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.

In 2015, the World Meteorological Organisation (WMO) reported that the global average amount-of-substance fraction of carbon dioxide exceeded the symbolic 400 $\mu mol\ mol^{-1}$ threshold and it is unlikely to return to this level in our lifetimes. To support governments verifying emissions and demonstrating national reduction targets, it is crucial to discriminate between the natural and various manmade sources of greenhouse gases. This requires accurate measurements of baseline concentrations and contributions resulting from emission events. However, separating man-made 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.

There has been a significant research effort worldwide to set up a metrological infrastructure to provide traceable measurements of carbon dioxide isotope ratios to the delta scale, since all isotope measurements must refer to this. The stable isotope standard for oxygen and carbon, NBS 19, was developed in 1982 at NIST from a white marble slab of unknown origin and was used to define the primary VPDB scale. In 2006 new guidelines were published for $\delta^{13}C$ calibration, including a recommendation to additionally use an assigned $\delta^{13}C$ value for the LSVEC (lithium carbonate) reference material to obtain an improved two-point calibration. However, NBS 19 is now exhausted and LSVEC has suffered stability issues, both posing serious challenges to maintaining continuity to the primary scale and reducing offsets between laboratories from calibration. The IAEA has taken great care to maintain continuity to the primary scale by producing IAEA-603 (replacement of the highest, $\delta^{13}C_{VPDB}$ scale-defining NBS 19). While numerous speciality laboratories are working to provide a second scale anchor for the $\delta^{13}C_{VPDB}$ scale, a replacement for LSVEC has not yet been made available.

This project is driven by an overwhelming demand from the atmospheric monitoring community for improved and more widely available isotope ratio reference materials of carbon dioxide and methane which are traceable to the primary scales and meet the uncertainty requirements for assessing changes in atmospheric composition. These reference materials are required to ensure carbon dioxide reference materials are produced with smaller uncertainties which is essential for underpinning global monitoring and meeting WMO-GAW requirements. Currently, there is no infrastructure i.e. methods and instruments to deliver carbon dioxide and methane gas reference materials with the required uncertainties to underpin global observations, which compromises 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. As access to reference materials that link measurements to the delta scale are limited, work to test and verify new methods to determine absolute values of isotope ratios for ^{13}C-CO_2 and ^{18}O-CO_2 are of paramount importance.

In addition to producing reference standards for calibration, metrology is required to ensure advances in spectroscopy (i.e. Isotope Ratio Mass Spectrometry – IRMS, and Optical Isotopic Ratio Spectroscopy -OIRS) result in field deployable techniques that have reduced uncertainties in order to meet uncertainty requirements set by World Meteorological Organisation.

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 $\delta^{13}C$-CO_2 and 0.05 ‰ for $\delta^{18}O$-CO_2 with target uncertainties of 0.05 ‰ for $\delta^{13}C$-CO_2 and 0.1 ‰ for $\delta^{18}O$-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 and results

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

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 16ENV06 SIRS and develop capabilities within the consortium to improve the traceability chain and the understanding of the influence of different parameters in gravimetric preparation on isotopic fractionation. The new methods being developed will deliver improved 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.

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

The use of different calibration approaches and standards have contributed to inter-laboratory measurement offsets of up to 0.5 ‰ for δ^{13}C, and 13 ‰ for δ^{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 δ^{13}C and δ^{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.

This project will develop gas reference materials of methane with a repeatability of 0.02 ‰ for $\delta^{13}C\text{-}CH_4$ and 1 ‰ for $\delta^{2}H\text{-}CH_4$ and with target uncertainties of 0.2 ‰ for $\delta^{13}C\text{-}CH_4$ and 5 ‰ for $\delta^{2}H\text{-}CH_4$, traceable to the VPDB and VSMOW/SLAP scales respectively.

Absolute carbon dioxide isotope ratio measurements towards SI traceability

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 $^{13}C\text{-}CO_2$ and 0.1 ‰ for $^{18}O\text{-}CO_2$.

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

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.

This project will develop spectroscopic methods and calibration approaches with a target precision of 0.05 ‰ for $\delta^{13}C\text{-}CO_2$ and $\delta^{18}O\text{-}CO_2$, 0.2 ‰ for $\delta^{13}C\text{-}CH_4$ and 1 ‰ for $\delta^{2}H\text{-}CH_4$.

Impact

The new infrastructure to be developed in this project to underpin measurements of the isotopic composition of atmospheric carbon dioxide and methane will provide high accuracy and comparable data to separate the various man-made sources and natural contributions of greenhouse gases in the atmosphere. This will assist governments in the development of accurate emission inventories to comply with legislation (e.g. Kyoto protocol and (Conference of Parties) COP 21), inform new policies, enhance abatement strategies and mitigate emissions to prevent damaging climate change. This work will also have an impact on the quality of life and the health of European citizens. It will reduce measurement uncertainty, resulting in cheaper compliance with directive 2008/50/EC on air quality and allowing better monitoring success of mitigation policies.

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. In addition:

- 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

This project addresses global challenges and there is strong European focus because industrial and domestic activities are major sources of greenhouse gases. This has been recognised by the Kyoto Protocol which commits its parties by setting internationally binding emission reduction targets.

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).

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.

Global society needs better information to address the problem of rising concentrations of greenhouse gases in the atmosphere. Agriculture, forestry, tourism and recreation will all be affected by changing weather patterns as a result of climate change. Human health impacts are expected to place additional economic stress on health and social support systems. Damage to infrastructure (e.g., roads, railways and bridges) from extreme weather events is expected to increase. Therefore, independent globally coherent information is essential, and this project will provide the underpinning work to achieve that.

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.

List of publications

Project start date and duration:		1 September 2020, 36 months
Coordinator: Professor 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		
Internal Funded Partners: 1 NPL, United Kingdom 2 DFM, Denmark 3 INRIM, Italy 4 LGC, United Kingdom 5 PTB, Germany 6 TUBITAK, Turkey 7 VSL, Netherlands 8 VTT, Finland	External Funded Partners: 9 AL, Spain 10 Empa, Switzerland, 11 JSI, Slovenia 12 MPG, Germany 13 RUG, Netherlands 14 UEF, Finland	Unfunded Partners:
RMGs: -		