InGOS Workplan for Trans-National Access

April 1, 2013

1 Project Information

- *Project Name*: Deployment of an automated quantum cascade laser instrument at Mace Head station for online monitoring of the four isotopomers of the major greenhouse gas nitrous oxide.

- *Duration of the project*: June 5 to July 1 (25 Research Working Days)

- *Name of infrastructure requested*: TNA-2: Access to InGOS stations - Mace Head, Ireland

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2 Background

Nitrous oxide is an important greenhouse gas and the dominant anthropogenic ozone-depleting substance emitted this century [2, 9]. The concentration of N_2O in the atmosphere is rising at a rate of around 0.2-0.3% year^{-1}; the current concentration of ∼320-330 ppb is around 20% higher than the preindustrial concentration of ∼270 ppm [5, 1, 11]. However, the processes contributing to this increase and the overall N_2O budget are poorly understood. Further studies are needed to determine which sources are the major contributors to the rise in atmospheric N_2O, in order to fully understand potential impacts and options for mitigation.

Recent studies have shown that isotopologue measurements have great potential to unravel the sources, sinks and chemistry of N_2O [11, 5, 4, 13]. The intramolecular site preference of ^{15}N can distinguish between different sources (eg. [7, 12, 10]), as well as constraining stratospheric exchange and sink processes [14, 6]. However, traditional flask sampling methods provide only low-time resolution data, which can mask seasonal and interannual variability [4]. Spectroscopic measurements with quantum cascade laser tunable infrared laser differential absorption spectroscopy (QCL-TILDAS), in combination with preconcentration of N_2O from ambient air, have the potential to provide high frequency, high precision data on the site-specific ^{15}N and ^{18}O isotopic composition of N_2O [3].

In close collaboration with Aerodyne Research, Inc., we have developed a low maintenance, cryogen-free preconcentration system that will allow remote, long-term measurements of N_2O isotopomer ratios at the Mace Head Station. Our system is unique in providing high-precision measurements of both site-specific ^{15}N and ^{18}O isotope ratios without the need for high-maintenance CO_2 removal traps.

3 Objectives

The aim of this project is to set up the instrument, known as Stheno-QCL-A1, at the Mace Head Station in Ireland, in order to isotopically characterise N_2O variability at high frequency and detect diurnal, seasonal and meteorological variations in sources, sinks and transport. The working instrument has been developed at the Massachusetts Institute of Technology, and its precision and accuracy have been compared to traditional isotope ratio-mass spectrometry (IR-MS) with a wide range of calibration standards. The instrument was developed under the NSF grant MRI-R^2 (R. Prinn, S. Ono and D. Nelson) with the specific intention of making long-term measurements at one of the five primary AGAGE measurement stations.

The Mace Head site is ideal for making these measurements due to the high data quality, the level of infrastructure and the support of PI Prof. Simon O'Doherty and station operator Gerard Spain. The site's exposure and location provide a unique environment to study fluxes and concentrations of trace gases in both marine and continental air. Comparison to the N_2O measurements made at Mace Head since 1978 [8] provides an opportunity to assess data quality, and the range of other trace gases measured at Mace Head will enrich the interpretation of the N_2O isotopomer measurements.

4 Methods and Materials

Our preconcentration and QCL-TILDAS system will be installed at the Mace Head station. We have discussed the space and power requirements of the instrument with the station operator Gerard Spain, and the instrument has been reconfigured to fit in the available space. An air compressor and a zero air generator have been purchased to minimise gas requirements; a tank of medical air for a trapping standard as well as a concentrated working standard are required for calibration and data quality monitoring. For initial calibration, we will also bring two small high-pressure tanks of primary standard to conduct an on-site calibration. The calibration is a simple procedure that will be repeated as often as necessary during the initial stages of the measurements. We will provide tubing to set up an inlet as close as possible to the current air inlet, so that the air sampling is comparable and simultaneous. The instrument requires very little regular on-site maintainance: pump oil and seals will need changing every 1-2 years, and we will provide extra traps and filters that may need changing after several years. For remote control, troubleshooting and access to data, the instrument will need a permanent connection to the internet. The data overview and analysis will be managed by E. Harris and S. Ono from the Massachusetts Institute of Technology, and A. Wenger from the University of Bristol.

5 Implementation

Task	Location	Begin	End
Instrument reconfiguration for Mace Head deployment	MIT	15.03.2013	03.04.2013
Training of A. Wenger (Uni. Bristol) to operate instrument	MIT	15.04.2013	26.04.2013
Final test measurements of ambient Boston air	MIT	04.04.2013	21.05.2013
Packing and shipping of the instrument	MIT	22.05.2013	05.06.2013
Travel of E. Harris to Mace Head		05.06.2013	06.06.2013
Installation of the instrument and inlet	Mace Head	06.06.2013	14.06.2013
Calibration and initial testing	Mace Head	14.06.2013	19.06.2013
First measurements of Mace Head air and associated trouble-shooting	Mace Head	20.06.2013	28.06.2013
Second calibration	Mace Head	28.06.2013	30.06.2013
Return travel of E. Harris to Boston		30.06.2013	01.07.2013
Continuous measurements of ambient air	Mace Head	01.07.2013	-

The deployment of Stheno-QCL-A1 at Mace Head will require the full-time presence of Dr. Eliza Harris at the Mace Head site from the 6^{th} of June to the 30^{th} of June, 2013 (25 days). Most of the project costs, including development and shipping, are covered by the NSF grant and the AGAGE network; we request an InGOS TNA2 travel budget for Dr. Harris of €500 and a daily subsistence allowance of €50 x 25 days (€1250), for a total of €1750.

6 Expected results and possible risks

This data will be the first long-term high resolution measurements of all four N_2O isotopomers. The project is expected to contribute significantly to improving our understanding of the sources, sinks and chemistry of N_2O in the atmosphere. The timeseries obtained will allow identification of changes in the sources of atmospheric N_2O in the background continental and oceanic air reaching Mace Head, and will be particularly useful in constraining the stratospheric sink term as well as diurnal and seasonal changes in sources.

The initial results of this project, concerning the precision and accuracy of the instrument and comparison to IR-MS, are currently in preparation and will be submitted for publication in summer, 2013. This publication will establish the validity of the method and the calibration to international isotope standards, allowing the results to be compared to other isotopomer studies in different locations. The first atmospheric results - from testing in Boston and the first Mace Head data - will be submitted for publication by the end of autumn, 2013. This paper will present isotopologue variations relative to the concentrations of other trace gases and meteorological parameters, as well as any visible

diurnal or short-term cycles. Once the instrument has run for 1-2 years, a discussion of monthly and seasonal cycles will be possible, and following the acquisition of <5 years of data, longer-term trends related to changing sources and other effects such as ENSO cycles will be assessed and published.

The Prinn group at the Massachusetts Institute of Technology has strong connections to all other stations of the AGAGE network, as well as to modelling groups at the UK Met Office and the University of Bristol. The group also works in connection with other international researchers measuring N_2O isotopomers in the USA, Japan and Europe. The data obtained from this project will be available for collaborative work with these and other groups, and will also become freely available as part of the AGAGE network following initial publications.

References

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