO and CH_4 fluxes over southern Africa were estimated to 3.64±2.58 $gCO.m^{-2}.month^{-1}$ and 1.46±0.79 $gCH_4.m^{-2}.month^{-1}$, respectively. Finally, GEM emission fluxes was estimated here to $3.06x10^{-5}$ ± $3.86x10^{-5}$ g $GEM.m^{-2}.month^{-1}$. These results were confronted, for each species, to a seasonal emission scenario computed by taking into consideration the main sources and sinks of CO_2, CO, CH_4 and GEM in southern Africa. The emission fluxes computed the RTM were in adequation with the emission scenario for CO_2 and CO, however were on average 5.4 and 17 times higher than the emission scenario for CH_4 and GEM respectively.

References :

Gaudry, A., Polian, G., Ardouin, B., & Lambert, G. (1990). Radon-calibrated emissions of CO2 from South Africa. *Tellus B, 42*, 9–19.

13 Measuring atmospheric O_2 and CO_2 gradients above a boreal forest to derive $O_2$and CO_2 fluxes and ER signals

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We measured O_2 and CO_2 at two heights above a boreal forest, in Hyytiala, Finland, to get a better understanding of the diurnal variability of both O_2 and CO_2 and their O_2:CO_2 ratio, called the Exchange Ratio (ER). O_2 was measured with a fuel cell instrument (Oxzilla) and CO_2 with an NDIR instrument (Uras). We evaluate two methods to calculate the ER of the boreal forest: based on one measurement height, were the slope of the fitted line through the concentrations of O_2 and CO_2 is ER_{atmos} or based on the vertical gradient of O_2 and CO_2 where the ratio of the resulting surface fluxes is the ER_{forest}. By using ER_{atmos}, we found that entrainment creates unrealistic values for a signal that represents the ER of a forest. We therefore found that the fluxes-based approach (ER_{forest}) gives more accurate values of the forest ER compared to ER_{atmos}. We found ER_{forest} values between 0.84 ± 0.26 and 1.03 ± 0.05. We also compared several approaches to calculate the O_2 surface flux, based on the gradient method, and show which approach gives the most accurate flux estimate. From ER_{forest}, we determine the ER signals of both photosynthesis (ER_a) and respiration (ER_r) and use these signals to separate the Gross Primary Production and Total Ecosystem Respiration from Net Ecosystem Exchange. This shows the potential of how atmospheric O_2 can be used as tracer for CO_2 fluxes, but also shows the importance of using the most accurate derivation of the ER signal with the correct measurement setup.

14 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. A prime example of this are the recent CFC-11 papers by Rigby et al. [2019], Park et al. [2021] and Montzka et al. [2021], that utilised data from both the NOAA and AGAGE networks to identify the source region responsible for the global increase in this banned chemical, and the subsequent reduction in emissions. 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 20+ years comparisons (now more than 500 individual comparisons) of

non-CO_2 greenhouse gases (totalling more than 45 species) have been carried out twice yearly and presented at meetings of scientists of the Advanced Global Atmospheric Gases Experiment (AGAGE) 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 previous GGMT meetings summarising the methodology and resultant output, with detailed results from selected comparisons and new comparisons that have been performed. While the presentation will focus primarily on the major greenhouse gases, 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 also be given.

Montzka et al., A decline in global CFC-11 emissions during 2018-2019, *Nature*, 590, 428-432, https://doi.org/10.1038/s41586-021-03260-5, 2021.

Park et al., A decline in emissions of CFC-11 and related chemicals from eastern China, *Nature*, 590, 433-437, https://doi.org/10.1038/s41586-021-03277-w, 2021.

Rigby et al., An increase in CFC-11 emissions from China inferred from atmospheric observations, *Nature*, 596, 546-550, https://doi.org/10.1038/s41586-019-1193-4, 2019.

15 Evaluation of regional atmospheric CO_2 inverse modeling over Asia

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Asian terrestrial ecosystems have been experiencing rapid warming and land-use changes in recent decades. As a result, significant changes in the terrestrial carbon cycle are expected in Asia but significant uncertainties have been reported in estimating the magnitude of terrestrial carbon budgets. Recent studies utilizing atmospheric inversion systems suggest that the unrealistic simulation of atmospheric transport in the current global inversion system could be one of the main sources of uncertainty. To improve the estimate of Asian terrestrial carbon budgets, this study develops a nested atmospheric inversion system in Asia using the GEOS-Chem adjoint model which has higher horizontal resolutions of 0.5°x0.626° than that of the standard global inversion system (4°x5°). The Orbiting Carbon Observatory (OCO-2) XCO_2 measurements are used for data assimilation and the Greenhous Gases Observing Satellite (GOSAT) XCO_2 measurements are used to evaluate the performance of global and nested inversions. Results show that the nested inversions improve the overall representation of observed XCO_2 concentrations with a reduction of RMSE by 10˜15 % compared to the standard global inversion during 2018. However, the improvement was not significant (or even decrease) in East Asia and South Asia during the spring and summer, respectively, when the number of OCO-2 data is relatively small. In the presentation, the direction of improving the performance of regional inversion will also be discussed by showing the seasonally varied sensitivity of CO_2 surface fluxes to OCO-2 measurements over Asia.

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16 Analysis of source distribution of high carbon monoxide and aerosol events using airborne and surface observations in South Korea

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Korean Meteorological Administration (KMA)/ National Institute of Meteorological Sciences (NIMS) firstly established the King Air 350 aircraft platform for in situ measurements for atmospheric chemical compositions such as CO_2, CH_4, CO and aerosol since 2018 (Fig.1). Anmyeon-do (AMY, 36.54°N. 126.33°E), a World Meteorological Organization/Global Atmosphere Watch Program (WMO/GAW) regional background station in South Korea, provides continuous observations of GHGs (CO_2 and CH_4), CO, and aerosol at the surface and vertical profiles within 0.5-9 km that are also collected by the aircraft (Fig.2). The vertical profiles collected in 2019 were analyzed using meteorological parameters such as vertical velocity and boundary layer height (BLH), and a strong relationship was observed among them, however, a vertical distribution influenced by unexpected strong pollution plume did not exhibit strong relationship with vertical velocity and BLH. On November 16, we captured a strong CO and aerosol signal within the boundary layer and at about 2 km, where vertical profiles of the aerosol scattering coefficient at 550 nm were simultaneously observed with the same vertical structure. We identified the origins and source types of the pollution plume stratification for CO and aerosol. We also analyzed surface in-situ observations of particle size distributions and reactive gases (NOx, O_3, and SO_2) as well as XCO and aerosol optical depth measurements from tropospheric monitoring instrument (TROPOMI) and moderate resolution imaging spectroradiometer (MODIS) satellite, respectively. The high CO and aerosol event within the boundary layer, including observations at the surface site, was attributed to domestic burning sources such as biofuel for vehicles. The convective uplifting of industrial fossil fuel emissions from Eastern China was responsible for the high air pollution in FT. Atmospheric pollution plume stratification in the troposphere should be considered for future radiative forcing studies to improve air-quality forecasting in this region.

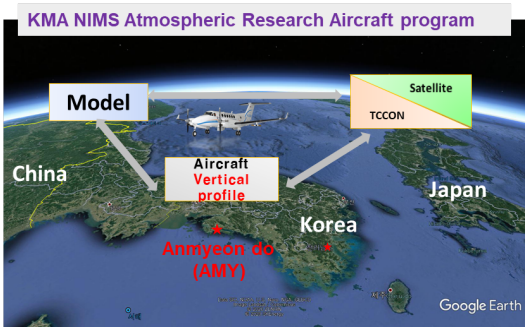

Fig. 1. The Korean Meteorological Administration (KMA) / National Institute of Meteorological Sciences (NIMS) research aircraft program was designed to obtain vertical profiles of atmospheric chemical compositions such as CO_2, CH_4, CO, and aerosol at Anmyeon do station, a WMO/GAW regional background site on South Korea. The vertical distributions could be utilized to verify model simulations and remote sensing data, also provide the seasonal climatology of atmospheric chemical compositions after long-term data were collected.

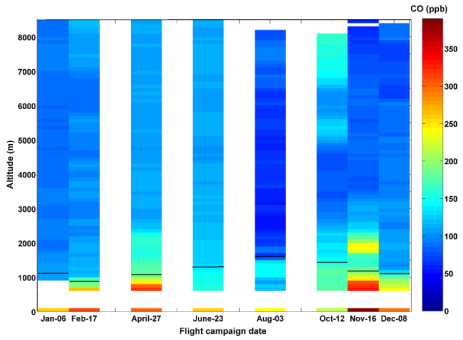

Fig. 2. Vertical distributions of CO dry mole fraction averaged at an altitude of 100 m bin for all 1-day flight spiral missions conducted over the AMY region for 2019 are shown. Totally eight 1-d flight missions were conducted during 2019. Since the minimum reaching altitude of King Air is around 500 m above mean sea level, the ground *in situ* measurements matching with flight time were shown in this figure as well. The black line represents boundary layer height (BLH) for each flight campaign.

17 A view of the European carbon flux landscape through the lens of the ICOS atmospheric observation network

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The Integrated Carbon Observation System (ICOS) network of atmospheric measurement sites produces standardized data on greenhouse gas concentrations at 39 sites in 14 different European countries. The network is continuously expanding and with it our understanding of the CO_2 flux landscape mainly through use of the measurements in regional inversion models. A characterization of the combined influence regions (footprints) of the current network offers insight to how well it represents different ecosystems and associated fluxes. We are interested in this for Europe as a whole, and will present various analyses at site, country, and continental level that quantitatively assess the ICOS network monitoring capacity. Relatively unmonitored areas and ecosystems are identified and visualized in "monitoring potential maps" which are intended to support network expansion decisions. *Relatively* well-monitored countries, such as Germany, will show little monitoring potential when considering Europe as a whole, and therefore we show how for national network expansion, the analyses can be limited to individual countries (figure 1b). This type of map can also be used to highlight relatively unmonitored areas with relatively high (anthropogenic) emissions, as well as to identify individual sites that uniquely monitor specific aspects of the European carbon cycle (e.g., coniferous forest fluxes at Scandinavian sites).

Our tools, accessible at the ICOS Carbon Portal Jupyter service to anyone, make it possible to analyze any network configuration with existing and/or hypothetical sites. Furthermore, considerations of hypothetical sites for network expansion decisions can be supplemented by output from Carbon Portal tools that characterize footprints of individual sites. A future avenue for these types of analyses will be to support network design within cities, which will require different datasets and other types of footprints.

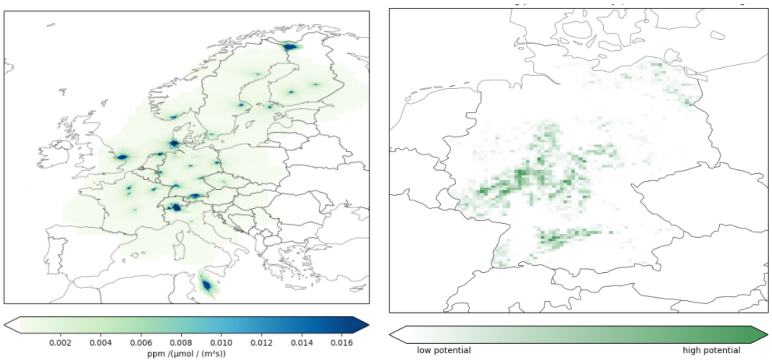

Figure 1. a) Network footprint of current ICOS network b) Monitoring potential map broad leaf forest Germany

18 Amazonia as a case study to compare measurements and inventories

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Amazonia hosts the Earth's largest tropical forests and has been shown to be an important carbon sink over recent decades. This carbon sink seems to be in decline, however, as a result of factors such as deforestation and climate change. Here we investigate Brazilian Amazonia's carbon budget and the main drivers responsible for its change into a carbon source and compare it with the Brazilian inventory results. We performed 742 aircraft vertical profiling measurements of lower-tropospheric concentrations of carbon dioxide and carbon monoxide at four sites in Amazonia from 2010 to 2020. We find the total carbon emissions for the Brazilian Amazon, fire emissions, and the Net Biome Exchange during this period and compare them with the inventory published information from the Brazilian government. The last National Communication from Brazil to UNFCCC (2020), related to the period 2010-2016, estimated 0.67 $PgCO_2$/year as the LULUCF net emission for the Brazilian Amazon. And specifically for the year 2016 0.27 $PgCO_2$/year. Our measurements and column integration technique produced the result of 0.92 $PgCO_2$/year for the Brazilian Amazon, during the period 2010 to 2016 and for the year 2016 the emissions of 1.53 $PgCO_2$/year, a very dry year. In our study, the period between 2010-18 produced the results of 0.78 $PgCO_2$/year, but in the next 2 years, when the deforestation control was almost totally removed and the deforestation increased by 60% and 70% during 2019 and 2020, respectively, the emissions increase to 1.17 and 1.34 $PgCO_2$/year for the same years, presenting a carbon emission increase of 50% and 70% respectively. Over the past 40 years, eastern Amazonia has been subjected to more deforestation, warming, and moisture stress than the western part, especially during the dry season, with the southeast experiencing the strongest trends. We explore the effect of climate change and deforestation trends on carbon emissions at our study sites and find that the intensification of the dry season and an increase in deforestation seem to promote ecosystem stress, increase in fire occurrence, and higher carbon emissions in the eastern Amazon. This is in line with recent studies that indicate an increase in tree mortality and a reduction in photosynthesis as a result of climatic changes across Amazonia. Since climate change is impacting the carbon sink capability it is recommended an annual report from inventories and measurements, because these changes have the potential to affect significantly the global carbon budget.

Reference: Gatti et al., 2021 Nature, https://doi.org/10.1038/s41586-021-03629-6

19 Community tools for developing integrated observation sets: ICP2 and Obspack

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Over the last several decades many laboratories have begun programs to measure atmospheric greenhouse gas concentrations in an effort to better assess and understand background levels and regional fluxes. Additional observations are critical to modeling efforts and to our understanding of these gases impact on the environment, but are only useful if they can be merged with existing measurements. This presentation will highlight two tools that NOAA offers the measurement community to assist with this objective.

To detect bias in measurements it is fundamental to conduct routine, ongoing comparisons with independent measurements. There are a variety of strategies used by laboratories to isolate and compare different parts of the complete measurement path. These include co-located sampling to assess the entire measurement procedure as well as comparison activities designed to target and test aspects of the measurement path, for example, the scale transfer assessment by the WMO Round Robin experiments. Dedicating resources to develop tools to analyze and review results of these comparisons can be difficult for both new and established programs. The NOAA Inter-Comparison Program (ICP2) is a web based tool that is freely available to the community for comparing datasets with co-located NOAA data as well as data from other available programs. We will discuss recent updates, future plans and ways programs can use this informative tool.

As critical as producing quality data is, what happens to the data next is just as important. One of our most fundamental responsibilities as data providers is to make that data available to the public for research, educational and other scientific purposes. The ObsPack data distribution system was introduced nearly a decade ago as a means of normalizing data formats, providing context for interpretation with self describing metadata and ensuring proper attribution for data providers with robust citation and attribution instructions. We will discuss ongoing efforts to standardize this format so that ObsPack formatted datasets can be produced in a consistent way by individual labs.

20 EM27/SUN Measurements of Greenhouse Gases in Seoul

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Anthropogenic emissions from fossil fuel combustion increase the concentration of greenhouse gases in the atmosphere which has a significant impact on the global climate. To better manage atmospheric greenhouse gases, it is necessary to monitor and quantify emissions at all spatial scales, from national to regional and urban levels. In addition to using satellites providing global coverage with high space and time resolutions, several recent studies have measured the column-averaged concentrations of greenhouse gases using ground-based portable remote sensing Fourier transform infrared (FTIR) spectrometers. This study analyzes the column-averaged dry air mole fractions of CO_2, CH_4, and CO (XCO_2, XCH_4, XCO) in the atmosphere over Seoul using two ground-based FTIR spectrometers, EM27/SUN, which is the first to be done in South Korea. In addition, we compare our measurements with the Orbiting Carbon Observatory-2 (OCO-2), Orbiting Carbon Observatory-3 (OCO-3), and Sentinel-5 Precursor TROPOspheric Monitoring Instrument (TROPOMI). Together, this study aims to identify the three-dimensional structure of greenhouse gases in Seoul using remote sensing measurements, which has been difficult to do due to the absence of domestic greenhouse gas observation satellites, and use it for various studies in the future such as greenhouse gas behavior mechanisms, plume detection, and emission monitoring and verification.

This research was supported by the R&D Program for Oceans and Polar Regions of the National Research Foundation (NRF) funded by the Ministry of Science and ICT(NRF-2020M1A5A1110493).

21 Source attribution of urban methane in Seoul, South Korea

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Megacity Seoul, with their complex infrastructures, is recognized as one of the major methane sources in South Korea. Understandings of methane emission in urban area are still limited because the most of methane emissions are estimated by the approximated methane emission, not by the measurements. To quantify the methane source in urban area, this study focuses on mobile measurements of methane using the electric vehicle In Seoul, South Korea. Methane observations for the twenty-five districts in Seoul collected once a week from January 2022 using the LI-7810 CH_4 trace gas analyzer. The mobile measurements are mainly conducted at the roads, old residential area, commercial area, water treatment facilities, landfills, power plants, sewer networks in Seoul. The mobile measurements in this study show that major methane sources in Seoul are identified from the natural gas bus, shopping malls, old apartments, power plants, and water treatment facilities. The areas near to the methane source show the 200 to 3,000 ppb higher enhancements above background methane level (2,000-2,200 ppb). Our findings suggest that the large portions of methane source in urban area are still missing in the National Greenhouse Gas (GHG) inventory. To quantify better quality of national GHG inventory, it is required to precede the precise GHG observations.

This work was supported by Brain Pool Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (No.2019H1D3A1A01101988)

22 Non-Contact, Low-Cost Regional Greenhouse Gases Detection via 3D Laminated Graphene-Based Photoelectric Construct

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Greenhouse gas (GHG) monitoring is very important in responding to global climate change, but modern greenhouse gas measurement equipment is expensive, bulky, and installed in some areas, so there is a limit to real-time response. In addition, it is difficult to measure the atmospheric composition of living space due to the problem of the detection method used in the measuring device and the limitation of observation due to spatial and operational contingency. Here, we report a graphene-based photoelectric detector that provides low-cost and high-precision monitoring of GHGs regardless of the proximity of the gas to the sensor unit. Graphene photodetecting material stacked under high temperature and high pressure conditions, designed as a three-dimensional element to optimally absorb light energy passing through the greenhouse gas layer. As a result, the photoelectric detector showed accurate reactivity to 216 ppm of carbon dioxide, 0.06 ppm of carbon monoxide, and 0.88 ppm of a mixed gas of methane and carbon dioxide. More interestingly, when the incident light of 12 μW/cm^2 passed through the carbon monoxide atmosphere of 1.09ppm, it showed a high reactivity of 45

Keywords: graphene, greenhouse gas, photoelectricity, detector, low cost, sensitivity

23 CSIRO Aspendale site move: Implications and opportunities.

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CSIRO Aspendale, the home of Australia's atmospheric observations since 1953, is scheduled to close in 2023 with all staff and facilities to move to a new location. This plan has prompted a science strategy driven review of the infrastructure and functionalities currently located at Aspendale and a lengthy process of laboratory design and consultation. This move, while challenging, is an opportunity to renew our infrastructure and instrumentation to position CSIRO to best address future challenges.

Here we will outline:

- the science review process, strategy outcomes and "20-year" vision
- the key functionalities identified and infrastructure requirements
- pre-move work - new location investigations and site clean up
- laboratory design and consultation process and preliminary plans

We do this to:

- prompt discussion - where will GHG measurement technology be in 20-years? And what laboratory infrastructure will that require?
- highlight the challenges such a move brings
- gather feedback from the wider measurement community and draw from their collective wisdom

24 ICOS Cities Integrated city observatories for innovative greenhouse gas measurements

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The time has come to develop a long-term perspective for city observatories in connection with the European research infrastructure landscape. PAUL aims to support the European Green Deal by solving specific scientific and technological problems related to the observation and verification of greenhouse gas (GHG) emissions from densely populated urban landscapes. These are fossil fuel emissions hotspots and are therefore at the heart of emission reduction efforts globally.

ICOS Cities aims to increase our understanding of specific needs of greenhouse gas emission assessment in urban environments by comparing available and novel observational approaches and implementing an integrated concept for a city observatory. The unique feature however is an innovative approach promoting the co-design principles to create services, models and observations between city administrators and scientists from multiple disciplines including social and governmental sciences.

This project will open the door for services for cities that support evidence-based climate action-related decisions and strategic investments. The objectives are as follows:

- Bring together and evaluate different observational approaches to determine fossil fuel CO2 emissions in cities.
- Develop research infrastructures further, and provide concepts to facilitate science and services.
- Collaborate with city stakeholders and engage citizens in co-designing services that are required for GHG monitoring in order to validate the implementation of the Paris Agreement
- Increase our understanding of specific needs of GHG assessment in urban environments and create a service portfolio for setting up an urban greenhouse gas observatory.

25 Towards implementing an optical method for N_2O analysis at the CCL

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The NOAA Global Monitoring Laboratory has served as the CCL for nitrous oxide since 2003. In that capacity, we have used gas chromatography with electron capture detection to define, implement, and transfer the WMO N_2O calibration scale. While this method has served the WMO/GAW community well, achieving a scale transfer uncertainty of 0.2 ppb (2-sigma), advances in optical methods for N_2O analysis offer superior performance. We have explored N_2O analysis for calibration purposes (dry air in aluminum cylinders) using two different optical analyzers, looking at linearity, repeatability, and stability. We will report on these studies, as well as experiments investigating the impact of argon in the matrix gas of gravimetrically-prepared standards.

26 Monitoring large CO_2 emissions on a facility-level by satellite

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To achieve carbon neutrality by 2050, accurate estimation of CO_2 emissions is needed. It is especially required for large point sources such as power plants or heat plants, not only because they are the sources of massive amount of CO_2 emissions, but also they are the targets of newly developing carbon reduction technologies. Therefore, many countries, including South Korea, stipulate large emitters to report their annual CO_2 emissions based on bottom-up approach, which is to estimate CO_2 emissions by multiplying energy consumption and the corresponding emission factors. However, discrepancies between true and the reported emissions may occur due to limited data, non-reported or omitted activities, or incomplete/undeveloped emission factors. As one way to resolve such discrepancies, Intergovernmental Panel on Climate Change (IPCC) mentioned top-down approach, which is to assess CO_2 emissions based on its atmospheric concentrations, in their 2019 Refinement to the 2006 Guidelines. In applying top-down approach, satellite has broadened its usage from constraining CO_2 emissions only on a global scale to estimating CO_2 emissions on a facility level. In this study, we estimated facility-level CO_2 emissions and the emission uncertainties of large CO_2 emitters of South Korea based on atmospheric CO_2 concentrations retrieved from Orbiting Carbon Observatories-2 (OCO-2) of NASA. We determined plume candidates as the area that showed significant enhancement in CO_2 concentration and estimated facility-level CO2 emissions by applying simplified Gaussian plume model, which takes wind speed, wind direction and atmospheric stability into account. Uncertainties arising from errors related to satellite observation, wind speed, wind direction and background setting were aggregated to calculate total emission uncertainties. For some cases, we were able to compare our estimated CO2 emissions with the reported ones. Our study demonstrated satellite can be useful in monitoring large CO_2 point sources.

This research was supported by the R&D Program for Oceans and Polar Regions of the National Research Foundation (NRF) funded by the Ministry of Science and ICT(NRF-2020M1A5A1110493)

27 Side by side comparisons of FTIR and CRDS analysers for CO_2 and CH_4 in air: persistent biases and dealing with water vapour

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GAW compatibility requirements for measurements of CO_2 and CH_4 in background clean air are 0.05/0.10 ppm for CO_2 in the southern/northern hemispheres and 2 ppb for CH_4. This accuracy is dictated by the needs of transport models to resolve the scales of large scale sources, sinks and fluxes of these climate-critical trace gases. Realising these compatibility limits across different instruments, measurement technologies and site locations is a very challenging task.

We have run three extended periods of side by side simultaneous measurements of Spectronus FTIR and Picarro CRDS analysers on the Australian research ship and mobile GAW site RV Investigator, at Kennaook/Cape Grim GAW station, and in the lab at the University of Wollongong. We see persistent biases between analysers of up to 0.4 ppm CO_2 and 2 ppb CH_4 . In all cases analyser calibrations are referenced to the same calibration gases and the analysers agree within GAW compatibility limits when measuring dry gases.

For air samples, in the FTIR the sample air is dried before measurement, while the CRDS measures ambient or partly-dried air and uses a correction for the water vapour effect. In this work we have investigated the treatment of water vapour in these measurements – the effects of drying in the case of FTIR, use of a chiller and improving the water vapour correction in the case of CRDS. The work is still ongoing but we suspect the existing CRDS droplet test-based water vapour corrections may not be accurate enough to meet the demanding GAW compatibility requirements.

28 A study on equivalence evaluation for continuous measurements of greenhouse gases with GC analysis method

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As global warming has become a social and economic issue, the World Meteorological Organization (WMO) is operating a Global Atmosphere Watch (GAW) program to monitor green house gases. About 100 countries are participating in the GAW Programme and there are now over 400 regional stations monitoring green house gases like CO_2, CH_4 and N_2O. These observations are important data for creating scenarios for climate change status and future climate change. Therefore equipment validation and establishing standards for quality assurance are important. In addition, since moisture in the atmosphere is known to affect the accuracy of the measured values, research on the influence of moisture is needed for accurate measurement. Therefore, in this study, the continuous gas analyzer commonly used in greenhouse gas observing stations was compared with the GC analysis method, and a comparative test was conducted on the accuracy of the measured values and the relative accuracy between equipment. In addition, the effect of moisture on the measured value was tested, and we compared how the removal of moisture from the pretreatment device affects the results.

29 High methane sources in the outskirt of metropolitan are detected by aircraft and mobile observations

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Atmospheric methane concentrations are largely contributed by anthropogenic emissions. We conducted both aircraft and mobile measurements in February and March 2021 and found high methane concentrations in the atmosphere over the outskirt of metropolitan areas. The observed methane emissions are 200 to 380 ppb (10% to 20 %) higher than in the surrounding area and are on averagely 12.6% ~ 16.5% higher than the monthly average methane level at the Mauna Loa Observatory in Hawaii. We used a tracer dispersion model combined with the Weather Research and Forecasting model and Stochastic Time-Inverted Lagrangian Transport model (WRF-STILT) to find the emission sources. The WRF-STILT model calculates the footprints of methane-based on meteorological variables at local hotspots of methane. Based on the analysis of results, high methane concentrations are associated with complex sources from facilities located near the metropolitan areas, i.e., intensive pig farm areas, industrial complexes, and landfill areas. We also found unknown high levels of methane concentrations over unknown landfill areas, but these are not accounted into the current methane inventory. The study highlights the current low level of understanding of domestic methane emissions and the importance of methane monitoring systems to achieve carbon neutrality.

30 Development of a dynamic calibration system for COS in air mixture at ambient levels

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COS has recently received increased attention as a potential tracer for carbon cycle because COS is irreversibly taken up by photosynthesis of plant vegetation unlike carbon dioxide. Due to this unique feature, COS can be used to estimate gross primary production (GPP) from local to global scale based on atmospheric observation. However, long-term atmospheric measurements have been very limited. A lack of reliable standard gas of COS at ambient level (ca. 500 ppt) is one of the major reasons. In this study, we developed the dynamic calibration system which can generate COS reference gas at atmospheric mole fraction level accurately. The system uses gravimetrically-prepared standard gas containing ~5 ppm COS, which is known to be relatively stable. The parent gas is diluted more than 2000 times with pure nitrogen using thermal mass flow controllers with rigorous pressure control. The mass flow rates of the parent and diluent gases are measured with high-precision flow meters, and the flow ratios are used to calculate mole fractions of COS in the diluted gas mixture. In this presentation, we will show the detail system configuration and results from experiments for evaluating dilution performance including repeatability, reproducibility, and linearity as well as for validating dilution accuracy. These results demonstrated that the developed dilution system is capable of dynamically generate reference gas standards of COS at the atmospheric level accurately, which allows to detect long-term trends in atmospheric COS.

31 International comparison of isotope ratio measurement capabilities for CO_2: From pure CO_2 to CO_2 in air samples

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During 2021, the BIPM and the IAEA conducted the international comparison CCQM-P204 on samples of four pure CO_2 with nominal carbon isotope delta values, $\delta^{13}C_{VPDB}$, of -42 ‰, -35 ‰, -9 ‰and -1 ‰. The level of agreement amongst the participants over this extended range will be discussed, and lessons learned from this exercise will be incorporated into the next international comparison on CO_2 in air samples, to be organized in 2023.

The need for improved quality infrastructure and appropriate reference gases for CO_2 isotope ratio measurements has been a driver for recent research and development activities within the National Metrology Institutes, and the decision of the Gas Analysis Working Group of the CCQM to plan an international comparison (CCQM-P204) of capabilities of measurements of these quantities. As part of the comparison, BIPM prepared 120 comparison samples (30 of each CO_2 gas) in 12 batches of 10 and, together with the IAEA, monitored the homogeneity and stability on a subset of 24 samples. The IAEA assigned the isotopic composition of one sample per batch on the VPDB scale with traceability via the IAEA-603 carbonate reference material. The BIPM sample preparation facility is able to blend different pure CO_2 sources to achieve a target $\delta^{13}C_{VPDB}$, using accurate flow measurements.

Analytical measurements (Dual Inlet IRMS) in both institutes demonstrated excellent homogeneity and stability of the samples, with variances reaching less than 0.005 ‰, ensuring the level of agreement between participants as a function of nominal value could be correctly demonstrated. Extensive information provided by the nineteen participants will allow the coordinators to develop recommendations for achieving accurate isotope ratio measurements using the two methods employed: IRMS and IRIS (Isotope Ratio Infrared Spectroscopy). The comparison will also identify any differences in implementing traceability to VPDB and the needs for harmonization of practices to reduce inter-laboratory variances. Lessons learned from this comparison will be incorporated into the next exercise to be conducted by the BIPM on CO_2 in air samples in 2023, for which an automated CO_2 extraction system has been developed and is being validated with reference materials prepared by the NPL. In this next comparison, participants will be invited to send two samples of their choice, within the carbon delta values -42 ‰and 1 ‰, and CO_2 amount fraction range between 350 umol mol^{-1} and 800 umol mol^{-1}. Expert laboratories routinely performing $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ measurements of carbon dioxide in the atmosphere will be invited to participate in the exercise.

32 UAV atmospheric mapping applications using an improved low-cost NDIR sensor

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Unmanned Aerial Vehicles (UAVs) provide a cost-effective way to fill in gaps between surface in-situ observations and remote-sensed data from space. In this study, a novel portable CO_2 measuring system suitable for operations on-board small-sized UAVs has been developed and validated. It is based on a low-cost commercial nondispersive near-infrared (NDIR) CO_2 sensor (Senseair AB, Sweden), with a total weight of 1058 g, including batteries. The system performs in situ measurements autonomously, allowing for its integration into various platforms. Accuracy and linearity tests in the lab showed that the precision remains within ± 1 ppm (1σ) at 1 Hz. Corrections due to temperature and pressure changes were applied following environmental chamber experiments. The accuracy of the system in the field was validated against a reference instrument (Picarro, USA) onboard a piloted aircraft and it was found to be ± 2 ppm (1σ) at 1 Hz and ± 1 ppm (1σ) at 1 min. Due to its fast response, the system has the capacity to measure CO_2 mole fraction changes at 1 Hz, thus allowing the monitoring of CO_2 emission plumes and the characteristic of their spatial and temporal distribution. Details of the measurement system and field implementations are described to support future UAV platform applications for atmospheric trace gas measurements.

33 Measurements of stable carbon isotope ratio of methane at Hateruma Station, Japan

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Hateruma island is the southernmost inhabited island of Japan. As the place is in the downwind of the continental East Asia in winter, arrivals of air masses of continental origin cause synoptic-scale variations (i.e., high-concentration events in CO_2, CH_4 etc.). We have collected air samples so as to coincide with such high-CH_4 events, and those air samples have been analyzed for stable carbon isotope ratio of CH_4 (δ^{13}C-CH_4) since December 2017 by using a continuous-flow preconcentration and isotope ratio mass spectrometry system. In this study, we present our experimental method for δ^{13}C-CH_4 analysis including our attempts to assure data quality. We prepared a compressed dry air as a working standard as well as a set of three surveillance cylinders (CH_4 in synthetic air) that cover a wide range of δ^{13}C-CH_4 values (from -68 to -26 per mil VPDB). Two-year measurement records show that the three surveillance cylinders have indicated no significant drifts. and that the standard deviations of the measured values for the individual cylinders are about 0.1 per mil. It is also observed that the span of our δ^{13}C-CH_4 measurement (difference of the measured values of the cylinders with high and low δ^{13}C-CH_4) has been constant over time. Although temporal drift needs to be monitored for a longer period, we consider that performance of our system is satisfactory to identify synoptic-scale variations at Hateruma island and to infer δ^{13}C-CH_4 signatures of the continental CH_4 sources.

34 On-demand comparisons of CO_2 in air standards and scale relationships

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The operation and validation of facilities for on-demand comparisons of CO_2 in air standards (BIPM.QM-K2), across the range (350 to 800) μmol/mol and the determination and monitoring of CO_2 in air scale relationships (BIPM.QM-K5) will be described.

Generating the highest precision measurements of CO_2 in air requires adopting the scale approach to metrological traceability and with the expected increase in demand for such measurements, for example around urban areas, instigating the development of local scales that permit reporting of results on one common scale. The conversion of CO_2 in air amount fraction values from one scale to another requires the scale relationships to be well known, noting that the requirement for internal consistency of standards within a scale, such as the WMO-CO_2-X2019 scale, is at the 0.01 μmol/mol level, and consistency between different scales should not exceed the 0.02 μmol/mol level [1]. The on-demand comparison, BIPM.QM-K5, is being designed with the support of the CCQM Task Group of Greenhouse Gas Scale Comparisons [1], to determine and monitor scale relationships. The BIPM facility for the comparison is based on two ensembles of 9 standards, over the range (350 to 800) μmol/mol, that have been value assigned by the manometric system maintained at the BIPM. High precision measurements of the internal consistency of standards within an ensemble with a laser-based instrument that targets the major CO_2 isotopologue, and measured values of isotope ratios within the standards, allows CO_2 amount fraction scale values to be determined for that ensemble of standards. The ensembles can then be compared with each other and other scale defining standards to determine their relationships.

The BIPM manometric system will also be used to compare SI traceable amount fractions of CO_2 in air standards, with the facility operating with repeatability reaching 0.02 μmol/mol and standard measurement uncertainties of 0.1 μmol/mol, and on-demand comparisons available as BIPM.QM-K2. The performance of the facility is undergoing final validation within the CCQM-P225 study, with comparison with independent primary standards from 6 laboratories including NOAA, which fulfils the role as the WMO CCL. The facilities and progress with comparison exercises will be presented.

[1] CCQM-GAWG Task Group on GHG Scale Comparisons (CCQM-GAWG-TG-GHG) https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-gawg-tg-ghg

35 Re-evaluation of long-term atmospheric $^{14}CO_2$ records of the Heidelberg cooperative background air sampling network

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Atmospheric $^{14}CO_2$ observations are important boundary constraints in many fields of biogeochemical sciences, where ^{14}C is applied as a tracer or for dating purposes. For global carbon cycle research, consistent and long-term $^{14}CO_2$ time series are particularly valuable as they are used to study exchange and mixing processes in the different compartments of the carbon cycle.More than 60 years ago, the first atmospheric $^{14}CO_2$ measurements were conducted in the Heidelberg Radiocarbon Laboratory. This led, in the course of the 1980s, to the establishment of a global cooperative background air sampling network for high-precision atmospheric $^{14}CO_2$ observations. One remarkable feature of this network is that the sampling and analysis methods have been refined but never fundamentally changed from the 1970s until today. This supports the long-term consistency of the observations and allows for consistent re-evaluation of the historical time series. We have revisited the historic atmospheric $^{14}CO_2$ measurements of the Heidelberg Radiocarbon Laboratory. Therefore, the raw data from the early '80s onwards were transferred to the ICOS Central Radiocarbon Laboratory database and re-evaluated in the same way as ICOS $^{14}CO_2$ data are evaluated today. We investigated the calibrations of the gas proportional counters and their link to the international ^{14}C scale via different working standards used from the '80s until today and derived corresponding calibration uncertainties. We discuss the reproducibility of the $^{14}CO_2$ measurements and their temporal change using multiple analyses and other quality control measures. The re-evaluated $^{14}CO_2$ background air records were compared to available background $^{14}CO_2$ records from other laboratories to identify potential inter-laboratory differences. Thereby the analysis period in 2010/11 could be identified, in which the measurements of the Heidelberg Radiocarbon Laboratory are systematically elevated. The time period in question was narrowed down by analysing archived $^{14}CO_2$ samples from the network, and the affected analyses in the questionable period were flagged. Selected re-evaluated long-term $^{14}CO_2$ records of the Heidelberg cooperative sampling network were published on the ICOS Carbon Portal and are freely accessible. The publication of the remaining $^{14}CO_2$ records is in progress.

36 Assessment of international standards on the carbon isotope VPDB scale

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Carbon isotope measurements are now commonplace in nearly all scientific fields, from palaeoclimate, medical, forensic, through to atmospheric research. In some fields like food adulteration studies, carbon isotope analyses may be applicable to legal proceedings. In others, like atmospheric sciences, very small natural variations need to be detected and inter-laboratory measurement compatibility goals are high (δ^{13}C-$CO_{2(atm)}$: 0.01 ‰). Stringent standardisation of carbon isotope measurements is especially important in these instances.

In case of carbon isotope measurements the primary standard is a calcium carbonate called NBS19, which defines the Vienna-PeeDee Belemnite scale (VPDB). Since 2006 LSVEC, a lithium carbonate has been used as a second anchor point on the VPDB scale.

Unfortunately LSVEC is isotopically unstable and NBS19 is no longer available to the wider scientific community. IAEA-603 has replaced NBS19, and two separate studies have been made that propose replacement materials for LSVEC. One was led by IAEA producing IAEA-610, 611 and 612 calcium carbonates, and the other by USGS proposing USGS44 calcium carbonate as a LSVEC alternative. Whether these new VPDB carbon isotope scale affecting standards will lead to a scale revision is under discussion in expert meetings. In the meantime, more data needs to be produced to provide a solid information base for any future decision that may be taken by for example IAEA experts, or the Commission on Isotopic Abundances and Atomic Weights (CIAAW).

Here we assess instrumental challenges that affect carbon isotope value assignment to calcium carbonate standards. We compare different approaches to the phosphoric acid reaction which is required to produce CO_2 from calcium carbonates. Furthermore we assess the impact of analyzing identical CO_2 samples in different laboratories. Finally, in the course of this study, we marry the proposed LSVEC replacements produced through separate attempts, IAEA-610, -611, -612 and USGS44, and discuss advantages and disadvantages of a possible future carbon isotope scale revision.

37 OBS4CLIM: French investment for an Integrated Observing System for the Atmosphere - Description of the greenhouse gases component

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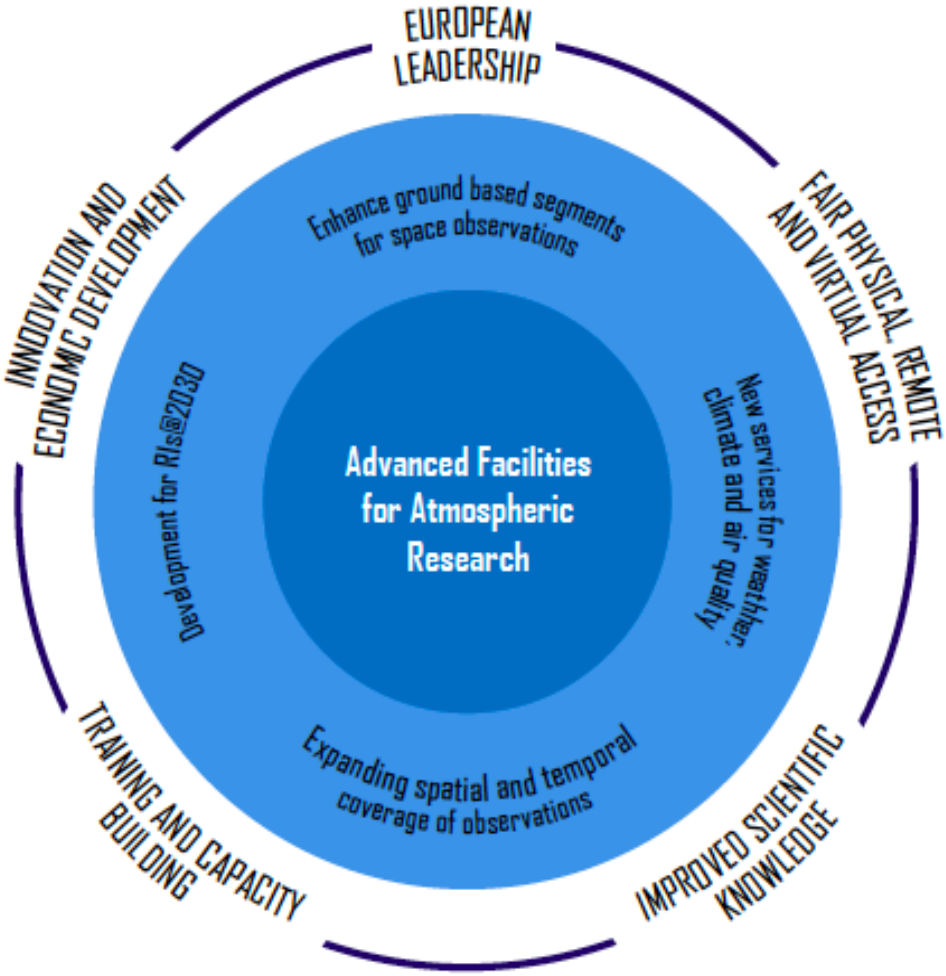
OBS4CLIM is a project led by 18 partners coordinated by the CNRS aimed at developing the innovation of the three French components of European research infrastructures (IR) in the field of the atmosphere: ACTRIS, IAGOS, and ICOS. OBS4CLIM is the EquipEx project of the entire atmosphere community at the national level, and will allow the three French IR mirrors (ACTRIS-FRANCE, IAGOS-FRANCE, ICOS-FRANCE) to meet the new challenges posed to Earth observation and to provide their users with qualified and relevant datasets, as well as innovative services. The project is organized in four actions:

- Support in-situ observations for the validation of satellite data.
- Strengthen the provision of data and services for air quality, climate and meteorological services.
- Extend the spatial and temporal coverage of observations and complete the research platforms.
- Prepare IRs for new observation technologies.

The poster will present the investments specific to greenhouse gas measurements, and the interactions with other observation programs. The main developments for greenhouse gases concern total column and vertical profile measurements, isotopic measurements, the use of mid-cost sensors, flux measurements, and the development of a new generation of analyzers with a view to measurements on board TGVs on national territory, as well as on board commercial aircraft within the framework of IAGOS. The OBS4CLIM program is organized in close collaboration with national observation sites as well as the centers of expertise part of the IRs. It is also developed in consultation with the national data center to ensure traceability and the dissemination of observations to users.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New services for weather, climate and air quality
Expanding spatial and temporal coverage of observations
Development for RIs@2030
Advanced Facilities for Atmospheric Research

38 Seven years of measurements of atmospheric methane at the Chacaltaya GAW regional station

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Continuous measurements of methane concentrations were made at the Chacaltaya GAW station (5240 m a.s.l.) in the Bolivian Andean Cordillera since 2015. During this period two high-precision Picarro-CRDS analyzers were used at the station, regularly calibrated with internationally certified gases (WMO X2004A) via the LSCE primary scale. The site has a privileged location not only for its altitude but also because it can sample air masses arriving from the near Altiplano (3 800 m a.s.l.), the Amazon, the Pacific Ocean, and the nearby metropolitan area of La Paz/El Alto (˜2 million of inhabitants). The complex topography of the region represents a challenge for deconvoluting the origin of the air masses and therefore to understand the sources and/or processes associated to the measurements made at Chacaltaya. The influence of the local atmospheric planetary boundary layer is clearly seen in the measurements, especially in the late morning, but collocated measurements of other atmospheric components as carbon monoxide or equivalent black carbon has proven that identifying free-tropospheric air masses is not an easy task. Here we show some results from the analysis of back trajectories obtained from using high and medium-resolution numerical weather models in order to identify the most important areas that influence air masses arriving to Chacaltaya, as well as satellite products, like TROPOMI and other related products as GFED4.1s and WAD2M to characterize and interpret daily, seasonal and interannual behavior of the methane concentrations observed at the station.

39 MIRO Analytical's MGA10: A single device for green-house gas and air quality monitoring

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Monitoring of air pollutants and greenhouse gases with high precision and selectivity is important to identify their sources and sinks, develop reliable models to predict air quality and ultimately to combat air pollution and climate change.

MIRO Analytical's new trace gas analyzers are capable of monitoring up to 10 gases simultaneously. These analyzers use direct laser absorption spectroscopy and combine several Quantum Cascade Lasers as light sources. The analyzers provide highest precision combined with best selectivity thanks to their operation in the mid-infrared spectral range. By monitoring green-house gases (CH_4, N_2O, CO_2) and air pollutants (NO, NO_2, CO, NH_3, SO_2, O_3) our analyzers can serve as an all-in-one solution for ambient air monitoring.

Due to their compactness, high precision and stability our analyzers are well-suited for installation in monitoring stations as well as for mobile monitoring. The multi-compound ability opens new possibilities for emission source attribution and for studies of interactions of different trace gases. In this contribution we will shortly introduce the new MGA10 multi-compound gas analyzer and will present examples of measurement campaigns that were recently performed by our customers.

40 Long-term performance of a dual-laser absorption spectrometer for measurement of $\delta^{13}C$, $\delta^{18}O$, and $\Delta^{17}O$ of CO_2

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We present an overview of the long-term performance of our Stable Isotopes of CO_2 Absorption Spectrometer (SICAS) since it was taken into use in 2017 at the Centre for Isotope research (CIO) in the Netherlands. The SICAS is used for measuring the $\delta^{13}C$, $\delta^{18}O$, and excess $\delta^{17}O$ or $\Delta^{17}O$ ($\Delta^{17}O = ln\ (1 + \delta^{17}O) - \lambda * ln\ (1 + \delta^{18}O)$) and the total CO_2 mole fraction of whole air atmospheric samples (Steur et al., 2021). Calibration of stable isotope measurements using spectroscopy can be done using measured isotopologue amounts or using measured delta values in a whole air matrix (Griffith, 2018). We have evaluated the accuracy and precision of the two calibration methods for various air samples and CO_2 reference materials on the SICAS.

For daily calibration of SICAS measurements we use a suit of high-pressure cylinders filled with dried air at various CO_2 mole fractions. The cylinders were measured for the CO_2 mole fraction at the CIO using cavity ringdown spectroscopy (CRDS) linked to the WMO-2019 scale, while the stable isotope composition was measured by the Max-Planck-Institute for Biogeochemistry in Jena (for $\delta^{13}C$ and $\delta^{18}O$ linked to the JRAS-scale) and the Institute for Marine and Atmospheric research in Utrecht (for the $\delta^{17}O/\delta^{18}O$-ratio needed to determine $\Delta^{17}O$). To check the agreement between our in-house reference scale and the international VPDB-CO_2 scale we measured several CO_2 primary reference materials on the SICAS. To do so, pure CO_2 was produced from NBS-19, IAEA-603 and USGS-44 and subsequently diluted to 400 ppm in CO_2 free air. Work is on-going on optimising the dilution process so we will be able to establish our own isotope scale for the SICAS, directly linked to the primary reference material(s), and coupled to IRMS CO_2 measurements conducted at the CIO.

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41 The Parisian component of ICOS Cities

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¡strong¿The Parisian component of ICOS Cities¡/strong¿

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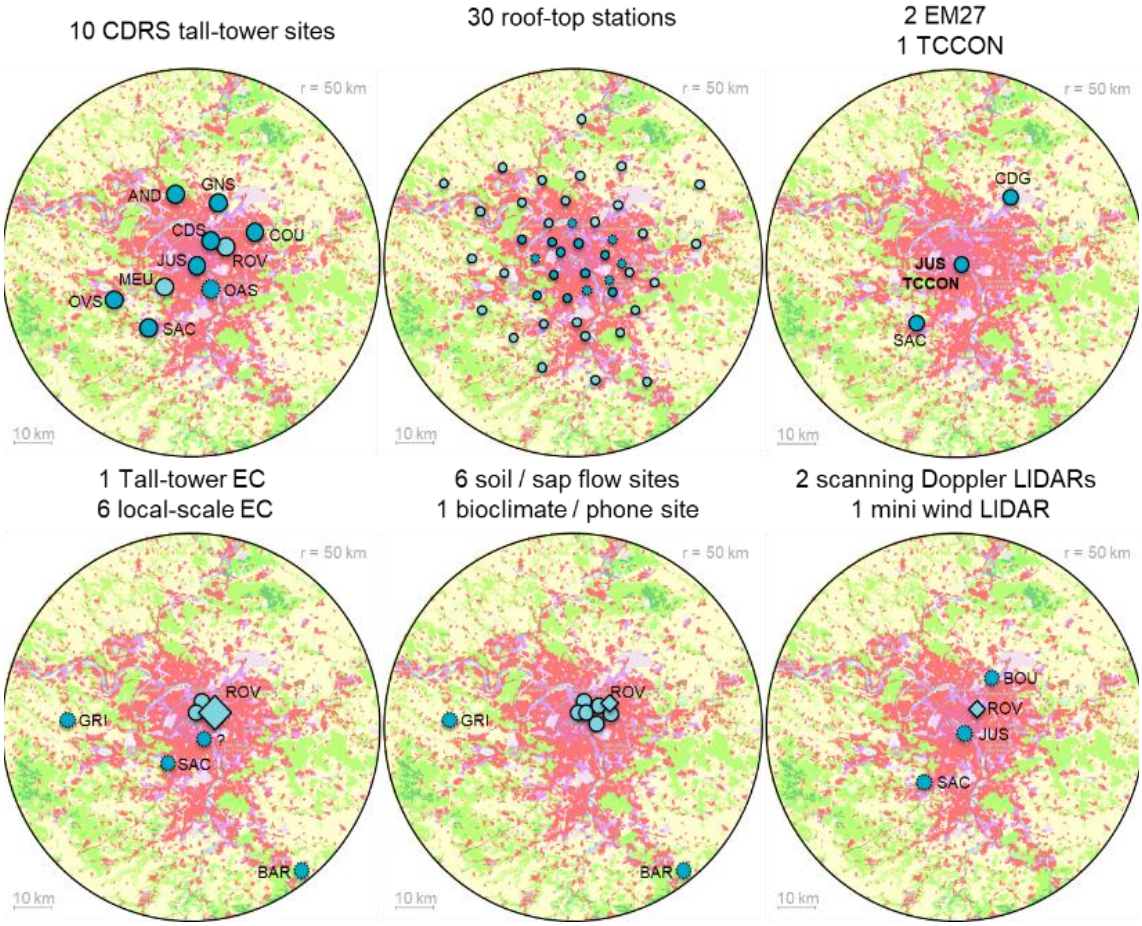
Urban areas contribute to a large share of global and European fossil fuel emissions. Cities are therefore at the heart of emission reduction efforts. The ICOS Cities project (www.icos-cp.eu/projects/icos-cities-project) will develop systematic observations to continuously monitor greenhouse gas emissions and emission reductions in urban areas. In order to test the feasibility of different observational and modelling approaches three cities of different size have been selected to develop pilot observatories: Paris, Munich, and Zürich.

We will present the observation program currently being established in Paris. Starting in October 2022, the project will provide continuous and grab sample data for a period of 2 years. The project's observation network will include: 10 high-precision CO_2, CH_4 and CO measurement sites; 30 intermediate precision CO_2 measurement sites, including ˜5 with air quality measurements; 3 to 4 measurement sites for total columns of CO_2, CH_4, CO; 7 flux measurement sites by eddy-covariance, one of which is on a high tower about 100m high; 6 ecosystem measurement sites; and up to 7 sites equipped with doppler wind lidars. Among the measurement sites, two high towers located on the outskirts of Paris will measure, in addition to greenhouse gases, several tracers such as NOx, black carbon and Radon-222. Regular samples will also be taken at these sites, as well as at the ICOS tower in Saclay, 20 km to the south-west of Paris, for the measurement of $^{14}CO_2$ by the

ICOS Central Radiocarbon Laboratory. The poster will present in particular the strategy for evaluating sensors and measurement sites, as well as the collaborations set up between ICOS-Cities and other European projects such as RI-URBAN and URBISPHERE which will deploy other types of atmospheric observational systems in Paris ahead of the 2024 Olympic Games.



42 Gravimetric Constraints on the Absolute Stability of the SIO O_2 Program $\delta(O_2/N_2)$ Scale

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The Scripps O_2 program has been measuring changes in the O_2/N_2 ratio at background sites since the early 1990s. In order to maintain a 30+ year time series this requires successful propagation of declared values from one tank to another. To minimize this source of error, the program has maintained a heterogeneous suite of long-term reference cylinders, referred to as primaries, comprised of tanks with varying volumes and materials. To correct our scale for long-term drift we assume that any shared drift among the primaries is due to scale drift from the secondaries, fit a curve to the observed primaries, and apply it as a correction to samples. This approach assumes that the primaries are not drifting, and means that any primary cylinder drift will be imposed onto the observations as an artifact. Keeling et al (2007) discussed potential sources of primary cylinder drift and constrained them to the degree possible, using some physical assumptions. To further this analysis we have revisited measurements of gravimetric standards made at various times throughout the lifetime of the program. We discuss an analysis of two sets of gravimetric standards, one prepared in 1992-1993 by R. Keeling in the lab of Jim Elkins, and the other prepared in 2017-2018 by N. Aoki. Since the cylinders themselves may drift with usage, we only consider the first measurements after preparation of each set. To complement this two point anchor, we also use a simplified forward model of our scale propagation. The two sets of gravimetrics imply a drift of the SIO O_2 program S2 scale of -10 $\pm$21 per meg over 26 years. While this is still compatible with a scale drift of 0, we speculate that this is likely due to long-term surface reactions in the steel primaries, based on the observed relative drift between steel and aluminium cylinders with different surface treatments. We discuss these findings within the context of the estimated uncertainty of the S2 scale, updated from the Keeling et al (2007) analysis.

Aoki, et al., 2019. "Preparation of primary standard mixtures for atmospheric oxygen measurements with less than 1 μmol/mol^{-1} uncertainty for oxygen molar fractions". *Atmos. Meas. Tech.*, 12, 2631-2646.

Keeling et al., 2007. "On the long-term stability of reference gases for atmospheric O_2/N_2 and CO_2 measurements". *Tellus*, 59B, 3-14.

43 21th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2022) – Utrecht – 19-21 September 2022

simona latchabady
LSCE
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21th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2022) – Utrecht – 19-21 September 2022 Urban and tropical EM27/SUN network for satellite validations, observations and verification of greenhouse gas emissions

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The EM27/SUN instrument is a FTIR spectrometer allowing to retrieve total atmospheric column abundance of CO_2, CH_4, CO and H_2O. Its major strength is to be easily transportable, therefore it can be used for short-term campaigns, as well as for long-term deployment, or used in projects framework. The LSCE is currently involved in two projects in which the EM27/SUN instruments will be deployed in different environments for different purposes.

The OBS4CLIM project aims at deploying four EM27 by 2023 at observatories located in tropical and background regions for long-term observations and satellite validation purposes.

The PAUL (Pilot Applications in Urban Landscapes) project aims at evaluating different observational approaches to determine CO2 emissions from large cities, such as Paris. A chosen strategy consists in evaluating the Paris carbon budget by coupling total column measurement to inverse modelling. In the PAUL framework, two EM27 are deployed in a north to south transect of Paris, in addition to the Paris TCCON site.

The rapid growth of this EM27/SUN network requires developing tools to ensure data quality and availability. Therefore, LSCE has developed:

- An automatic data treatment chain based on PROFFAST (developed and maintained at KIT) which has three calculation steps: pre-processing, cross-section calculation, and spectra inversion. Several models are used as a priori profiles (GGG2014, GGG2020, and CAMS) allowing to retrieve daily data in near real-time to ensure rapid problem detection and thus high data availability. Moreover, the data processing has been parallelized to obtain a short computation time.

- Automatic enclosure systems to protect the instrument from a rough environment. This system allows increasing drastically the daily observations and data availability.

In the proposed poster, we will present in detail these two major developments that are necessary to obtain a robust network providing semi-continuous observations in near real time. Future improvements and feedback will also be presented. Finally, results from sensitivity studies to the used models for data retrieval, that are based on our numerous EM27/SUN observations, will be shown.

44 The NOAA High-altitude Operational Returning Uncrewed System (HORUS) for Atmospheric Observing

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NOAA's Global Monitoring Laboratory facilitates the global collection of high-accuracy, in situ balloon-borne measurements of ozone and water vapor to approximately 30 km above mean sea level with long-standing records dating back to 1967 and 1980, respectively. The development of NOAA's balloon-borne AirCore atmospheric sampling system (circa 2011) has enhanced these stratospheric observational records with the ability to derive calibrated, near-total column trace gas profiles of carbon dioxide, methane, carbon monoxide, nitrous oxide and sulfur hexafluoride traceable to World Meteorological Organization trace gas standard scales, alongside stratospheric profiles of chlorofluorocarbons and halons. AirCore trace gas profiles collected on a monthly basis over the past eleven years comprise one of the longest-standing observational records of stratospheric trace gases in the world. They contribute significantly to our understanding of atmospheric composition and dynamics in the stratosphere, global model evaluation of trace gases, and surface and space-borne remote sensing evaluation efforts. The requirement for AirCores to be quickly and efficiently recovered upon landing for analysis of air samples and cost recovery of instrumentation, however, is one limiting factor in expanding AirCore sampling to more remote regions.

Driven by the need to both expand AirCore trace gas sampling locations and improve its feasibility of recovery, we have combined the idea of a low-cost, portable small uncrewed aerial system with small-balloon (3000 g) technology to develop a custom glider platform capable of returning balloon-borne scientific equipment from the stratosphere in a controlled manner. With the ability to efficiently recover and reuse high-quality atmospheric sensors from altitudes that manned aircraft are incapable of reaching, this platform has the potential to transform high-altitude atmospheric observing capabilities; to expand profiling locations to climate-relevant regions over land or at sea; to increase satellite evaluation efforts in remote regions and to potentially improve upon weather and climate forecast model predictions with the ability to return and re-calibrate balloon-borne sampling and measurement systems. Over the past two years, the NOAA High-altitude Operational Returning Uncrewed System (HORUS) and its technology has been designed, developed, successfully tested to 75,000 ft above mean sea level, and brought to an operational technology readiness level. We detail these efforts, necessary next steps toward operational HORUS flights in the United States, and the value of this observing platform for global, low-cost atmospheric observing in the upper troposphere and lower stratosphere.

45 Detection of Hazardous Air Pollutants and Greenhouse Gases at Ultra-trace Levels using Broad Band Cavity Ring Down Spectroscopy

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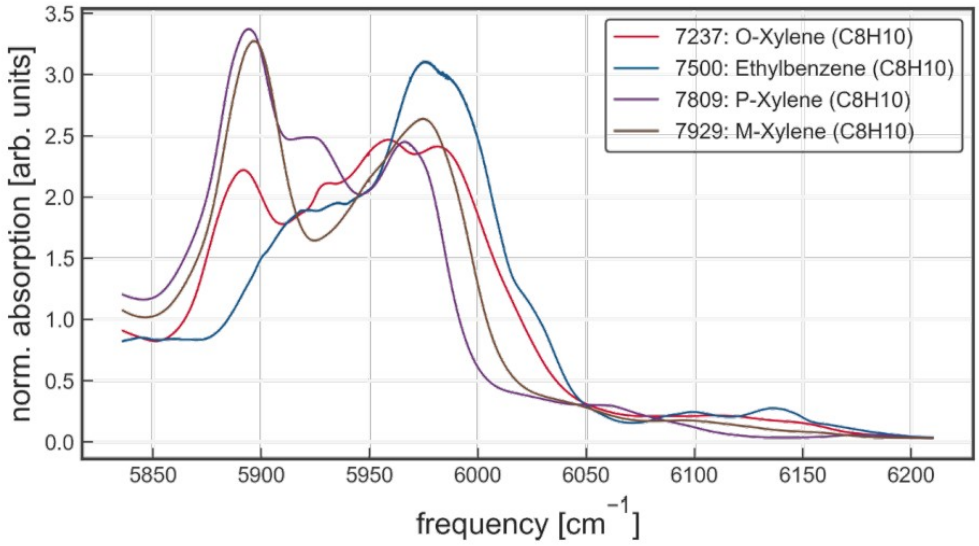
Hazardous Air Pollutants (HAPs) comprise a list of gaseous compounds that have long been recognized to have an adverse effect on human health or on the environment. Despite their importance, there are few measurement techniques suitable for the measurement of HAPs. The analytical techniques that do exist are poorly suited to field deployment, due to poor detection sensitivity, insufficient time resolution, and/or challenging and costly field deployment. In recent years, robust laser-based instrumentation has been developed for environmental pollutants such as formaldehyde and hydrogen sulfide and well as greenhouse gases. Laser-based instruments are simple to deploy, requiring minimal calibration, and provide data in real-time. However, these instruments can only measure small compounds, with fewer than 6-8 atoms, due to the spectroscopy of larger compounds, which do not have the narrow (< 1 nm) spectral features that can be scanned with commonly available lasers. We present a new laser-based instrument for measuring HAPs, based on a novel spectroscopic technique called Broad Band Cavity Ring Down Spectroscopy (BB-CRDS). Using semiconductor lasers and a high-resolution wavelength monitor, we can collect a non-uniform sequence of wavelengths in a ˜100 nm band covering much of the C-H overtone band, with targeting accuracy of 0.25 picometers. When coupled to a high finesse optical cavity, hundreds of unique spectral points can be collected in about a second, enabling the real-time analysis of a dozen or more volatile organic compounds (VOCs), selected from a growing library of 100+ compounds. Here, we present field results collected with a prototype BB-CRDS analyzer that measures the BTEX compounds (benzene, toluene, ethyl benzene, and the three isomers of xylene), along with ammonia, hydrogen sulfide, an array of alkanes, and other common atmospheric constituents (GHGs).


7237: O-Xylene (C8H10)
7500: Ethylbenzene (C8H10)
7809: P-Xylene (C8H10)
7929: M-Xylene (C8H10)
norm. absorption [arb. units]
frequency [cm^{-1}]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
5850
5900
5950
6000
6050
6100
6150
6200

46 Progress on understanding the stability and transfer uncertainty of scales maintained by the CCL at NOAA

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Understanding the stability of scales maintained by the CCL and the uncertainty of the scale transfer from the CCL is critical for long term monitoring of greenhouse gases in the atmosphere to ensure observed trends and spatial gradients are real. NOAA as the WMO/GAW CCL for CO_2, CH_4, N_2O, SF_6, and CO strives to maintain scale stability over decadal time scales and to disseminate the scales with low enough uncertainty to allow WMO/GAW participating organizations to meet the targeted network compatibility goals. The uncertainty of the scale transfer is typically not the limiting factor for meeting these targets as other issues in the sample collection / measurement path dominate. However, the underlying scale stability and the scale transfer uncertainty need to be understood to allow the other factors to be assessed.

We present on-going work at the CCL to evaluate the stability of our scales, the uncertainty of transferring the scales to other laboratories and general QC protocols. The stability of the scale implementation is assessed with both internal target tanks and external comparisons over various time scales. The scale transfer uncertainty is dependent on the measurement systems used along with influences due to gas handling, matrix effects, and cylinder stability. Target tanks and the internal use of the scales on NOAA measurement systems can be used to understand and begin to quantify these issues and determine the scale transfer uncertainty over time.

47 A new system to measure N_2O site preferences in air samples, demonstrated on N_2O extracted from agricultural drainage waters

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Mole fractions of nitrous oxide are increasing in the atmosphere, mostly due to anthropogenic emissions following increased use of N fertiliser. Isotopomers of N_2O provide insights on microbial processes leading to N_2O formation. The Site Preference (SP, $\delta^{15}N\alpha$ – $\delta^{15}N\beta$) is reported 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, where the reported differences in site preference between end members is on the order of 30 ‰.

We present a new analytical tool based on a commercial Los Gatos Research N2O1A-23e-EP analyser that we modified from continuous-flow to discrete sample mode. Air samples, and reference gases are injected into a mixing volume in a first step. N_2O-free air can also be injected in various proportions, to match mole fractions between sample and reference gases without altering the isotopic composition. Accurate pressure control results in constant amounts of samples/reference gases after the dilution step. Finally, gases are expanded from the mixing volume into the analytical cell, where they are analysed for 10 minutes per injection. We present technical challenges and the solutions we found, enabling measurements with a reproducibility of SP on the order of 0.3 ‰at 1000 ppb N_2O.

The measurements are currently calibrated using USGS51 and USGS52 standards in N_2O-free air mixtures, by correcting for the offset in measured versus target isotope ratios. We are exploring the application of the recently proposed calibration scheme based on absolute isotopologue mole fractions, using gravimetric standards prepared from synthetic N_2O-free air and isotopically calibrated N_2O

We demonstrate the capability of our new system and the level of information such data provide from the analysis of N_2O extracted from agricultural drainage waters.

48 Influence of fractionation of CO_2 and air during preparation of a standard mixture

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NMIJ/AIST — AIST — AIST — NMIJ/AIST
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Within the WMO/GAW community, a CO_2 scale determined using a manometric method by NOAA have been used as a consistent reference to which all measurements are compared, allowing changes of CO_2 mole fractions to be measured with precisions. However, to make it robust, the scale should be validated using other method such as a gravimetric method. We have been challenging to establish CO_2 scale for atmospheric CO_2 observation by a gravimetric method. In the process, we found that CO_2 scale deviated according to adsorption to a cylinder's surface and fractionation of CO_2 and air during the preparation of standard mixture through a multistep dilution. We conducted a study to fully understand the carbon dioxide (CO_2) adsorption and the fractionation of CO_2 and air during the preparation. Decanting experiments to continuously measure CO_2 mole fraction in a CO_2/Air mixture exiting from a cylinder were conducted to evaluate the CO_2 adsorption to the internal surface of the cylinder. As the cylinder pressure was reduced from 11.0 to 0.1 MPa, the CO_2 molar fractions in the mixture flow leaving from the cylinder increased the CO_2 molar fractions by 0.16 ± 0.04 μmol mol^{-1}. By applying the Langmuir adsorption-desorption model to the measured data, the amount of CO_2 adsorbed on the internal surfaces of a 10 L aluminum cylinder when preparing a standard mixture with atmospheric CO_2 level was estimated. The influence of the fractionation was evaluated by a mother–daughter transfer experiment that transfer CO_2/Air mixtures from a cylinder to another evacuated receiving cylinder. The mother–daughter transfer experiments showed that the deviation of CO_2 mole fraction was caused by the fractionation of CO_2 and air in the process of transferring a source gas (a CO_2/Air mixture with a higher CO_2 molar fraction than that in the prepared gas mixture). Additionally, we established a method to prepare standard mixtures by diluting the pure CO_2 with the air only once, to avoid fractionation during the preparation. The CO_2 molar fractions in standard mixtures prepared by diluting pure CO_2 with air three times was evaluated based on the standard mixtures prepared using the established method. It indicates that the deviation is larger than a compatibility goal of 0.1 μmol mol^{-1}, which has been recommended by the World Meteorological Organization (WMO).

49 Laboratory comparison and progress on the development of community reference gases for carbon and hydrogen isotope ratios in atmospheric CH_2

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Umezawa et al. 2018 have highlighted significant inter-laboratory differences in both carbon and hydrogen isotope ratio measurements of atmospheric CH_4. The main cause of these differences is that a common set of unique reference gases has not been available since these observations begun. As the next best solution, laboratories developed local VPDB and VSMOW scale realisations for d^{13}C-CH_4 and d^2H-CH_4 in air, respectively. BGC-IsoLab and NIWA are pursuing a project to develop a prototype suite of reference gases for CH_4 in air, where isotopically calibrated CH_4 is diluted with CH_4-free air to atmospheric mole fractions. We will present updates on technical developments to calibrate the isotopic composition of pure CH_4, and on the preparation of CH_4-free air. It is the overall goal to make such reference gases available to the atmospheric monitoring community.

Furthermore, we present updates on the ongoing round robin for isotope ratios in atmospheric CH_4 (RR-CH4-i). RR-CH4-i has been initiated by NOAA GML, INSTAAR and NIWA and comprises of a suite of four cylinders. The composition of the gas mixtures was purposely chosen to amplify typical analytical challenges, thereby testing for the sensitivities of individual laboratories to the variability in natural samples. The RR-CH4-i results uniquely demonstrate the design of a future suite of community reference gases that would be most impactful. RR-CH4-i is underway since 2019 and has been measured by eleven laboratories so far, with seven further laboratories on the list.

50 WCC and QA/SAC activities and GHG observation by 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) for carbon dioxide (CO_2) and methane (CH_4) in Asia and the South-West Pacific within the framework of the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO). As part of the WMO/GAW quality assurance system, WCC-JMA has a fundamental role in helping to ensure the traceability of GAW network measurements to the WMO primary standard through comparison campaigns.

WCC-JMA organized six rounds of the CH_4 reference gas inter-comparison experiments from 2001 to 2022 as one of the WCC activities in Asia and the South-West Pacific in cooperation with NOAA (WMO/CCL, USA), CSIRO (Australia), NIWA (New Zealand), CMA (China), KMA/KRISS (Republic of Korea), IITM (India), MRI (Japan), NIES (Japan), AIST (Japan), NIPR (Japan), and Tohoku University (Japan); the seventh round is still in progress (Figure 1). The results of the fifth in Japan and the sixth in Asia were issued as GAW reports (GAW Report 263 and 264, respectively) in the WMO Library. We acknowledge all the participants for supporting our WCC-JMA activities.

In addition to the activities as GAW Central Facilities, JMA has made long-term continuous observations of atmospheric concentrations of major greenhouse gases such as CO_2 and CH_4 at Minamitorishima GAW Global Station (MNM) since the 1990s (Figure 2). Since 2011, other major observation laboratories in Japan also have been conducting systematic measurements of not only atmospheric CO_2 and CH_4 but also O_2/N_2 ratio, stable isotopes of CO_2 and other trace gas species which JMA doesn't observe at MNM. In this context, we can investigate the consistency in the observation results of CO_2 and CH_4 by comparing the data between JMA and these laboratories.

In 2020, JMA started the observation of the Hydrofluorocarbons (HFCs), which are known as highly potent greenhouse gases, at MNM as it relates to the Kigali amendment to Montreal protocol that restricts the production and emission of HFCs. The data is available from WMO/GAW World Data Centre for Greenhouse Gases (WDCGG). https://gaw.kishou.go.jp

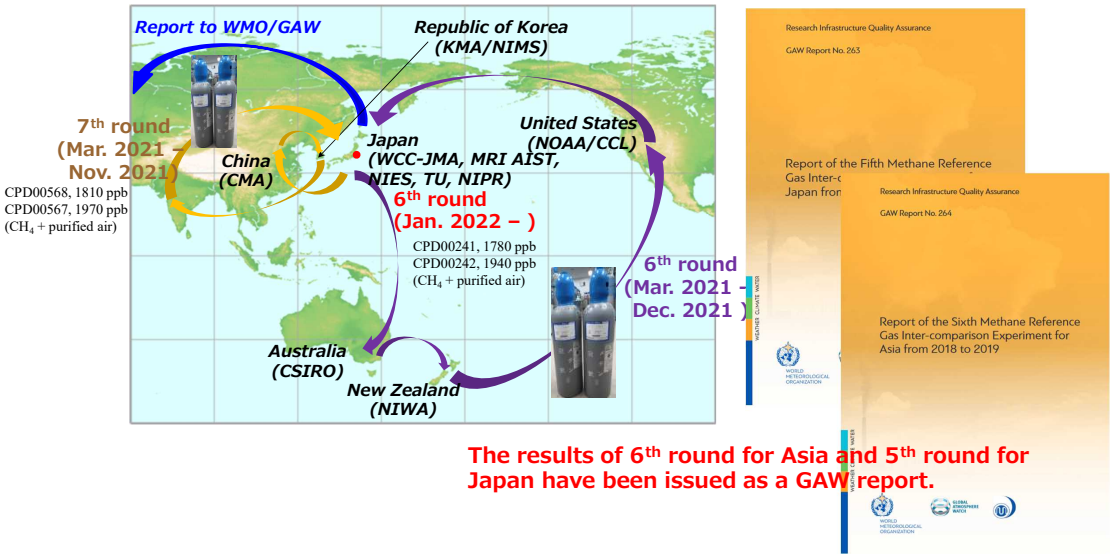

Figure 1. The overview of the reference gas inter-comparison and the reports of the recent results of CH_4 reference gas inter-comparison experiments published as GAW Report No. 263 and 264.

Figure 2. Minamitorishima (red circle) is one of the 30 GAW global stations in the world.

51 40 years of atmospheric CO_2 measurements in Hungary

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Continuous atmospheric carbon dioxide mole fraction measurements were started in Hungary on 5 June 1981. The base of the measurements was the K-puszta regional background air pollution monitoring station operated by the Hungarian Meteorological Service, where the monitoring continued until July 1999. In 1994 a tall tower site (Hegyhátsál) was also equipped for the long-term monitoring of CO_2 and other greenhouse gases. Both K-puszta and Hegyhátsál provided data for the WMO GAW program. The overlapping monitoring was started at the Hegyhátsál tall-tower greenhouse gas monitoring station, the present Hungarian ICOS atmospheric site (HUN), in September 1994. The five years of parallel measurements at the two sites 220 km away from each other allowed us to evaluate the spatial representativeness of the measurements and the limits of the combination of the two data series. Hegyhátsál is also a site for the NOAA cooperative global flask air sampling network, which provides a permanent quality control tool for the in situ measurements. Besides the presentation of the monitoring sites, the poster also presents the trend in concentration and the changes in the seasonal cycle at these mid-continental stations, as well as their similarities to and deviations from the global tendencies.

52 Adding DOI to observation data and enhancing WDCGG website functions

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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, which has been operating since 1990. It serves to collect, archive and distribute data on such gases (e.g., CO_2, CH_4, CFCs and N_2O) and other related gases (such as CO) in the atmosphere, which are measured under GAW and other programmes. All of these services are available on the WDCGG website (https://gaw.kishou.go.jp), which was redesigned in 2018.

WDCGG has begun assigning DOIs for the dataset on WDCGG in 2021 to promote dataset utilization in accordance with the GAW Implementation Plan 2016-2023. Data contributors for WDCGG can get the DOI of the registered dataset, uniquely determined by the observation element, organization, and station, if they request. DOI is also given to the merged dataset for each gas species containing all data contributed by fixed and mobile stations (Figure 1). The individual DOI is issued for the merged dataset fixed annually, so it can be useful to refer the used dataset in analysis and to retest the results of previous studies.

In addition, since the last GGMT, WDCGG has added the following functions to improve the utilization of the website.

- Start of providing data in NetCDF format
- Enhancement of search function for ground-based observation data
- Addition of a combination search function for ground-based observation stations and mobile observation stations
- Unification of drawing data and addition of animation in quick look maps for satellite data
- Addition of animation of temporal changes in latitudinal distributions of greenhouse gases

WDCGG is focusing on improving the search functions to find observation data, so that the user can find easily the targeted data in time and space. The station search functions help visually users to find both the ground and the moving platforms. The mixing ratios of data within the searched area can be confirmed by color.

The data submitted to WDCGG are used for global analysis for key greenhouse gases in the WMO Greenhouse Gas Bulletin, which is annually published before COP. Detailed data and analysis are also provided in WMO WDCGG Data Summary. We believe that these publications/activities meet the expectations for updated information on greenhouse gas levels and would support continued observational and research activities as well as expanding data availability.

WDCGG plans to continue improving its services for the collection, archiving and distribution of data worldwide to support the monitoring of climate change and policy

making, thereby helping to reduce environmental risks to society. Currently, we are working on issues such as integrating the GAW IDs into WIGOS Station Identifiers (WSIs) and introducing a frame to add data quality information to each observational data following the GGMT2019 recommendations.

We would like to acknowledge all the data contributors and users for supporting our WDCGG activities.

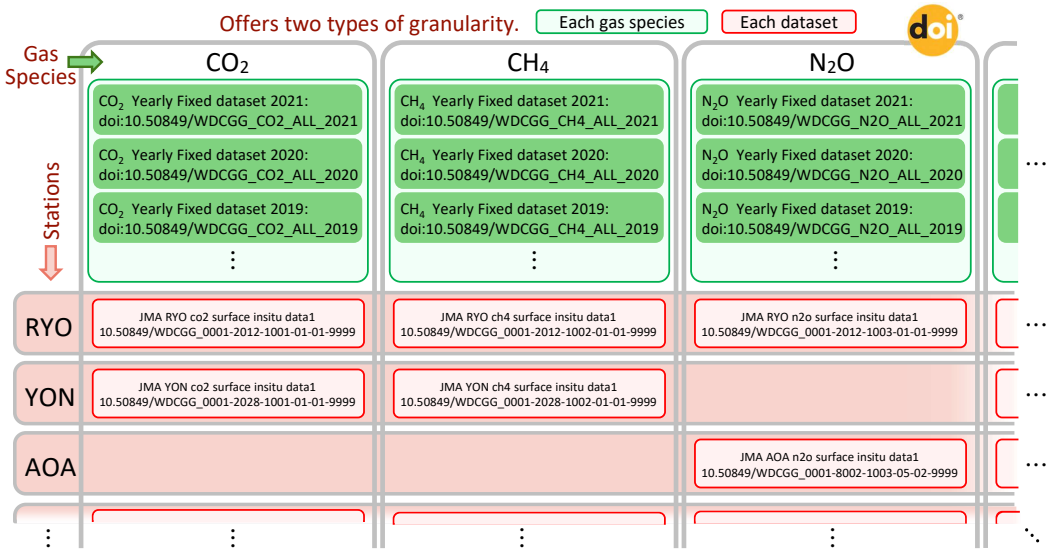

Figure1. WDCGG has begun assigning DOIs for the dataset on WDCGG (Mar. 25, 2021). Offers two types of granularities for DOIs. That is, a DOI for each gas species, and one DOI for each dataset. Contributors can request WDCGG DOI issuance for datasets that do not already have original DOI issued by contributors.

53 Dense Monitoring Networks to Observe Greenhouse Gases in Korea

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Atmospheric concentration observations are used in verification of greenhouse gases (GHG) emission inventory. In addition, atmospheric concentration observations are effective tools to evaluate the policy for reduction GHG emission. GHG monitoring in Seoul, Korea have been conducted to figure out the characteristics of GHG concentration and emission in urban area. The Ministry of Environment, the republic of Korean, plans to expand and rebuild GHG monitoring networks using ground, high-altitude and satellite observation of air quality. In this presentation, we introduce the development plan of GHG monitoring networks composed by ground, high-altitude and satellite observation in Korea. Furthermore, implementation method of constructing networks is also provided with examples in urban areas. Finally, Korea Carbon Budget Map project using monitoring networks is explained.Enter description here.

54 Looking inside the carbon sequestration of bamboo forests in Anji (China) with an observation-based approach

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As a perennial plant within the grass family, bamboo usually grows faster than native tree species. It has a high potential for catching atmospheric carbon, with further sequestration and transformation into durable products. However, the capacity of bamboo forests to sequester carbon and its potential depending of the land management and environmental conditions remains poorly explored. To find out, the WMO is trying to develop a methodology for objectively assessing the carbon sequestration potential of bamboo forests. The project investigates the carbon sequestration of a typical bamboo forest in the east of China with a novel observation-based methodology, coupled with a range of atmospheric tracers to identify the fluxes attributions (CO_2, COS, CO, ^{14}C-CO_2). Instead of applying the traditional inventory to estimate carbon emissions/uptakes, this study will provide new information on individual carbon-cycle processes of the bamboo forest and on the most promising tracers to study regional CO_2 fluxes. Based on atmospheric observations of CO_2 concentration, modelling systems and analysis tools could be further utilized to derive carbon fluxes of the bamboo forest with consideration of different management practices and environmental conditions.

55 Comparison of δ^{13}C-CO_2 and δ^{18}O-CO_2 measurements: An update of the results from the IAEA CLASSIC experiment and the WMO round robins.

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More than 20 years ago, a round robin exercise using high-pressure tanks of air and canisters of pure CO_2 for the measurement of the stable isotopic composition of CO_2 in air was funded by the IAEA. The exercise was CLASSIC (Circulation of Laboratory Air Standards for Stable Isotope interComparisons) and in addition to measuring the CO_2 stable isotopic composition (δ^{13}C-CO_2 and δ^{18}O-CO_2), the four laboratories (CSIRO Oceans & Atmosphere, INSTAAR, Scripps Institute of Oceanography and Tohoku University) also measured the CO_2 and N_2O mole fractions in the air tanks. Over a four-year period, five high-pressure tanks of air and two low-pressure canisters of pure CO_2 were circulated between the laboratories. A duplicate set of high-pressure air tanks was maintained and analysed at CSIRO during the circulation period, and all tanks are now maintained and analysed at CSIRO as part of their surveillance strategy.

The four laboratories also participate in the WMO/IAEA round robin (RR) exercises and, over the time since the circulation of the CLASSIC tanks, have made a number of changes to their calibration and data analysis procedures that have resulted in changes to the values reported for the CLASSIC tanks and for past RRs.

We will present revised results, compare these with past results, and discuss what we learn from this revisiting of past comparison exercises.

56 Development of a centralized quality management system for ICOS Atmosphere

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The Integrated Carbon Observation System (ICOS) is a research infrastructure for quantifying and understanding the carbon balance of Europe and its neighboring regions. ICOS consists of 14 European member and observer countries with currently 150 registered stations distributed in national networks of atmospheric, ecosystem, and marine sites. It provides long-term standardized observations measuring carbon fluxes from ecosystems and the oceans, and greenhouse gas mixing ratios in the atmosphere. All ICOS stations have to undergo a rigorous assessment prior to receiving the official ICOS label. To be labeled, new stations are thoroughly evaluated over several months to optimize the experimental settings and standard operation procedures, train the operators, detect and fix problems and, finally, ensure high quality data. Currently, 36 labeled stations form the ICOS Atmosphere network. The ICOS Atmospheric Thematic Centre (ATC) has developed data products and tools that are available to station operators to screen and qualify the data. Final fully quality controlled data (Level 2) also go to a plenary data review by the Monitoring Station Assembly (MSA) before their publication. Even if a set of automatic data check is already available, the operators still have to rely mostly on their own expertise to determine if their data are within acceptable range of quality. During the last year, a working group composed of Principal Investigators (PIs) and ICOS ATC has been refining quality indicators to support the station Pis in reviewing their data and to early detect measurement issues. A centralized traffic light summary panel has been created to alert PIs in such cases so that action can be taken and the high quality of the produced data be re-established. For now, three categories are covered: data availability, target and calibration gas performances, and uncertainties. The evaluation of the sampled air quality (e.g. through comparison with flask samples, other instruments, study of the gradients for tall tower, results of the intake line tests, ...) and an intended issue tracker to transparently follow issues between PI and ATC will be added at a later stage. We present here the different indicators with their thresholds and the strategy to translate the sum of indicators into a global assessment of the current performance of a site as well as concrete examples of stations. This new tool will help ICOS Atmosphere stations to maintain their high quality standards, to learn from the past and mutually from the other stations and even to improve the overall quality of data.

57 Characterizing regional methane emissions from the oil and gas sector using non-methane hydrocarbons

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Methane is a potent greenhouse gas but its sources remain poorly quantified in the Eastern Mediterranean and Middle East (EMME) region. Light alkanes, such as ethane (C_2H_6), are co-emitted by fossil fuel (oil and gas) activities and are promising tracers for quantifying the methane emissions from this sector. Cyprus is an ideal location for studying the composition of air masses of varied origin and for characterizing different emission source signatures at a regional scale. A Picarro analyzer and two field-based Gas Chromatography Flame Ionization Detectors (GC-FID) were deployed and an extensive dataset is generated. Our aim is to use these observations for identifying regional and local anthropogenic methane sources, for assessing tropospheric concentrations, while evaluating the significance of long-range transported versus local sources. Continuous methane observations were performed between February 2020 and December 2021 at a suburban background site of the capital city of Nicosia in Cyprus. NMHC (C_2-C_{12}) measurements were also performed on the same site between February and December 2021, and include both anthropogenic (alkanes, alkenes, aromatics) and biogenic (isoprene, monoterpenes) compounds that help in the separation of sources originating from different sectors. Our initial results suggest strong local methane and NMHC sources. We also provide evidence for long-range transport, using the observations obtained during a 3-month field campaign using a Mobile Laboratory (MoLa) deployed at the south-eastern edge of the island between December 2021 and February 2022. The aim was to study the contribution of methane emissions from Middle Eastern oil and gas operations while minimizing the influence of local (island-based) emissions. Our measurements will ultimately provide a better understanding of pollution sources at local and regional scale in the Eastern Mediterranean region.

58 Measurements of atmospheric CH4 at regional stations of Korea Meteorological Administration/ Global Atmosphere Watch Programme: characteristics and long-term changes

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To quantify CH_4 emissions policy-relevant spatial scales, the Korea Meteorological Administration (KMA) started monitoring its atmospheric levels in 1999 at Anmyeondo (AMY), and expanded monitoring to Jeju Gosan Suwolbong (JGS) and Ulleungdo (ULD) in 2012. The monitoring system consists of a Cavity Ring Down Spectrometer (CRDS) and a new cryogenic drying method, with a measurement uncertainty of 0.7–0.8 ppb. To determine the regional characteristics of CH_4 at each KMA station, we assessed the CH_4 level relative to local background (CH_4), analyzed local surface winds and observed CH_4 with bivariate polar plots, and investigated CH_4 diurnal cycle. We also compared the CH_4 measured at KMA stations with those measured at the Mt. Waliguan (WLG) station in China and Ryori (ROY) station in Japan.

CH_4xs followed the order AMY (55.3±37.7 ppb) >JGS (24.1±10.2 ppb) >ULD (7.4±3.9 ppb). Although CH_4 was observed in well mixed air at AMY, it was higher than at other KMA stations, indicating that it was affected not only by local sources but also by distant air masses. Annual mean CH_4 was highest at AMY among all East Asian stations, while its seasonal amplitude was smaller than at JGS, which was strongly affected in the summer by local biogenic activities. From the long-term records at AMY, we confirmed that the CH_4xs source changed from the past (2006 to 2010) to recent (2016 to 2020) years in East Asia. Especially in northern China, CH_4xs were mainly attributed to burning activities such as fossil fuel during 2006–2010, but mainly by biogenic activities during 2016–2020, as shown by decreasing $\delta^{13}CH_4$ value in the same region. isotopic data. CH_4 emissions in the southern part of China and in local regions in Korea were enhanced by biogenic signals. We confirmed that long-term high-quality data can help understand changes in CH_4 emissions in East Asia.

59 High-precision airborne measurements of N_2O, CH_4, CO_2, CO using active AirCore

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Making accurate airborne measurements is challenging for long-lived greenhouse gases, which is especially the case for nitrous oxide (N_2O). Here we present the development of a new active AirCore system that is capable of continuously collecting air samples aboard aircraft for accurate mole fraction measurements of N_2O, CH_4, CO_2 and CO. The active AirCore consists of a extasciitilde285 m thin-wall stainless-steel tube with a volume of ˜4.3 L, a pump, a mass flow controller, and an electronic control unit, which weighs ˜6 kg. Furthermore, the AirCore can be pressurized to ˜ 1.6 bar to obtain a maximum air sample of ˜ 7 standard liters. The collected air samples were analyzed in series by two cavity ring-down spectrometers (CRDS) for mole fractions of N_2O, CO_2, CH_4 and CO. Five flights were performed with the new active AirCore aboard a lightweight SkyArrow aircraft over the Groningen and Utrecht regions in 2020, with each flight lasting ˜ 2.5 hours. For four flights of them, both the active AirCore and a commercially available LICOR-7810 analyzer for high precision CH_4 were flown together. The in situ LICOR CH_4 measurements were used to optimize the AirCore retrieval algorithm. The optimized AirCore CH_4 showed a high agreement with the in situ LICOR CH_4 measurements, with a mean difference of LICOR minus AirCore CH_4 ranging from -1.64 ppb to +0.18 ppb for the four flights. With a typical storage time of 4 hours, the spatial resolution with a typical flight speed of 40 m/s is determined to be 1.7 km, 1.9 km, 1.6 km and 1.8 km for N_2O, CH_4, CO_2 and CO, respectively. The new active airborne AirCore system provides a robust means to obtain accurate airborne measurements of N_2O, CH_4, CO_2 and CO, and can be useful to quantify regional emissions of greenhouse gases.

60 Historical CO_2 and CH_4 time series on the European continent

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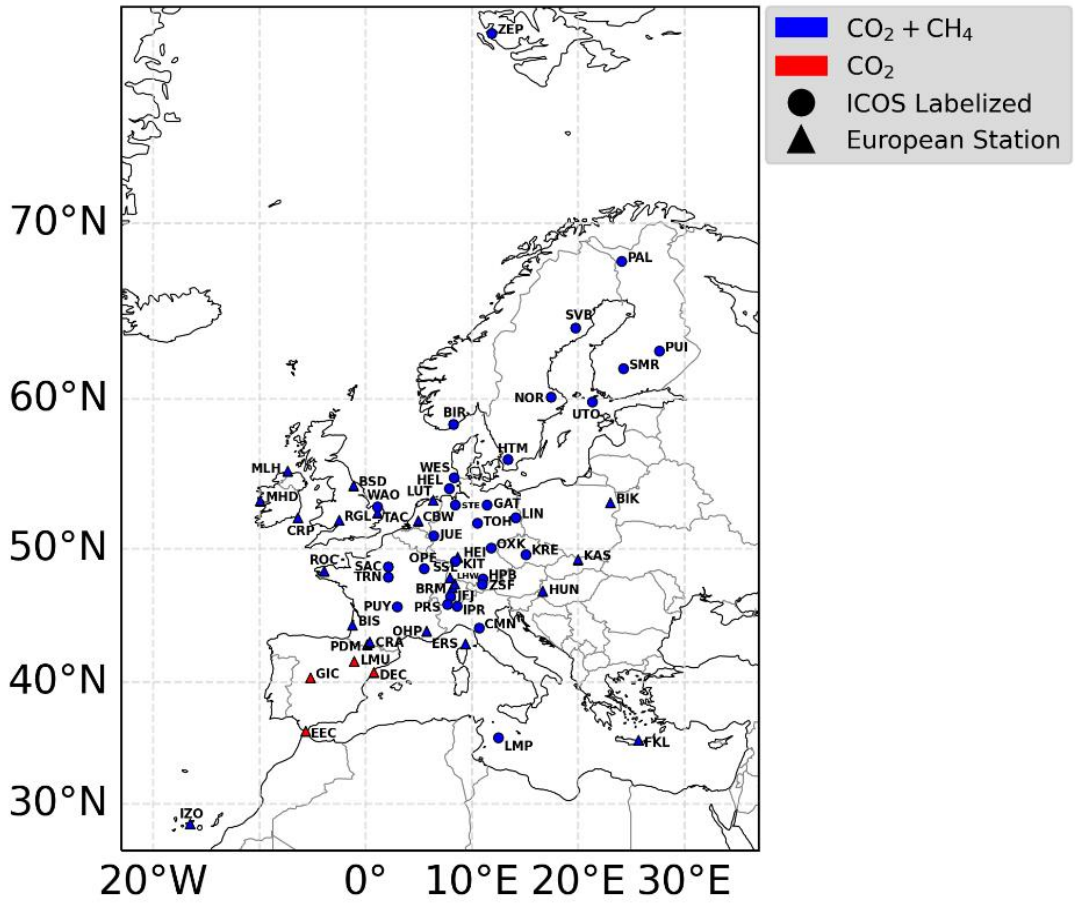
Many research institutes are involved in the monitoring of atmospheric concentrations of CO_2 and CH_4 on the European continent. The Schauinsland (Germany), Monte Cimone (Italy) and Izana (Spain) stations were pioneers in Europe with continuous measurements started in the 70s or early 80s of the previous century. By 2000, the European network included only 7 continuous CO_2 and CH_4 measurement stations, compared to 60 stations at present, without counting urban CO_2 networks that are emerging since a few years. Among these stations, 35 of them are now labeled in the ICOS research infrastructure (plus one in the southern hemisphere), and a few more have initiated the labeling process. ¡span lang="en"¿The ICOS research infrastructure makes it possible to standardize measurement protocols in its stations, as well as the dissemination of data through the ICOS Carbon Portal, including near-real time data (delay less than 24 hours). However, the finally quality controlled ICOS dataset does not cover all European stations, and only goes back to 2015. In collaboration with the European stations PIs, we have therefore decided to organize a collection of all European CO_2 and CH_4 data, with the aim of providing users with a updated formatted data set each year. This dataset accessible on Carbon Portal will be fully compatible with the OBSPACK data product, and will also be made available to users via the WDCGG database. The level of compatibility of the measurement protocols of stations not labeled ICOS will not be at the level applied to ICOS stations, and will not allow, for example, to provide data in NRT mode or to provide the traceability available from ICOS stations. However, an effort is being made to collect metadata such as the measuring instruments and reference scales used, and to organize verifications of the signals measured through comparison between stations. We will present the organization of this effort coordinated by the ICOS-ATC and ICOS-CP, as well as a first evaluation of the decadal and seasonal cycles from the recorded data which represent in total more than 800 years of CO_2 measurement and 600 years of CH_4 at 60 stations.


$CO_2 + CH_4$
CO_2
ICOS Labelized
European Station
70°N
60°N
50°N
40°N
30°N
20°W
0°
10°E
20°E
30°E
ZEP
PAL
SVB
PUI
SMR
NOR
UTO
BIR
HTM
MLH
WES
HEL
LUT
BSD
WAO
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GAT
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OPE
HEI
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HPB
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PUY
PRS
IPR
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CMN
OHP
PDM
CRA
ERS
LMU
GIC
DEC
EEC
LMP
FKL
IZO

61 The characteristics of atmospheric SF_6 and emission changes during 2017-2020 in Korean Peninsula

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The most powerful greenhouse gas, Sulfur hexafluoride (SF_6), has the global warming potential of SF_6 is 22,800 over a 100-year time horizon. The global atmospheric abundance of SF_6 has been well characterized, however, East Asian contribution to global budget is still uncertain. In this work, we used near surface in-situ measurements of SF_6 from 3 regional background stations in Korea from 2017 to 2020. As the Anmyeondo (AMY), Jeju Gosan (JGS), and Ulleung-do (ULD) stations locate at the western, southern, and eastern boundary of South Korea, respectively, the stations provide information to understand SF_6 source regions in not only Asian continent but also Korean peninsula. We analyzed the background changes and influences of local meteorological effect. The annual average increase of SF_6 at three stations is about 0.3 ppt per year, which is similar with the trend of global background. We also quantified the regional enhancement of SF_6 from each site and investigated the potential source regions using back-trajectory analysis. It turns out there are two major source regions located in the central part of Korea and the central part of China.

62 Metrology Lab of the ICOS Atmospheric Thematic Center: Role in ICOS and platform for GHG instrument performance assessment.

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Since its inception, ICOS is aiming to provide harmonized high precision data for advanced research on carbon cycle and greenhouse gas (GHG) budgets over Europe. For that purpose, the ICOS Atmosphere Thematic Centre (ATC), located at LSCE in Gif-sur-Yvette, France, has evaluated and implemented, in collaboration with the National Networks, standard protocols for GHG measurement and the corresponding data processing. Any GHG instrument deployed in the ICOS atmospheric network initially passes at the ATC MLab to verify its compliance with the performance specifications defined in ICOS, via a standard protocol. With such metrological assessment activity over the last decade, ICOS ATC MLab has tested hundreds of GHG instruments/sensors, ranging from prototypes to proven systems, according to standards in connection with manufacturers, research labs and institutions. This ICOS activity which is relevant to guaranty the data quality and maintain ICOS knowledge on state-of-the-art GHG metrology, tends to become also a reference for GHG benchmarking.

After presenting the metrological assessment protocol with some use cases, the presentation will focus on the interest of such standard "benchmarking", especially with the emergence of new applications, new actors in the domain.

63 Design and performance assessment of "Mid Cost" CO_2 sensor system for urban monitoring network

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In the framework of the ICOS Cities – PAUL, a H2020 European project aiming to assess different techniques and methodologies to better estimate the CO_2 emission in urban area, the LSCE and Origins.earth are developing and deploying a network of 30 "mid cost" CO_2 NDIR sensors within Paris and its near suburb. In addition to few stations equipped with high precision spectrometers, such dense "mid cost" CO_2 sensor network allows a better monitoring of the complex spatial distribution of CO_2 gradient at a local scale. In order to represent larger footprint and avoid the direct measurement of very local CO_2 sources (e.g. traffic) difficult to handle by inversion model, these sensors are deployed at the roof level (between 25m and 180m agl). With such network configuration, the typical site to site CO_2 gradient observed in Paris is limited to few ppm and up to 10-20 ppm depending mainly to the meteorological conditions (wind speed, mixing layer height). In order to be able to monitor this atmospheric signal, the "mid cost" CO_2 sensors accuracy target has been set at 1 ppm.

This presentation presents the results of the "mid cost" CO_2 sensor sensitivities test to environmental parameters (pressure, temperature, humidity) and metrological performance test conducted at the ICOS ATC Metrology Lab (at LSCE), the related calibration and quality control strategy to meet the performance objective and the integration done to provide a stand-alone sensor box (so called AtmoBox) suitable for operational network.

64 Tracking the origins of atmospheric CO_2 in Seoul, South Korea using ^{14}C and ^{13}C

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More than 70% of global CO_2 emissions from fossil-fuel combustion occur in urban areas. Therefore, assessment of urban CO_2 emissions is essential to make an effective solution to mitigate global climate change. In this study, observations of atmospheric CO_2 concentration and its carbon isotope compositions (i.e., $\delta^{13}C$ and $\Delta^{14}C$) were conducted to understand the exact sources of urban CO_2. The observations were made at the city center tall tower, Namsan Seoul Tower (NST; 420m MASL), South Korea from July 2020 to April 2022. NST is the tallest tower located in the center of Seoul making it suitable to observe the typical characteristics of Seoul. Using $\delta^{13}C$ and $\Delta^{14}C$ data measured at NST, we intended to quantify the source (i.e., fossil-fuel and vegetation) of CO_2 enhancement in Seoul. In addition, the detailed origins of fossil-fuel sources were identified and their seasonal characteristics were assessed. More details of our study will be presented in the workshop. Our results of urban CO_2 attributions in Seoul can provide valuable insight for developing effective carbon mitigation strategies.

This work was supported by Korea Environment Industry &Technology Institute(KEITI) through "Climate Change R&D Project for New ClimateRegime.", funded by Korea Ministry ofEnvironment(MOE) (2022003560006).

65 High-resolution CO_2, CH_4, and NOx maps from urban to rural areas using mobile monitoring

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Mobile monitoring is conducted to estimate concentration changes with high spatio-temporal resolution according to various land-use type while moving through a wide range of regions. The CO_2, CH_4, and NOx mobile monitoring travels over 160 km crossing South Korea from urban to rural areas were performed 4 times in June 2022. The mobile platform was equipped with CO_2/H_2O trace gas analyzer (model LI-7815, LI-COR Environmental, NE, USA), $CH_4/CO_2/H_2O$ trace gas analyzer (model LI-7810, LI-COR Environmental, NE, USA), NO/NO2/NOx (nCLD AL2, Eco Physics, Swiss) ambient level gas analyzer, and GPS device (model AK-770, AscenKorea, Korea). Before and after mobile monitoring, in situ comparisons between monitoring instruments were performed for 30 minutes to determine offsets and background concentration. Based on these data, we attempted to identify the spatio-temporal concentration variations of CO_2, CH_4, and NOx, and concentration differences according to explanatory variables. The explanatory variables include land-use type, population density, traffic volume, terrain elevation, road type. Using linear regression analysis, the relationships between the observed concentrations at all measurement points and the explanatory variables were found. Through high-resolution CO_2, CH_4, and NOx concentration maps, high concentration regions can be found and concentration reduction policies can be proactively applied to these regions.

This work was supported by Korea Environment Industry &Technology Institute (KEITI) through "Climate Change R&D Project for New Climate Regime", funded by Korea Ministry of Environment (MOE) (2022003560006)

66 Comparison of atmospheric greenhouse gas measurements at two intake heights at the monitoring stations Zugspitze and Schauinsland in Germany

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The German Environment Agency (UBA) has been measuring greenhouse gases in the atmosphere at the mountain stations Zugspitze (2670 m a.s.l.) and Schauinsland (1205 m a.s.l.) for decades. More recent measurements with high temporal resolution show that even these remote stations can be influenced by local pollution events. In order to quantify and to reduce the influence of these local pollutions, additional greenhouse gas measurements were taken at both stations at higher altitudes or on a nearby tower.

At Zugspitze, CO_2, CH_4 and CO mole fractions in ambient air were measured at the Environmental Research Station Zugspitze-Schneefernerhaus and additionally on the mountain ridge about 150 m above Schneefernerhaus between October 2018 and October 2020. Comparison of these measurements shows that the measurements at the mountain ridge are less influenced by local pollution such as from snow blowers and snow groomers, but also that careful quality control of the Schneefernerhaus data can successfully remove this influence.

At Schauinsland, CH_4 and CO_2 mole fractions are measured at the station at 12 m height (above ground) and, since September 2022, additionally at 35 m on a nearby radio tower. Unlike the Zugspitze mountain station, the Schauinsland station is surrounded by forests and pastures. The comparison of the high frequent time series from different intake heights can provide insight into the local influence of the biosphere and the grazing livestock on the data.

67 Utilising vertical gradient information of greenhouse gases and meteorological measurements at eight German atmospheric ICOS Stations

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Eight ICOS Atmospheric tall tower stations across Germany have been operated by the German Meteorological Service (DWD) since 2015. At each station mixing ratios of carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), and nitrous oxide (N_2O), as well as meteorological parameters are continuously observed at 3 to 5 measurement heights (up to 341 m a.g.l.). High quality gradient measurements can be utilised as part of data quality control as well as to infer regional greenhouse gas flux estimates.

We show how vertical gradients are useful for station data quality control by comparing the measurements of the different heights under well-mixed conditions. Then, there should be no marked differences between the mixing ratios at different heights and leakage in a sampling line can potentially show up in form of a noticeable deviation in statistics.

Beyond the value for quality control purposes, local to regional greenhouse gas fluxes can be calculated using established methods from mixing theory to obtain flux estimates from gradient measurements. Here we show the first results of these flux estimates from the DWD tall towers, highlighting the potential and limitations of this type of data product for understanding greenhouse gas budgets.

68 Greenhouse gases measurements in Southern Ocean onboard the Marion Dufresne

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Over the last decades, important efforts have been done to develop environmental monitoring networks as for example the European ICOS network for greenhouse gases. Despite these improvements, there is still a lack of data in the southern hemisphere, and in particular above the oceanic areas. The MAP-IO project (Marion Dufresne Atmospheric Program Indian Ocean) launched in Autumn 2020, with the aim of studying the atmospheric composition and the ocean-atmosphere processes, represents a unique opportunity for greenhouse gases monitoring over the Indian Ocean.

The French oceanographic vessel Marion Dufresne has been equipped with a set of instruments dedicated to long term atmospheric monitoring. As part of this full instrumental package, a complete greenhouse gases (GHG) equipment set has been installed in November 2020, including a continuous high precision analyzer (providing CO_2, CH_4, CO measurements), a calibration and quality control setup and intake line and a GPS positioning system.

The measurement system is running continuously, and provides continuous series of data, in particular over the French Austral islands area which are visited four time a year at different seasons. We will briefly present the experimental set up, measurement protocol and data quality control and we will then focus on the results obtained over the last 18 months during the oceanographic scientific campaigns as well as during the logistical operations of the vessel. We will show and analyze the spatial distribution of GHG concentration, look at the seasonal amplitude and variability (comparing two years of data when available), compare the results with local monitoring stations (Amsterdam and La Reunion island for example), and also present first comparison with the CAMS model.

69 Characteristics of Atmospheric Greenhouse Gases in Urban and Background Areas in Korea

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More than 70 percent of global anthropogenic carbon are emitted in urban areas. South Korea emitted the ninth largest amount of carbon in 2019. Seoul, the capital of South Korea is one of the megacities that emit large amount of greenhouse gases in the world. Therefore, to establish a strategic policy for reducing emissions of greenhouse gases in Korea, characteristics of greenhouse gases' concentrations and emissions in urban areas should be identified. Several stations set up for observing background atmosphere since 1996, in Korea. To observe greenhouse gases in urban areas, greenhouse gases monitoring points have been installed at air quality monitoring stations by the Ministry of Environment, Korea, since 2021.

In this study, based on the differences in the concentrations of greenhouse gases at urban and background monitoring stations, the characteristics of atmospheric greenhouse gases in Korea are identified. Furthermore, we also introduce an integrated analysis method of greenhouse gases and air pollutants.

70 A new compressor system based on a Resato gas booster replacing the Rix SA-models for filling whole air reference cylinders

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For decades compressing ambient air into high pressure cylinders to serve as working standards has been done by using a modified oil-free compressor system based on the three-stage dive compressors model SA-3 and SA-6 from Rix (Rix, Emeryville, California, USA) described in detail by Mak & Brenninckmeijer (1994). In spite of the excellent performance of the Rix-systems over time, the compressor itself tended to be sensitive to regular failure due to mechanical stress and the breakdown of vital parts. Moreover, in 2017 the Rix company decided to stop production of their SA-3 and SA-6 sweet-air, oil-free compressors, apart from offering one last manufacturing run to serve the atmospheric science community. This prompted us to look for an alternative compressor system, which brought us to the oil-free air driven gas boosters offered by the company Resato International B.V. (Assen, The Netherlands). We have chosen an air-driven all stainless steel two-stage Resato booster (model B160-5-30). The Resato booster uses standard laboratory compressed air (1-7 bar) as driver gas and can compress air up to 210 bar. The valve seals are made of Teflon® (PFTE) or Viton® (FKM) and the high pressure piston seals are PFTE-based. A minimal sample air inlet pressure of 2 bar is required, which can be provided by any oil-free commercial compressor with a 50 L (or larger) pressure tank serving as a buffer volume. The booster than compresses by a factor of 1:5/1:30 (first and second stage) until it reaches a maximum set pressure, e.g. 200 bar. The drying steps are largely the same as the earlier Rix-setup (using coalescence and chemical traps to remove water) with the addition of a cryogenic cooler dryer after the first compression stage. Here we present a detailed overview of our system set-up and its performance. We have thoroughly tested the sample stability by comparing the composition of a so-called "mother tank" containing compressed ambient air (or nitrogen) with a "daughter tank" which was made by compressing the "mother tank" air into a smaller cylinder. So far, we tested the stability of CO_2, CH_4, CO, N_2O, COS, and the stable isotopes δ^{13}C-CO_2 and δ^{18}O-CO_2. Further tests include the O_2/N_2 ratio and certain halocarbons. We found tolerable biases on the order of -1 to -1.5% for CO_2, +4 to +9% for CO, and -0.4% for N_2O. A noticeable acceptation was COS which increased in our test by 24%. After filling 51 cylinders of various volumes (1-40 L) comprising a total of 185 m^3 of air, maintenance of the piston seals was required.

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71 NIST Low-Cost Sensor Greenhouse Gas Measurement Project

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To monitor urban greenhouse gas (GHG) emissions and fluxes in the Baltimore, Maryland and Washington DC metropolitan areas, the NIST Greenhouse Gas Measurements Program deployed a network of high accuracy monitors as part of the larger US Northeast Corridor Tower GHG network. These monitors provide CO_2 accuracy at the sub-ppm level, but their high cost limits the total number of monitors feasible in a network. To supplement these monitors and increase the network measurement density, NIST is developing a low-cost sensor package to monitor CO_2 and other meteorological parameters. The low-cost nature (˜ $3,000) of the package will allow for a wider deployment throughout the Baltimore/Washington region.

The goal of the low-cost sensor project is to design an easily deployable and scalable internet of things (IoT) network to monitor CO_2 at the 1-2 ppm accuracy level. Once this is achieved, ˜ 50 low-cost sensor packages will be deployed to supplement the existing high-accuracy network.

In this poster, we will present an overview of NIST's custom low-cost sensor packages based on commercially available components, station-supporting IT infrastructure, and scientific results from an inter-comparison between a low-cost sensor package co-located with a high-accuracy monitor. We will show examples of station construction, including custom hardware and software used to interface various GHG and meteorological sensors, and the challenges presented in calibrating commercially available CO_2 sensors with known reference gas standards. In addition, network performance will be discussed including network quality of service and station reliability. We will also highlight meteorological impacts on sensors, and statistical methods for correcting temperature, pressure, and relative humidity dependencies from CO_2 measurements in real time.

72 The NIST Northeast Corridor Tower GHG Network

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The NIST Northeast Corridor (NEC) Tower GHG Network spans the Northeastern US urban corridor from North Carolina to Maine. It is part of the NIST Urban Testbed Program; the other two urban testbeds are Los Angeles Megacity and Indianapolis/INFLUX. Currently, the NEC comprises a dense 12-tower network in Washington, DC and Baltimore, MD, nested within a regional network in the US Northeast. Our goal is to provide high-quality, high-accuracy carbon dioxide and methane observations that can be used in atmospheric inverse analyses to diagnose fluxes of these gases from the urban corridor.

The NEC testbed hosts additional observations and analyses aimed at quantifying GHG emissions, often complemented by outside researcher-led campaigns that leverage the existing long-term tower network observations. These include periodic aircraft campaigns focused on Washington DC, Baltimore, MD and New York City, NY, and the development of a low-cost sensor network in Washington, DC.

Here we present an overview and status update of the NEC tower network including recent scientific results, ongoing measurements, complementary observations, and future plans for the project. The goal of the testbed system is bringing emissions estimates derived using various methodologies into consensus, and we will also present examples of such compatibility between estimates for long-term methane trends in Washington DC and Baltimore, Maryland.

73 Reaching compatibility targets for d^{13}C of air-CO2 and methane: mission impossible or possible?

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In order to produce reliable GHG records based on data of different labs obtained over years, these datasets must be compatible. For this purpose, GGMT community introduced data Compatibility Targets (CTs) and stressed the need for robust calibrations and data compatibility over years. From one hand, strict CTs for δ^{13}C of air-CO_2 and methane (0.01 and 0.02 ‰, respectively) are at the limit of best performance of modern IRMS systems, so CT values are indirectly linked to overall data uncertainty. From another hand, modern metrology considers compatibility to be based on data uncertainty. Here, uncertainty may be considered as the range where "true" value is situated with 68 % or 95% certainty.

Next, RRs are widely used to demonstrate (dis-)agreements; these provide a snapshot which is valid for a particular year, for each RR. Up to date, RRs demonstrated discrepancies in δ^{13}C and δ^{18}O of air-CO_2 which largely exceed CT values (discrepancies in δ^{13}C up to 0.09 ‰[1, 2]). As these discrepancies imply problems with calibration and/or data treatment [1, 2], assessment of all other available data may be helpful.

First, CLASSIC intercomparison experiment demonstrated that discrepancies in δ^{13}C on pure CO_2 are larger than discrepancies in δ^{13}C(air-CO_2). That prompted calibration approaches to be based on air-CO_2 mixtures, so that CCL-isoCO_2 was created and started distributing calibration CO_2-air mixtures in 2009. Still, assessment of other calibration approaches and its relevance to data compatibility may be useful as well. CARIBIC-1 and CARIBIC-2 performed δ^{13}C(air-CO_2) measurements in 1999-2002 and 2007-2009 [3, 4]. In this project, independent calibration scheme was established, it was based on the use of primary reference material (that time - NBS19) and verification of all instrumental effects and corrections [3, 4]. Special attention was paid to decouple effects and identify uncertainty sources. As Quality Control, NIST CO_2 RMs 8562-8564 were analyzed. A retrospective data assessment demonstrates that δ^{13}C obtained on RMs 8562-8564 during CARIBIC-1 [4] agrees within ¡0.010 ‰with the values obtained during CARIBIC-2 at IRMM [3] and also with values obtained years later in another project, with calibrations based on the new primary RM IAEA-603 [5]. Since NIST RMs cover the δ^{13}C range from -3.7 to -41.6 ‰, that agreement proves correctness of tests for instrumental effects, calibration approaches and data treatment and also implies that reaching CT of 0.010 ‰for δ^{13}C(air-CO_2) is possible.

Current presentation will give re-analysis of approaches presented in numerous publications including papers by CCL-isoCO_2 and other laboratories.

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74 Evaluation of two algorithms for the automatic identification of spikes on continuous atmospheric observations of CO_2, CH_4 and CO

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Within the Integrated Carbon Observation System (ICOS) research infrastructure, a network composed of 36 labelled atmospheric stations is providing preliminary calibrated and automatically screened data in near-real time (i.e. with a 24-hour delay) and final fully quality controlled data of the atmospheric mixing ratios of greenhouse gases (CO_2, CH_4, N_2O) and CO. In this framework, an automated procedure to detect the occurrence of "spikes", i.e. sudden and short-lasting increases in GHG mixing ratios due to very local emissions, is required to separate local influence from regional and global signals. While some categories of data usage (e.g. inverse modeling) need to exclude spikes from their analysis, the information provided by spikes can be useful to investigate the impact of local emissions. Moreover, the capacity to automatically detect spikes facilitates the data quality control operations of the station Principal Investigator (PI) and further optimize the data harmonization among stations.

For these reasons, a working group including station PIs and the ICOS Atmospheric Thematic Center (ATC) has been launched within the ICOS Atmosphere Monitoring Station Assembly (MSA) to assess the effectiveness of two widely used spike detection algorithms ("Standard Deviation - SD" and "Robust Extraction of Baseline Signal – REBS" methods). A subset of different typologies of ICOS stations (continental, coastal and mountain) and one urban station were considered to test the algorithms and to perform sensitivity and comparative experiments.

For the period 2019 – 2020, both algorithms have been applied to time series of 1-minute averages of CO_2, CH_4 and CO. A sensitivity study on the algorithm settings was conducted to assess the impact (i) on the fraction of data detected as spikes, (ii) on the

monthly mean values and (iii) on the seasonal and diurnal cycles.

For each station and atmospheric species, case studies to assess the performance of the detection algorithms by the station PIs were selected. Moreover, for a subset of sites, a dichotomous analysis was performed to compare the results of the manual detection performed by the PIs with the automatic detection performed by the algorithms.

Preliminary results suggested that defining one optimal combination of algorithm and setting for all the considered sites and for all the atmospheric species is challenging but that the agreement between manual and automatic spike detection substantially increased when only higher amplitude spikes were targeted.

75 Comparing emerging methods for source identification and emission quantification of methane emissions at municipal solid waste landfills

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In recent years, methane emissions have shifted into the focus of mitigation action. In 2021, Canada and over 100 other countries joined the Global Methane Pledge, which aims to reduce global methane (CH_4) emissions by 30% below 2020 levels by 2030. Globally, the waste sector is a major source of anthropogenic CH_4 with the lion's share contributed from municipal solid waste landfills. To understand and unlock the mitigation potential of such facilities, it is critical that current emission reports are compared to the plethora of emerging atmospheric monitoring techniques.

As a first step, Environment and Climate Change Canada has conducted measurements of multiple landfills with one extensive experiment where different measurement techniques were deployed at the same facilities. The techniques included: surface emission monitoring using hand-held detectors (SEM5000), mobile measurements of CH_4 enhancements downwind of the site using a bike, a car, a small unmanned aerial vehicle (sUAV), and spectral plume imaging from an aircraft platform. Furthermore, two solar-tracking Fourier Transform Spectrometers were used to quantify total column enhancement of methane downwind of a site, and a scanning Laser Dispersion Spectroscopy system provided continuous horizontal multi-directional column measurements. In a later experiment, commercial and home-made low-cost sensors were also tested to continuously track CH_4 enhancements from the landfill.

The core objectives of this comparison study was to 1) test the ability of different techniques to locate emission hotspots on the facilities, and 2) provide estimates of facility-wide CH_4 emissions that can be compared to annually reported emissions.

We found that SEM, walking, driving and sUAV surveys reliably identified emission hot spots on simpler (closed) landfill sites and also found major sources on larger active landfills. Emission rate retrieval for both landfill types from downwind vehicle surveys was successful, while sUAV data were able to estimate emissions from hotspot areas of the landfills. The aircraft-based system was limited to detecting the part of the emissions that correspond to the larger plume of the active landfill site and likely missed the smaller diffusive sources. Data from the continuous scanning laser system and the low-cost sensor study indicate that those techniques can track strong changes in emissions over the course of days to months, however, a reliable method for retrieving facility-wide emission estimate is still being developed.

Future studies will be extended to a larger set of landfills to be able to provide insights into how the site design influences hotspot distribution and overall emissions.

76 PERFORMANCE ASSESSMENT OF THE MOBILE G4301 CAVITY RING-DOWN SPECTROSCOPY ANALYZER AND PRACTICAL FEEDBACK FROM FIELD MEASUREMENTS

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Carbon dioxide (CO_2) and methane (CH_4) are the most important greenhouse gases, and there is an increasing need to measure these greenhouse gases with mobile measurement devices. Picarro's G4301 Cavity Ring-Down Spectroscopy (CRDS) analyzer is a high-performance, light-weight, portable, battery-powered gas concentration analyzer that has enabled real-time measurements of CO_2 and CH_4 in challenging environments in the field of ecosystem [1]–[3], soil science [4] , glaciology [5], limnology [6] and indoor air quality [7]. Here we evaluate the performance of this portable greenhouse gas analyzer in laboratory test and share practical feedback from field measurements.

The performance of the G4301 analyzer was assessed at the Metrology Laboratory (MLab) that is part of the Atmospheric Thematic Center of ICOS. The MLab regularly tests greenhouse gas analyzers that are used within the European monitoring network ICOS (Integrated Carbon Observation System). We will present CO_2 and CH_4 performance data on the continuous measurement repeatability (CMR), the short-term repeatability (STR), the long-term repeatability (LTR), the ambient temperature sensitivity, the inlet pressure sensitivity, and the built-in water vapor correction.

To assess the mobile performance of the analyzer in various deployment configurations, it was tested during balloon flights and ground-based measurements.

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77 30 years of atmospheric methane measurements at Schauinsland Stations in southern Germany : Analysis of trends in mole fraction and emissions derived with radon-tracer method

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Schauinsland is one of the stations with the longest methane in-situ measurement record in Europe. Since 1991, the German Environment Agency (UBA) has continuously measured the CH_4 mole fraction at the Schauinsland station (47°55', 7°55'E, 1205 m above sea level). The monitoring station is a continental mountain station located in the German Black Forest 1000 m above the Rhine valley. Four different instruments (gas chromatographs and CRDSs) were used during the 30-year measurement period. For this study, all data were carefully checked for influences from local sources and for consistency. Radon activity in the atmosphere is measured by the Federal Office for Radiation Protection (BFS).

The trend in atmospheric CH4 mole fraction at Schauinsland, follows the marine background station Mace Head, with a mean continental excess of 26 ppb CH4 during the last 20 years. The Schauinsland CH4 record shows mean seasonal and diurnal variabilities of 31 ppb and 7 ppb, respectively. In a second step of the data analysis, we use the hourly CH_4 and ^{222}Rn measurements to derive with the radon tracer method monthly CH_4 emissions in the catchment area of Schauinsland station. These CH_4 emission estimates show clearly a decrease of more than 30 % from the years 1990s to the more recent years 2007-2021. The major decrease of the CH_4 emissions is observed between 2000 and 2006. Regional and national emission inventories for the region Baden-Württemberg or from UNFCC report for the same period a considerable larger CH_4 reduction of 55-60 %, which is mostly related to the sector waste treatment.

Enter description here.

78 Quantification of methane emission rates in southern Germany using mobile measurements

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The detection and quantification of urban CH_4 emissions is still a challenge due to the complex and heterogeneous distribution of emitters, i.e. leakages in the natural gas grid, waste and wastewater treatment, and biogas plants. Mobile measurements at street level, with cars or bicycles, are a good way to detect methane sources. In this study, we present mobile CH_4 measurements performed in in several cities in Southern Germany. We focused on the leak detection in a small and medium size city (Schwetzingen and Heidelberg) with a population of 20000 and 200000 inhabitant, respectively.

In addition regular mobile measurement campaigns were conducted in the plume of point sources like biogas plants, landfills and waste water treatment plants and gas compressor station with the aim to quantify methane emission. Here we applied a Gaussian plume model, which was tested with several CH_4 release experiments. The results of the city and point source CH_4 emission rates are compared to emission factors used in the national emission inventory.

Enter description here.

79 Updates from the Los Angeles Megacity Carbon Project

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The Los Angeles Megacity Carbon Project (LA Megacity) network, one of three urban testbeds established by the US National Institute of Standards and Technology (NIST), focuses on monitoring greenhouse gas (GHG) emissions in the South Coast Air Basin (California, US). The current *in situ* network of 12 sites provides high precision CO_2, CH_4, and CO observations from Picarro cavity ring-down spectrometers (models G2301 or G2401) equipped with partial drying using a Nafion dryer and operated with automation and data processing through GCWerks software. Three of the sites are equipped with Picarro G5310 analyzers for high-precision measurements of N_2O and CO, operated in collaboration with the California Air Resources Board. The LA Megacity testbed provides a comprehensive dataset for estimating the GHG emissions from an area population of ˜13 million, and aims to help gauge the success of attempts to reduce GHG emissions in this region.

Here, we present recent developments in the LA Megacity network, some concurrent with the Northeast Corridor (NEC) network, including; the implementation of the NOAA/WMO CO_2 X2019 scale, propagation of the NOAA/WMO calibration scales to field tanks prepared at Scripps, first public release of the *in situ* CO observations in the LA Megacity network, implementation and analysis of a 2-point calibration scheme on the *in situ* dataset, improvements to the data processing algorithm at building sites to remove signals from building contamination, and a new estimate of the background concentrations in the basin based on "upwind" observations from the San Clemente Island and Victorville sites, as well as a summary of other recent scientific results.

80 The Sausage ICP: 20 years of inter-laboratory flask-air comparison data

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Many laboratories contribute data sets to the global monitoring of CO_2 and other greenhouse gases in the atmosphere. These measurements need to be accurate and compatible as they are often used together to constrain estimates of global atmospheric trends and fluxes. Any spatial differences due to measurement biases between laboratories can bias their source and sink flux estimates. The respective levels of scientifically required data agreement have been regularly updated by the GGMT Expert community and recommendations made to reach this compatibility. This data agreement could be derived from the respective laboratories' measurement uncertainty estimates. However, there is a risk that measurements are biased by unidentified systematic errors. One method to assess the true data agreement is comparison exercises involving two or more laboratories. A variety of approaches are practiced including co-located sampling, shared flasks, or round robins. They differ in their frequency, the parts of the entire flask observation procedure that they represent, the mole fraction range assessed, and the number of paricipants.

The "Sausage Flask Intercomparison" program was initiated by Heidelberg University in 2002 and is being continued by the ICOS Flask and Calibration Laboratory. It has involved up to 10 flask analysis laboratories, each using their established methods for atmospheric flask whole air sample measurements. It aims to perform comparisons 4-6 times per year which span the range of mole fractions typically observed in the atmosphere at the time of the comparison. Network flasks regularly used within each participating program are sent to the ICOS central facility to be filled from three cylinders of compressed atmospheric air spanning these mole fraction ranges. A set of flasks is flushed in series then filled with one of these cylinders air to ensure consistent composition in each flask. This procedure excludes the uncertainty contribution from individual sample collection procedures. A critical evaluation of the approach is presented to ensure that the observed inter-laboratory differences can be considered as representative measurement and scale offsets between laboratories for samples of their entire station network.

We present up to 20 years of results from this ongoing exercise for multiple gas species

measurements. The data provide a quantitative record of the overall agreement of the participating laboratories. They allow to identify mole fraction dependent inter-laboratory differences. In some cases, they document small systematic offsets between laboratories that are stable over time; in others, these differences exhibit a temporal development. Comparing individual laboratories' data with NOAA GML data reveal that laboratories' average measurement agreements are mostly close to the target compatibility goals for some species but that these goals remain a challenge for others. The comparison results give the participants information to realize issues they might have with specific measurements and thus can help to address such problems. They can also serve as basis to valuate the individual measurement uncertainty estimates.

These results do not include all aspects that may contribute to errors in atmospheric observation but they do present information to assess whether the combination of data sets from various laboratories is appropriate for specific investigations.

81 MACARON : Marseille-Aix-en-Provence metropolis Carbon Atmospheric Research program and Observation Network for improving CO_2 and CH_4 emission estimates.

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The MACARON research program and observation network aims at improving bottom-up estimates of CO_2 and CH_4 emissions of the Aix-Marseille metropolis (AMm) area through top-down approaches. The AMm, located south-east of France in the Sud-PACA region, is the second most populated area of France after the Paris megacity. According to the emissions inventory delivered by the regional air quality monitoring agency ATMOSUD, regional CO_2 emissions are estimated to represent 45.5 $MtCO_2$/yr ie ˜15% of national emissions, with 55% coming from the AMm area. These emissions are mainly attributed to the industrial and energy production sectors (70%), followed by the traffic sector (15%) and building uses (8%). Biofuels represent 4% of the AMm biogenic CO_2 emissions, estimated to be 1 $MtCO_2$ and produced by traffic (37%), waste sector (36%), building uses (20%), industry (5%) and agriculture (2%). According to ATMOSUD, regional CH_4 emissions represent 2.7 $MteqCO_2$/yr i.e. ˜4.6% of national CH_4 emissions, with 0.8 $MteqCO_2$/yr coming from the AMm (i.e. 30.4% of regional emissions) , mostly from the waste sector (78%), followed by the industry/energy sectors (6%) and agriculture (6%).

Emission estimates from bottom-up inventories need to be assessed independently for reducing their uncertainties and for stakeholders to taking efficient mitigation actions. These uncertainties can reach several tens of percents for some emission sectors. This objective can be achieved through top-down approaches. Within the ANR COoL-

AMmetropolis project coordinated by Aix-Marseille University / IMBE (https://www.imbe.fr/anr-cool-ammetropolis.html) in link with the ATMOSUD observation program, and including regional ICOS-France stations, a dedicated atmospheric urban/industrial network has been developed to assess independently CO_2 and CH_4 emissions from the AMm, including two ICOS-France background sites (OHP, since 2014 and ERSA, since 2013), one ATMO-SUD/IMBE urban site in the center of Marseille (MRS, since 2016), one IMBE site in the industrial area of Fos-Berre (PDB, since 2021), and one ICOS-France/IMBE peri-urban site in the forest of Fontblanche, ˜20 km east of Marseille (FBL, since 2007).

All sites have been equiped with CRDS analyzers and meteorological sensors. Furthermore, OHP and MRS are equiped with aerosols Lidars and photometers to retrieve the boundary layer height. Timeseries have been analyzed to address the diurnal, synoptic and seasonal variability of CO_2 and CH_4 and to infer CO_2 and CH_4 urban/industrial plumes in the area of study.

On top of these continuous observations, field campaigns based on radiocarbon and 13C measurements have been carried out to assess the partitioning of the different activity sectors to CO_2 emissions and natural emissions. Multi-tracers approaches based on simultaneous CO_2, CO, NOx, VOCs and black carbon measurements have also been carried out to discriminate sources.

The results obtained so far will be presented and compared to other urban/industrial studies, focusing on urban/industrial greenhouse gas variability and plume assessment, boundary layer height quantification and greenhouse gas sources attribution.

Furthermore, mobile methane campaigns are planned in the coming months to identify point sources CH_4 plumes and location. Finally, a CO_2 mesoscale modeling framework is under progress for developing CO_2 emission reduction scenarios in synergy with local stakeholders. These perspectives will be presented.

82 Mobile methane measurement in UK cities – partitioning sources and comparing spectroscopic analysers

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Royal Holloway's mobile greenhouse gas laboratory MIGGAS has been deployed to measure and identify the source of fugitive methane emissions in UK cities, including London and Glasgow. In the UK both the distinct $\delta^{13}C$ isotopic signature (˜-40‰) and ethane:methane ratio (˜0.05) of pipeline gas can be used to partition this from other methane sources, and the measurements show that emissions in both cities are dominated by gas pipeline leaks.

Five different spectroscopic analysers have been deployed in a vehicle to simultaneously measure methane mole fraction in order to compare ability to resolve leaks and identify the size of methane enhancements from a mobile platform. Very small leaks can be resolved using a 10 Hz analyser, which may be missed with lower measurement frequencies. There is a wide range in peak heights between analysers with different measurement frequencies and cavity sizes. To estimate emissions using mobile measurements consideration needs to be given to the instrumentation, driving speed and model used to avoid under or over estimating emissions.

83 Beyond the GGMT Greenhouse Gas Measurement Guidelines: Guidelines for National and Urban Greenhouse Gas Emission Monitoring and Assessment

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The GGMT community has worked for many years to provide careful guidelines for high quality measurement of greenhouse gases and associated isotopes and tracers, and this effort has been supported by WMO and it's Global Atmospheric Watch (GAW) programme. Further, the WMO Integrated Global Greenhouse Gas (GHG) Information System (IG^{3}IS) initiative has worked to document and promote the value of an integrated approach for estimating GHG emissions that combines activity-based emissions information with model analyses of atmospheric mole fraction measurements.

A primary function of IG^{3}IS is to improve the relevance and value of emissions information for decision-makers. A key step on that path is to assess and document the current best research practices to guide stakeholders as well as practitioners to enhance the capacity of nations, states, cities, and industries to target significant emission reduction opportunities and track the success of these policy measures. This effort includes documenting state-of-the-art methodologies, recommendations for their application, known challenges and limitations, and future opportunities for improvement.

In June 2022, IG^{3}IS completed the first edition of the Urban Greenhouse Gas Emission Observation and Monitoring Good Research Practice Guidelines. This document is authored by more than 50 researchers from across academia, national and international research organizations representing a range of countries and cities with expertise in urban greenhouse gas emissions research. IG^{3}IS intends to provide updates of these guidelines every two years, in a similar manner to the GGMT guidelines and the next iteration of our document will make a strong effort to provide information in a format more accessible to a broad range of stakeholder and decision-maker communities.

Later this year, IG^{3}IS will launch a similar effort to document national-scale emissions observations and monitoring, tapping the knowledge and experts from GGMT and the lessons learned during the creation of the Urban Guidelines. This presentation will discuss these IG^{3}IS efforts in the relation to the ongoing work of GGMT community. We will also discuss the potential for enhancements to GAW GHG measurements and IG^{3}IS efforts around the globe through a newly proposed effort of the WMO Commission for Observation, Infrastructure and Information Systems to develop and refine a concept for a Global GHG Measurement and Monitoring Infrastructure.

84 Status of the New Zealand atmospheric greenhouse gas observation network.

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The greenhouse gas observation network in New Zealand was initially developed to observe baseline air arriving off the ocean that was representative of large areas of the mid-latitude southern hemisphere. In more recent years the focus has shifted to include observations of air that has interacted across the country. This has allowed us to utilize inverse modelling techniques at a national scale for both carbon dioxide and methane to identify sources and sinks of these species and is coordinated within our CarbonWatch New Zealand programme.

To provide a better national coverage observation stations have been added that observe baseline input air flows, while others have been added to allow for specific sectors to be studied more closely that provide observation in key urban, forest and grassland areas.

Supporting the in situ observations we utilise a number of tracer species that assist in interpreting the processes involved in production and removal of greenhouse gases. Tracer techniques can provide insight into fossil fuel contributions, chemistry and the role of photosynthesis. The network flask collections provide air for laboratory studies of isotopic composition, and related species like carbonyl sulphide.

85 The revised INSTAAR data set for δ^{13}C-CO_2: How do we measure up to other stable isotope laboratories, and how can we work together to make the most of our data?

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INSTAAR's thirty-two year record of δ^{13}C-CO_2 and $\delta\ ^{18}$O-CO_2 from NOAA GML's Global Greenhouse Gas Reference Network is now tied to JRAS-06, which is directly traceable to the VPDB-CO_2 scale. This is an improvement to the INSTAAR data, both because it corrects calibration errors that had been in our 'local' scale realization, and because it moves us toward better comparability and compatibility with other stable isotope labs using JRAS-06. We also have improved our quantification of uncertainty. Metrics such as reproducibility of surveillance cylinders, pair differences of co-sampled flasks, and test flasks reflect the quality of the data from our high-throughput operation and the efficacy of our flagging routines. Finally, we investigate offsets with other labs measuring $\delta\ ^{13}$C-CO_2, and how these vary over time. Co-located measurements, same-air samples, and round robin comparisons provide the data we need to quantify our differences, merge datasets with appropriate error bars, and confidently use the global stable isotope dataset in dual tracer inversion models.

86 Quantifying combined uncertainties of δ^{13}C-CO2&δ^{18}O-CO_2 from 20-year calibration datasets: how good could we achieve in realization of VPDB-CO_2 scale via NBS19 etc. carbonates?

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To improve uncertainties in CO_2 flux estimation using multiple atmospheric observation records via inversion models, it is important to quantify the combined uncertainties for each individual components, including isotope tracers (δ^{13}C-CO_2 or δ^{18}O-CO_2). Combined uncertainty is quantified via propagation of the uncertainties associated with individual steps through a traceability path to the primary references.

The primary scale of δ^{13}C-CO_2 or δ^{18}O-CO_2 is VPDB-CO_2. One of the primary standard/reference is NBS19 (carbonate) with assigned isotopic values. To tie atmospheric δ^{13}C-CO_2 or δ^{18}O-CO_2 measurements to the primary scale, it needs linking the measurements to NBS19-CO_2 through all levels of standards via a traceability path as realization of VPDB-CO_2 scale.

A direct and clear traceability path in realization of VPDB-CO_2 scale has been utilized in ECCC's lab over the last 20 years for measuring CO_2 isotopes and BC isotopes. We use two levels of carbonate standards (NBS19 as the primary standard, NBS18 and two additional lab carbonates as the secondary standards). We calibrate/tie NBS18 and the two carbonates (Cal1 & Cal2) against/to the primary scale via NBS19-CO_2 on an annual basis (measuring them together against the same working reference gas), and then we use secondary standards to tie our atmospheric sample measurements to VPDB-CO_2 scale.

The overall measurement uncertainty includes the uncertainties from the two levels, i.e., calibration for secondary standards via NBS19-CO_2 and sample measurement against the secondary standards. Those uncertainties are usually associated with carbonate-CO_2 production via acid digestion, IRMS analysis, and air-CO_2 sampling/handling and CO_2 extraction etc.

In this presentation, we are going to focus on quantification of uncertainties at the first level, i.e., calibration of secondary carbonate standards against the primary standard (NBS19), a key step in realization of VPDB-CO_2 scale. A 20-year-record of δ^{13}C-CO_2 or δ^{18}O-CO_2 by three different IRMS instruments (i.e., MAT252 over 2001-11, IsoPrime over 2002-14, and MAT253 over 2012-22) will be presented. The overall uncertainties for the periods by individual instruments as well as over the entire period of 20-year will be quantified and discussed. Those results would facilitate answering the question: how good could we achieve in realization of VPDB-CO_2 scale over decadal time?

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87 Progress Toward a NOAA Commercial Aircraft Greenhouse Gas Measurement Program

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The NOAA Global Monitoring Laboratory (GML) is actively pursuing establishment of an insitu measurement program program for CO_2, CH_4, CO, and H_2O from a Boeing 737 commercial aircraft platform to greatly increase the number vertical profile measurements that are routinely collected over the U.S. and Arctic. Toward this goal, last year, NOAA GML participated in the Boeing ecoDemonstrator test flight program on a 737 aircraft to test potential sample inlets and identify candidate locations for housing instrumentation. During this program, three Picarro analyzers were flown in-parallel and made simultaneous measurements on air drawn from three different inlet configurations. Two of the inlets that were tested are those that are used by IAGOS and CONTRAIL, the European and Japanese commercial aircraft greenhouse gas measurement programs, respectively and the third inlet is a flush-mount that is used by NOAA's WVSS-II program, which collects water vapor data from commercial aircraft for improved weather forecasting. Data collected over 260 flight hours demonstrated remarkable compatibility for CO_2 and CH_4 among the three inlets throughout normal flight profiles. Large differences for H_2O and CO were shown from the engine bleed air sample configuration used by CONTRAIL, as expected. Small differences for CO_2 and CH_4 were shown between the flush-mount inlet used by WVSS-II and the Rosemount inlet used by IAGOS during vertical profiling between ground level and 12 km altitude. Identification of a viable inlet design is a critical step in the long-term effort by NOAA to build a commercial aircraft greenhouse gas measurement network.

88 Chasing the WMO CO_2 Compatibility Goal around the Southern Ocean

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The WMO GAW community has had a longstanding compatibility goal for CO_2 measurements of 0.05 ppm in the Southern Hemisphere. Making atmospheric CO_2 measurements to this level is challenging, and it has generally only been possible to achieve ˜0.2 ppm compatibility at best. Difficulties exist for any site, owing to challenges in maintaining and propagating calibration scales at this level of precision—but challenges are particularly acute for remote Southern Ocean stations with limited access for monitoring in situ instruments operating in harsh environments, and long and potentially cold storage of flask samples. Potential problems include laboratory scale offsets, drift in field reference standards, flask storage effects, room air contamination through leaks at fittings, and local terrestrial influences at coastal or island sites.

We evaluated 44 available CO_2 measurement records from surface stations south of 30 S, spanning the past four decades, for their ability to provide insight into Southern Ocean fluxes. We excluded records for a variety of reasons, including strong local terrestrial influences, shortness or sparseness of the records, and flask storage effects. Of those considered, we used measurements from 22 records in a recently published analysis (Long et al., Science, 2021). We used observations from NOAA, Scripps Institution of Oceanography, the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Laboratoire des Sciences du Climat et de l'Environnement (LSCE), the National Institute of Water and Atmospheric Research (NIWA), and the South African Weather Service (SAWS).

In collaboration with these data providers, we identified issues associated with local influences evident in diurnal CO_2 cycles over the Southern Ocean, and several inconsistencies related to flagging information conveyed in the ObsPack metadata. We also benefited from efforts already underway to correct for flask storage effects in the NOAA South Pole (SPO) and Syowa records, and to better reconcile the Scripps and NOAA/WMO CO_2 scales. Comparisons between NOAA, Scripps, and CSIRO records at SPO and Cape Grim (CGO), suggest 1-sigma compatibility of $\pm$0.10 ppm at SPO and $\pm$0.04 ppm at CGO for 20-year means, but larger values of $\pm$0.14 ppm at SPO and $\pm$0.12 ppm at CGO for monthly means.

The resulting data set was able to resolve clear latitudinal gradients in CO2 over the Southern Ocean, with deficits up to -0.5 ppm in summer and enhancements up to 0.2 ppm in winter, reflecting seasonal air-sea exchange. The summer gradients were able to constrain air-sea fluxes but owing to stronger atmospheric mixing, sparse observations, and measurement uncertainty, the winter gradients were not. Aircraft observations over the Southern Ocean have the distinct advantages of 1) being able to define spatial gradients using a single—or more typically multiple—instruments, thus greatly reducing compatibility errors, and 2) measuring vertical gradients that are much more sensitive to the underlying air-sea fluxes.

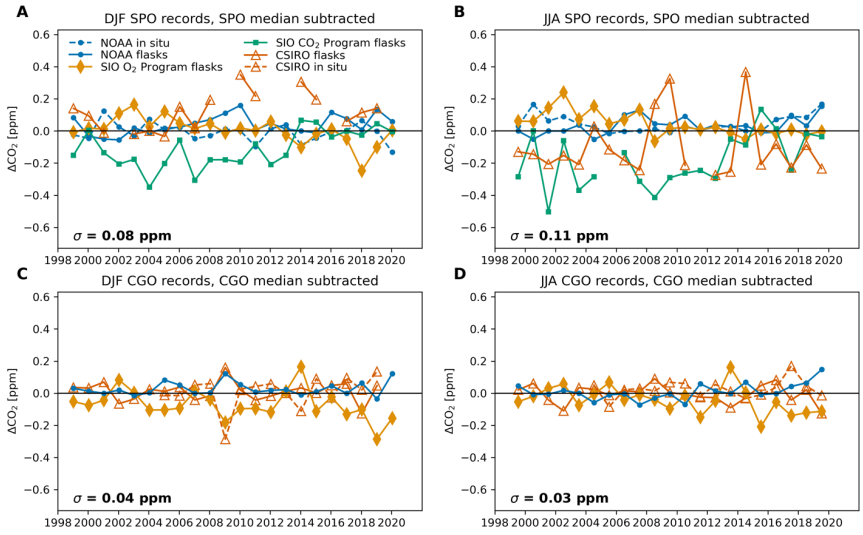

Figure. Comparison of seasonal records at South Pole Observatory (SPO) and Cape Grim Observatory (CGO). (Left) Summer and (right) winter CO_2 records at (**A, B**) SPO and (**C, D**) CGO. The sigma values given in each panel are the standard deviations of the 20-year mean values for each record. From Long et al. (Science, 2021).

89 A multi-pronged effort needed to enhance measurements of GHG vertical profiles

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For several decades, aircraft, and now balloon, vertical profiles of greenhouse gases (GHGs) have provided a critical constraint for satellite retrievals, forward and inverse models, and for our basic understanding of the carbon cycle and processes that drive changes in the atmospheric burden of GHGs. Despite the powerful constraint that vertical profiles provide, planned campaigns and routine profiling programs are globally sparse and insufficient given the challenges of interpreting remote sensing measurements and models that track the atmospheric composition of GHGs, which depend on significant bias corrections, highly accurate transport models and underlying ocean and land processes.

The technology is available for the rapid expansion of global atmospheric profiling, but it will require significant effort and international collaboration to achieve the spatial and temporal coverage needed to integrate surface and spaceborne GHG observations. Lessons learned from recent global aircraft campaigns, commercial and routine, light and heavy aircraft deployments, and balloon-based platforms provide us with robust measurement technology that enables an operational, instead of research-based, approach for capturing profiles of GHGs. We propose a multi-national, multi-institutional and multi-platform approach, which seeks to use both regular measurement campaigns as well as routine, site-based and flights of opportunity on high-use (e.g. commercial and government) aircraft. It is important that the global community recognizes this opportunity and acts together to leverage these new possibilities.

90 Greenhouse gas measurements onboard the Research Vessel Investigator – GAW's first mobile observatory

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The Southern Ocean is a globally significant region for understanding the climate system. It is a major sink of CO_2 and plays an important role in the N_2O budget. However, due to its vast extent, limited land surfaces and inaccessibility during much of the year, we have very few high quality, long-term observations of this near-pristine area.

The tropics are another climatically significant region of the globe where our understanding of carbon sources and sinks is severely limited by data paucity.

The RV *Investigator*, Australia's Marine National Facility has been operating with two atmospheric laboratories (one for aerosol and reactive gases measurements, one for greenhouse gases) since 2014 and has since been recognised as GAW's first mobile facility. The vessel makes regular trips across the Southern Ocean, to the ice edge of Antarctica, travels around the Australian coastline and undertakes voyages in Australia's tropical waters. The datasets from this observatory are helping deliver greater understanding of the atmospheric composition in under sampled parts of the planet.

We will here present some representative datasets and describe the changes in our sample handling and measurement technology over the past eight years. We will be highlighting lessons learned as CSIRO engages with the Australian Antarctic Division to instrument its new ice breaker, the RSV *Nuyina*.

91 Retrieving the global mean surface CO_2 level from the GAW in-situ network

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A sufficiently dense CO_2 observation network and comprehensive approach is critical to monitor changes in global CO_2 and support the development of climate policies to mitigate climate change. The WMO WDCGG archives and analyses the measurements from the WMO GAW observation network, the derived global mean surface CO_2 level includes uncertainty due to data extension. NOAA implemented a similar curve fitting and data extension method, while only represents the marine boundary layer. This study uses a method, semi-NOAA, and apply to almost all GAW stations, additionally also we apply the method to 3D CO_2 output from the CTeu model. The semi-NOAA setup results in the global surface average ranges from 339.13±0.38 ppm in 1980 to 413.05±0.16 ppm in 2020, in high agreement (r=1, RMSE=0.053 ppm) with the WDCGG approach without the external data extension to the increased network. CTeu output at station grids or all global grids results in higher global CO_2 mole fraction (˜0.59 ppm or ˜1.255 ppm) comparing to the estimates from station observations, however, all three show good agreement in their derive atmospheric growth rate. This implies that the sparsity of current CO_2 network is not an obstacle to monitor global surface CO_2 changes, while the restricted network likely underestimates the total global surface CO_2 mole fraction. We find that the global surface CO_2 mole fraction shows a clear linear relationship with atmospheric CO_2 mass, which implies that the global surface CO_2 GAW network can represent the signal of CO_2 change in atmosphere very well.

92 QA/SAC Switzerland and QA/SAC Japan contributions to the quality of GAW's greenhouse gas observations

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Within the GAW programme, systematic observations of high accuracy and full traceability are the key to scientific exploitation and reliable information for society, policy makers, and international conventions like the United Nations Framework Convention on Climate Change (UNFCCC). Of critical importance are long-term measurements to determine trends, variability and unexpected changes of atmospheric variables. In support of the observations, a quality assurance system based on Central Facilities is established, which are responsible for quality control, dissemination, scientific guidance, training and technical developments of the global network. A key role for the quality control in the GAW programme is played by the four Quality Assurance/Science Activity Centres (QA/SACs), which are currently operated in Germany, Japan, Switzerland and the United States. Overall, QA/SACs support the programme through the provision of an operating framework for GAW quality assurance activities, training and technical support, and the promotion of scientific exploitation of GAW data. The detailed terms of references for QA/SACs are defined in the GAW Implementation Plan. Due to the rather broad scope, QA/SACs usually focus on specific variables and/or geographical areas. Here, we present the activities of QA/SAC Switzerland, hosted by Empa, and QA/SAC Japan, hosted by the Japan Meteorological Agency (JMA), which are both supporting the observations of greenhouse gases, but in different regions of the world. Highlights and ideas for future collaboration are presented.

93 INT7020 project: Developing Capacity towards the Wider Use of Stable Isotopic Techniques for Source Attribution of Greenhouse Gases in the Atmosphere

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INT7020 "Developing Capacity towards the Wider Use of Stable Isotopic Techniques for Source Attribution of Greenhouse Gases in the Atmosphere" is an IAEA and WMO technical cooperation project aims at assisting countries in using stable isotopes to measure the release of greenhouse gases (GHGs) and accurately determine their source.

Countries around the globe made commitments under the Paris Agreement, the Kyoto Protocol and their respective national policies to reduce emissions of greenhouse gases. The IAEA and WMO, in the framework of this INT7020 project, supports countries with improving capacities in stable isotope analysis that is critical for determination of the origins of these greenhouse gases. Over several years, the project intends to establish regional training and analysis centers which will support laboratories from their respective regions with developing analytic capacities for the collection and the interpretation of gases data. The trained scientists will be able to inform decision makers and help authorities target their climate policies, dispel local myths about the reality of emissions, and build support for focused climate action. The establishment of a first regional training and analysis center has started in Argentina, while in parallel, the IAEA is developing reference materials for CH_4 isotopes, and is in the process of finalizing a Good Practice Document - Guidelines for measurements of isotopes in atmospheric CH_4 to characterize CH_4 sources.

The project aims to support the regions of the globe with lesser capabilities to collect, analyze and report isotopic data.