Publishable Summary for 19ENV05 STELLAR
Stable isotope metrology to enable climate action and regulation

Overview

Global warming is one of the greatest risks to society worldwide. To prevent stark changes to the Earth's climate, emissions of carbon dioxide and methane must be reduced, requiring discrimination between anthropogenic sources and natural contributions and emissions from different industrial sectors. This project will fill the traceability gap in the measurement of the isotopic composition of carbon dioxide and methane by providing an infrastructure for delivering gaseous reference materials and methods. This work is essential to provide governments with the data required to support inventory verification targets and enable pledges of emissions reductions to be demonstrated.

Need

Immediate action on greenhouse gas emissions mitigation is required to limit dangerous changes to Earth's climate. There is increasing international focus on meeting the United Nation's Paris Agreement signed by 197 countries in 2016, to prevent global temperatures from reaching 2 ˚C above pre-industrial levels by 2100, and ideally 1.5 ˚C. A report by the Intergovernmental Panel on Climate Change (IPCC) states that meeting this implies halving the annual global carbon emissions between now and 2030, and falling to zero by 2050. It is likely that even "negative emissions" (sinks of carbon dioxide) will have to be organised. Many of these components also influence the formation of tropospheric and depletion of stratospheric ozone, so are relevant to air quality (Directive 2008/50/EC) and climate.

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 and methane amount fractions is challenging and requires information on the isotopic composition, especially if man-made negative emissions start to play a role.

Currently, there is no infrastructure to deliver carbon dioxide and methane 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 and methane by developing gas reference materials, calibration methods and dissemination mechanisms, which are traceable to existing scales (e.g. VPDB - Vienna Pee Dee Belemnite - and VSMOW/SLAP - Vienna Standard Mean Ocean Water/ Standard Light Antarctic Precipitation) and the SI.

Additionally, metrology is also required to ensure advances in optical spectroscopy result in field deployable techniques that meet uncertainty requirements.

Objectives

The overall objective of this project is to fill a traceability gap in the measurement of the isotopic composition of carbon dioxide and methane by providing a new infrastructure able to deliver gaseous carbon dioxide and methane reference materials to meet the increasing demand to underpin greenhouse gas measurements. This project also strives to validate existing and develop new and field-deployable spectroscopy. The specific objectives of the project are:

1. To develop gas reference materials of carbon dioxide (pure and 410 µmol mol^{-1} in an air matrix) with a repeatability of 0.01 ‰ for $\delta^{13}C\text{-}CO_2$ and 0.05 ‰ for $\delta^{18}O\text{-}CO_2$ with target uncertainties of 0.05 ‰ for $\delta^{13}C\text{-}CO_2$ and 0.1 ‰ for $\delta^{18}O\text{-}CO_2$, ensuring traceability to the primary VPDB scale with stability of more than two years. In addition, to characterise IRMS scale contraction, establish the relation between the

VPDB-CO_2 and VSMOW-CO_2 scales for ^{18}O, and ^{17}O correction on carbon dioxide for methane isotope ratio measurements.

2. To develop gas reference materials of methane (pure and 1.85 µmol mol^{-1} in an air matrix) with a repeatability of 0.02 ‰ for $\delta^{13}C$-CH_4 and 1 ‰ for $\delta^{2}H$-CH_4 and with target uncertainties of 0.2 ‰ for $\delta^{13}C$-CH_4 and 5 ‰ for $\delta^{2}H$-CH_4, ensuring traceability to the VPDB and VSMOW scales with stability of more than one year.
3. To develop SI traceable methods for absolute isotope ratio measurements of carbon dioxide with uncertainties of 0.1 ‰ for $\delta^{13}C$-CO_2.
4. To develop and metrologically characterise field deployable spectroscopic methods and calibration approaches for isotope ratio measurements of carbon dioxide and methane with a target precision of 0.05 ‰ for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2, 0.2 ‰ for $\delta^{13}C$-CH_4 and 1 ‰ for $\delta^{2}H$-CH_4.
5. To facilitate the take-up of the technology and measurement infrastructure developed in the project by the measurement supply chain (accredited laboratories, CCQM), standards developing organisations (CEN, ISO) and end users (WMO-GAW, IAEA, instrument manufacturers, specialty gas industry).

Progress beyond the state of the art

Calibrating reference materials of carbon dioxide in air back to the reference standard (VPDB) as required for atmospheric monitoring, creates problems of traceability and reproducibility due to e.g. sampling. The Jena Reference Air Sets (JRAS) are stable isotope standards consisting of carbon dioxide generated from a calcite and mixed into CO_2-free air. These standards define the JRAS-06 scale that is closely linked to the VPDB-CO_2 scale. Currently, the production of gas reference materials using this method is limited and prohibitively expensive.

This project will build on the results of the EMPIR project SIRS (16ENV06) by developing independent capabilities for the whole traceability chain and an improved understanding of the influence of parameters in gravimetric preparation on isotopic fractionation. The improved method will deliver reference materials of carbon dioxide with a repeatability of 0.01 ‰ for $\delta^{13}C$-CO_2 and 0.05 ‰ for $\delta^{18}O$-CO_2 and with target uncertainties of 0.05 ‰ for $\delta^{13}C$-CO_2 and 0.1 ‰ for $\delta^{18}O$-CO_2, traceable to the VPDB-CO_2 scale.

The use of different calibration approaches and standards have contributed to inter-laboratory measurement offsets of up to 0.5 ‰ for $\delta^{13}C$, and 13 ‰ for $\delta^{2}H$ measurements of atmospheric methane isotopes. Currently, no methane isotope ratio gas reference materials exist that provide traceability to the VPDB and VSMOW/SLAP scales for $\delta^{13}C$ and $\delta^{2}H$, respectively, which meet the uncertainty and high-volume requirements to underpin global measurements. There is also no Central Calibration Laboratory (CCL) at the WMO-GAW level to ensure compatibility of global observations.

No absolute isotope ratio measurements traceable to the SI have been achieved thus far with the desired uncertainty due to insufficient methods and instrumentation. This project will develop SI traceable methods for absolute isotope ratio measurements of carbon dioxide with uncertainties of 0.1 ‰ for ^{13}C-CO_2 and 0.1 ‰ for ^{18}O-CO_2.

Introduction of relatively low-cost spectroscopic techniques has revolutionised the measurement of key greenhouse gas components in air by enabling continuous in-situ field measurements for quantifying sources and sinks at local, regional, and global levels. In tandem, existing validation routines, recommendations and traceability chains for field-deployable spectroscopic techniques that meet the precision specifications of IRMS are not yet available.

Results

Carbon dioxide gas reference materials (pure and 410 µmol mol^{-1} in air)

Technical capabilities have been developed to perform the carbonate -phosphoric acid reaction that forms the basis of the international VPDB scale for $\delta^{13}C$ and $\delta^{18}O$. MPG have scrutinised the system, to reach the "perfect synthesis". To this end, known carbonates (IAEA-603, MarJ1, NBS-19) have been used for the reaction, while several parameters have been varied, such as the degassing time of the phosphoric acid, the composition of the various materials in use and improved temperature control. The present status is that both the target uncertainties (0.05 ‰ for $\delta^{13}C$ and 0.1 ‰ for $\delta^{18}O$) and reproducibility (0.01 ‰ and 0.05 ‰, respectively) have been achieved, but that there appears to be an offset compared to previous results. If these offsets are real, they might lead to changes in the JRAS scale.

Several batches of CO_2 from IAEA-603 and MarJ1 have been produced, which will be measured at MPG. Results will show both the reproducibility of the RUG's phosphoric acid reaction, and a possible deviation between the reaction processes between the two laboratories. JSI is reproducing the original McCrea 1950 set-up, only at elevated temperature. Thereafter the analysis of the isotope ratios will use a continuous flow IRMS system. First results for $\delta^{13}C$ are satisfactory in terms of both the value and the reproducibility. For $\delta^{18}O$ the results still need considerable improvement. JSI will also be in the loop with MPG and RUG for sending and receiving CO_2 from the phosphoric acid reaction.

UEF have performed the phosphoric acid reaction in a classical setting but performed the isotope measurements using a Picarro optical Cavity Ring Down Spectroscopy (CDRS) system. This system's results are, however, CO_2 concentration dependent, so more work is needed before reliable $\delta^{13}C$ measurements can be performed.

NPL has prepared an air matrix free of CO_2 by synthesising air from the pure components (N_2 78.1 %, O_2 20.93 %, Ar 0.93 % and N_2O 330 nmol mol^{-1}). The pure source gases have been provided by AL. The composition has been verified by GC and CRDS using existing NPL standards. Determination of any traces of residual CO_2 and CH_4 is crucial for the integrity of the isotopic composition of the CO_2 (and CH_4) to be added. NPL has determined these residuals by the standard addition of diluted fractions of an NPL standard. Results show that the residual concentrations of CO_2 are in the 0.01-0.02 µmol mol^{-1} range. Even when assuming very negative δ-values for this CO_2, the influence on the $\delta^{13}C$ and $\delta^{18}O$ values will be < 0.01 ‰. NPL is in the process of shipping 10-12 cylinders of this synthetic air in high pressure cylinders to INRIM and TUBITAK. Institutes will add pure CO_2 (from the previous SIRS project) to reach an amount fraction of 410 µmol mol^{-1}. NPL itself will do the same.

Absolute carbon dioxide isotope ratio measurements towards SI traceability

LGC identified D-glucose as the most suitable compound to be used in the preparation of calibration mixtures. Purchasing of isotopically enriched glucose has been arranged in two stages. At the first stage, small amounts of ^{13}C-depleted and ^{13}C-enriched material were acquired. Their isotopic abundances and chemical composition were checked. At the second stage, larger amounts of these compounds were purchased. ^{13}C-depleted D-glucose has been delivered. A shipment of ^{13}C-enriched D-glucose is delayed and expected to arrive by June. The principle of the method is that measurements of the compounds themselves and, in addition, of a gravimetrically prepared mixture, enable one to determine the instrument's mass bias coefficients K, and following from that determination the absolute isotope abundances. PTB has concentrated on the mathematics of the equations to be solved, both for the more general case of true isotope mixtures, and the case of isotopologue mixtures, as is the case for CO_2. The calculations for these cases, both the values themselves and the full uncertainty budget, have been made available as Excel spreadsheets.

Methane gas reference materials (pure and 1.85 µmol mol^{-1} in air)

The inventory of methane sources has been completed. The easiest (and cheapest) route to span this range is to start with pure fossil and pure biogenic methane and mix these gravimetrically. It has been identified that methane from biogenic origin is much harder to obtain at the requested high purity. VSL, VTT, JSI, NPL and AL are in contact with potential suppliers.

NPL is developing the plans for the CH_4 to CO_2 combustion facility based on literature and purchased the furnace and Pt catalyst. Further, plans for the dynamic dilution system are being developed.

Spectroscopic methods for in-field isotope ratio measurements of carbon dioxide and methane

Strategies have been developed to measure $\delta^{13}C$-CO_2 and $\delta^{18}O$ -CO_2. PTB, VTT, DFM and RUG have identified different uncertainty contributions and defined strategies to quantify and reduce these uncertainties. These strategies include optimisation of the gas sampling, possible changes in electronics and optics, improvements in data processing including spectral acquisition, averaging and fitting, analysis of gas matrix effects and optimizing calibration routines. VTT began work on improving the precision of the field-capable CO_2 isotope analyser.

A step towards an improved protocol for metrological characterisation of OIRS has been taken by an OIRS-IRMS comparison by INRIM, NPL and RUG: Three cylinders with CO_2 in air at different isotopic composition were prepared, subsampled and analysed by IRMS and OIRS. The subsampling of the cylinders was performed to with assure the same sampling method for all subsamples and the resulting dataset showed a large agreement between the analysis with OIRS and IRMS with residuals below 0.07 ‰ VPDB for $\delta^{13}C$ and 0.04 ‰ VPDB-CO_2 for $\delta^{18}O$ -CO_2.

Key factors that limit precision and accuracy for OIRS analysers for $\delta^{13}C$-CH_4 and $\delta^{18}O$ -CH_4 have been studied. The partners (Empa, PTB, DFM, NPL) collected and provided a literature-based overview and discussion of different uncertainty contributions related to the spectrometer, the scale, data collection and processing and preconcentration (if applied). Additionally, the spectral line positions and line strengths of all analysers that are used within the project are provided. Further, the different analyser's spectral ranges were analysed with respect to the absorption of other interfering components such as CO_2, H_2O and N_2O to evaluate potential spectral interferences. This information forms the basis for an analysis of need for improved spectral line data, that already started and is ongoing. Further, the partners have defined requirements for gas reference materials for calibrating $\delta^{13}C$-CH_4 and $\delta^{18}O$ -CH_4 at ambient levels and calibrating at enhanced concentration (in particular for evaluating gas matrix and concentration effects).

Experimental and conceptual work has been performed to enhance the performance of the analysers for CH_4 measurements. These improvements by the partners (Empa, PTB, NPL, VSL) included optimisation of preconcentration, adjustments to the gas handling scheme, evaluation of the analysers spectral assignment and alternative calibration approaches as well as changes to the optical gas cell.

Impact

A website featuring summary material on the project can be found here: http://empir.npl.co.uk/stellarproject/.

The project has a committee of thirteen stakeholders from organisations such as CSIRO Oceans and Atmosphere, ABB LGR, BIPM, University of Wollongong, NOAA Global Monitoring Division, Max-Planck-Institute for Biogeochemistry, Licor, INSTAAR, University of Colorado and Institut fuer Umweltphysik.

The project now has a collaborator, the Physical and Chemical Metrology Department within the D.I. Mendeleev All-Russian Institute for Metrology (VNIIM). It is the leading Russian organization in the field of precise measurements in metrology and the major centre of national measurement standards in Russia.

Presentations on aspects of the project were made at the General Assembly 2021 (vEGU21: Gather Online) Copernicus meetings. Additionally, an introduction to the STELLAR project was presented at the Dneve Jožefa Stefana / Jožef Stefan Institute Open Day.

Impact on industrial and other user communities

This project will develop clear tangible outputs (i.e. new reference materials, instrumentation, calibration methods and recommendations), which will lead to a European-based calibration service integrated into the European Metrology Network (EMN) on Climate and Ocean Observation. The atmospheric monitoring community (e.g. the European ICOS and other networks, organisations such as WMO-GAW and academia) will have access to new traceable reference materials. The atmospheric monitoring community and instrument manufacturers will benefit from improved spectroscopy methods, which provide traceable measurements and improved specifications to match those provided by mass spectrometry. This will provide access to instrumentation (e.g. CRDS) that is more cost effective and more portable for field use. Instrument manufacturers will benefit from the supply of the next generation of accurate calibration standards for isotopic composition, which will ensure their instruments are traceable and provide valid data for atmospheric monitoring. This will increase market potential for their instruments. Speciality gas companies will benefit from traceability to support gas mixture production under accreditation, which will open new opportunities for reference mixtures for isotopic composition.

Impact on the metrology and scientific communities

Global comparability helps assess the real state-of-the-art in measurement. Metrology for stable isotopes of carbon dioxide and methane is a strategic priority for CCQM-GAWG, which the consortium has very good links with. Therefore, the research outputs (e.g. development of capabilities and reference materials) from this project will be presented to global experts in gas metrology at their meetings to advance the state-of-the-art in measurement science. The NMIs and external partners involved in this project will benefit from enhanced capabilities and primary reference materials which will lead to increased revenue from measurement services.

Such is the importance of underpinning isotope ratio measurements to the metrology community that a new working group (CCQM-IRWG) has been established to advance measurement science and support stakeholders. The project partners are actively involved in the activities of CCQM-GAWG and CCQM-IRWG. Outputs from this project will be presented to global experts from a diverse range of sectors (e.g. metrology, academia and industry). The development of reference materials for carbon dioxide and methane will support future pilot studies and key comparisons for global comparability, new calibration and measurement capability claims for isotopic composition. The consortium is well connected with the WMO community, the IAEA and the IUPAC-CIAAW.

Impact on relevant standards

The developments in this project will be used to revise existing standards by updating reference methods to allow isotopic analysis in documentary standards under ISO/TC158 (Gas Analysis) and CENTC/264 (Air Quality) and will improve comparability of atmospheric and stack measurements by end users.

Longer-term economic, social and environmental impacts

There are a variety of ways that climate change will have an economic impact. Some are gradual changes such as increased cooling costs for buildings, while others are more dramatic, related to the higher frequency of extreme weather events. The cost of inaction is vast. In a recent report, projections indicate that combined country-level costs (and benefits) add up to a global median of more than $400 in social costs per tonne of carbon dioxide. Based on the carbon dioxide emissions in 2017, that presents global impact of more than $16 trillion.

This project will have a direct impact on the environment and quality of life as it will underpin global monitoring, provide a greater understanding of the increasing influence of human activity on the global atmosphere and inform decisions on policy. It will allow European states to comply with current legislation requiring the measurement of components in ambient air which govern climate change and air quality. It will work towards meeting the requirements of the Kyoto Protocol and COP21 to reduce emissions of the most important greenhouse gases.

This project will have impact beyond the immediate community of laboratories concerned with monitoring long-term atmospheric trends. Examples include the impact on public health from future improvements in the accuracy and efficiency of the data acquired to meet the EU Air Quality Directives (e.g. 2008/50/EC).

List of publications

There are yet no publications.

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

<table>
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<tr><td colspan="3">Coordinator: Paul Brewer, NPL Tel: +44 (0) 208 943 6007 E-mail: paul.brewer@npl.co.uk
Project website address: http://empir.npl.co.uk/stellarproject</td></tr>
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1 NPL, United Kingdom
2 DFM, Denmark
3 INRIM, Italy
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