

InGOS Workplan for Trans-National Access

May 30, 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 N₂O 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 N₂O budget are poorly understood. Further studies are needed to determine which sources are the major contributors to the rise in atmospheric N₂O, 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 N₂O [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-R² (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 maintenance: 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 T. Röckmann from Utrecht University, E. Harris and S. Ono from the Massachusetts Institute of Technology, and A. Wenger from the University of Bristol.

5 Implementation

Task	Begin	End	Completed?
Instrument reconfiguration for Mace Head deployment at MIT	15.03.2013	03.04.2013	✓
Training of A. Wenger (Uni. Bristol) to operate instrument at MIT	15.04.2013	26.04.2013	✓
Final test measurements of ambient Boston air at MIT	04.04.2013	21.05.2013	✓
Packing and shipping of the instrument	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 at Mace Head	06.06.2013	14.06.2013	
Calibration and initial testing at Mace Head	14.06.2013	19.06.2013	
First measurements of Mace Head air and associated trouble-shooting	20.06.2013	28.06.2013	
Second calibration at 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 at 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 6th of June to the 30th 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 N₂O isotopomers. The project is expected to contribute significantly to improving our understanding of the sources, sinks and chemistry of N₂O in the atmosphere. The timeseries obtained will allow identification of changes in the sources of atmospheric N₂O 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.

Both the Prinn group at the Massachusetts Institute of Technology and the Röckmann group at Utrecht University have strong connections to the AGAGE network and other global monitoring networks, as well as to modelling groups at the UK Met Office and the University of Bristol. The groups also work in connection with other international researchers measuring N₂O isotopomers in the USA, Japan and Europe such as the Swiss Institute for Materials Science and Technology (EMPA). 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

- [1] J. Huang, A. Golombek, R. Prinn, R. Weiss, P. Fraser, P. Simmonds, E. J. Dlugokencky, B. Hall, J. Elkins, P. Steele, R. Langenfelds, P. Krummel, G. Dutton, and L. Porter. Estimation of regional emissions of nitrous oxide from 1997 to 2005 using multinetwerk measurements, a chemical transport model, and an inverse method. *J. Geophys. Res.*, 113(D17):D17313–, 2008.
- [2] IPCC. *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, 2007.
- [3] J. Mohn, B. Tuzson, A. Manninen, N. Yoshida, S. Toyoda, W. A. Brand, and L. Emmenegger. Site selective real-time measurements of atmospheric n₂o isotopomers by laser spectroscopy. *Atmospheric Measurement Techniques*, 5:1601–1609, 2012.
- [4] C. D. Nevison, E. Dlugokencky, G. Dutton, J. W. Elkins, P. Fraser, B. Hall, P. B. Krummel, R. L. Langenfelds, S. O’Doherty, R. G. Prinn, L. P. Steele, and R. F. Weiss. Exploring causes of interannual variability in the seasonal cycles of tropospheric nitrous oxide. *Atmospheric Chemistry and Physics*, 11(8):3713–3730, 2011.
- [5] S. Park, P. Croteau, K. A. Boering, D. M. Etheridge, D. Ferretti, P. J. Fraser, K. . R. Kim, P. B. Krummel, R. L. Langenfelds, T. D. van Ommen, L. P. Steele, and C. M. Trudinger. Trends and seasonal cycles in the isotopic composition of nitrous oxide since 1940. *Nature Geoscience*, 5(4):261–265, April 2012.
- [6] SY Park, EL Atlas, and KA Boering. Measurements of N₂O isotopologues in the stratosphere: Influence of transport on the apparent enrichment factors and the isotopologue fluxes to the troposphere. *JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES*, 109(D1), JAN 15 2004.

- [7] T. Perez, S. E. Trumbore, S. C. Tyler, E. A. Davidson, M. Keller, and P. B. de Camargo. Isotopic variability of n_2o emissions from tropical forest soils. *Global Biogeochem. Cycles*, 14(2):525–535, 2000.
- [8] R. G. Prinn, R. F. Weiss, P. J. Fraser, P. G. Simmonds, D. M. Cunnold, F. N. Alyea, S. O’Doherty, P. Salameh, B. R. Miller, J. Huang, R. H. J. Wang, D. E. Hartley, C. Harth, L. P. Steele, G. Sturrock, P. M. Midgley, and A. McCulloch. A history of chemically and radiatively important gases in air deduced from ale/gage/agage. *J. Geophys. Res.*, 105(D14):17751–17792, 2000.
- [9] A. R. Ravishankara, John S. Daniel, and Robert W. Portmann. Nitrous oxide (n_2o): The dominant ozone-depleting substance emitted in the 21st century. *Science*, 326(5949):123–125, October 2009.
- [10] RL Sutka, NE Ostrom, PH Ostrom, JA Breznak, H Gandhi, AJ Pitt, and F Li. Distinguishing nitrous oxide production from nitrification and denitrification on the basis of isotopomer abundances. *APPLIED AND ENVIRONMENTAL MICROBIOLOGY*, 72(1):638–644, JAN 2006.
- [11] Sake Toyoda, Natsuko Kuroki, Naohiro Yoshida, Kentaro Ishijima, Yasunori Tohjima, and Toshinobu Machida. Decadal time series of tropospheric abundance of n_2o isotopomers and isotopologues in the northern hemisphere obtained by the long-term observation at hateruma island, japan (running title: Tropospheric n_2o isotopomers). *J. Geophys. Res.: Atmos.*, pages n/a–n/a, 2013.
- [12] N Wrage, J Lauf, A del Prado, M Pinto, S Pietrzak, S Yamulki, O Oenema, and G Gebauer. Distinguishing sources of N_2O in European grasslands by stable isotope analysis. *RAPID COMMUNICATIONS IN MASS SPECTROMETRY*, 18(11):1201–1207, 2004.
- [13] N. Yoshida and S. Toyoda. Constraining the atmospheric n_2o budget from intramolecular site preference in n_2o isotopomers. *Nature*, 405(6784):330–334, May 2000.
- [14] Y. L. Yung and C. E. Miller. Isotopic fractionation of stratospheric nitrous oxide. *Science*, 278(5344):1778–1780, December 1997.