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

TNA-2: Access to InGOS stations (Mace Head)

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Introduction and Motivation

Nitrous oxide (N_2O) is an important greenhouse gas and the dominant anthropogenic ozone-depleting substance emitted this century [1, 2]. 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 [3, 4, 5]. 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 [3, 4, 6, 7]. The intramolecular site preference of ^{15}N can distinguish between different sources [eg. 9, 10, 11, 12, 13], as well as constraining stratospheric exchange and sink processes [14, 15, 16, 17]. However, traditional flask sampling methods provide only low-time resolution data, which can mask seasonal and interannual variability [18, 19]. 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 [20]. 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.

Scientific objectives

The aim of this project was to set up the instrument, known as Stheno-QCL-A1, at the Mace Head Station in Ireland, where it will measure N_2O isotope ratios at Mace Head station for the next two years. This will provide the first long-term, continuous data showing N_2O isotopic variability at high frequency, allowing measurement of diurnal, seasonal and meteorological variations in sources, sinks and transport. In combination with inverse modelling and the full spectrum of weather and pollution data available at Mace Head, the results will provide new insight into the atmospheric chemistry of N_2O, particularly the magnitude of troposphere-stratosphere transport. These results will also contribute to our understanding of seasonal and temporal variations in N_2O sources and hot spots, allowing a detailed assessment of sources and the development of targeted emission mitigation policies.

Reason for choosing station

The Mace Head site, shown in Figure 1, 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. The inlet tower (Figures 1 and 2) will minimise the impact of local emissions. Comparison to the N_2O measurements made at Mace Head since 1978 [21] 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. The Mace Head site is well characterised in terms of meteorology and source footprint, and past experience in inverse modelling at this site [22, 23] will facilitate the challenging project of incorporating isotopic tracers into these models.

Figure 1. Mace Head Atmospheric Research Station

Method and experimental set-up

The working instrument was developed at the Massachusetts Institute of Technology 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 precision and accuracy of the measurements have been compared to traditional isotope ratio-mass spectrometry (IR-MS) with a wide range of calibration standards. A calibration scheme has been developed to monitor precision and accuracy and allow correction to international the international isotopic standard scales (V-SMOW for $\delta^{18}O$ and air N_2 for $\delta^{15}N$), as summarised in Table 1. We are also participating in the interlaboratory comparison for N2O isotope measurements organised by the Swiss Institute for Materials Science and Technology (EMPA). An N_2O site-specific primary standard scale is not yet available.

	Trapping standard	**Quaternary**	**Tertiary**	**Secondary**
Type	Compressed air tank from Air Products	65 ppm N_2O tank from Air Products	Pure N_2O from Air Gas (Ref II)	65 ppm N_2O tank from *and* pure N_2O from Air Gas (Refs I & III)
Frequency	Between every 5-10 trapped samples	Between every sample	Daily to weekly	Monthly to yearly
Lifetime	Months – a year	< 5 years	5 – 10 years	> 10 years
Cross-calibration		Measured against Refs I & II	Measured with IR-MS in Ono lab and Yoshida lab	Measured with IR-MS in Ono lab and Yoshida lab

Table 1. Calibration scheme for N_2O isotope monitoring at Mace Head Station, Ireland

Preliminary results and conclusions

Figure 2. Stheno-QCL-A1 installed at Mace Head Station

The instrument was successfully deployed at Mace Head in June 2013, where it has now been running for two weeks (Figure 2):

- An air compressor and a zero air generator were installed 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.
- The instrument requires very little regular on-site maintenance: pump oil and seals will need changing every 1-2 years.
- The inlet is located at the top of the 20 m tower (Figure 3) near the air inlets for current instruments, so that the air sampling is comparable and simultaneous between instruments and the influence of local emissions is minimal.

Figure 2. The 20 m tower at Mace Head station and the N_2O instrument inlet

- Several small high-pressure tanks of tertiary and secondary standard were used to conduct an on-site calibration. The isotopic composition of the quaternary standard has been determined by measurement against Ref I and Ref II to be:

$$\delta^{18}O = 38.8 \pm 0.25 ‰$$
$$\delta^{15}N^{\alpha} = 1.80 \pm 0.18 ‰$$
$$\delta^{15}N^{\beta} = 0.63 \pm 0.26 ‰$$

  The tanks for the EMPA intercalibration exercise are set up for measurement once the instrument is stable.
- Both the laser instrument and the preconcentration unit were connected to the internet to allow remote control and access to data from Utrecht University and MIT. An automatic back up to a data server at Bristol University was set up to ensure data security.
- 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. Although an unexpected problem with one flow controller means that data will not be useful

for another week, the instrument has been taking measurements and all systems are running correctly. It is expected that at least one month of good quality, continuous data will have been taken by the end of summer 2013. An example of Mace Head ambient air data taken before the flow controller problem is shown in Figure 4.

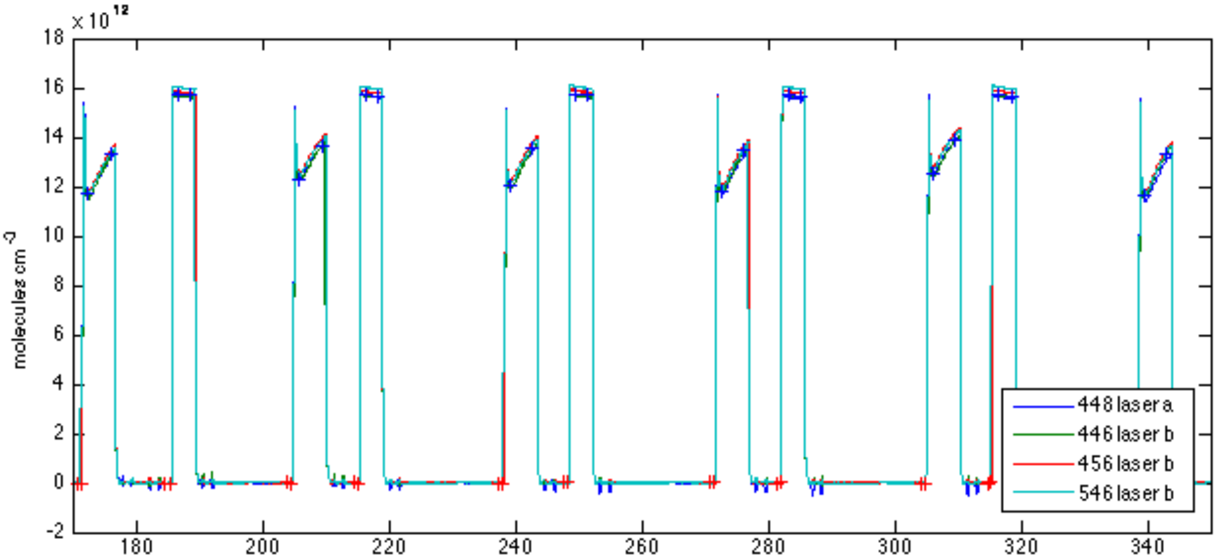

Figure 3. N_2O isotopocules measured with preconcentration/laser spectroscopy at Mace Head. Flatter peaks are reference gas and steeper peaks are ambient air. Time in minutes is on the y-axis.

Outcome and future studies

This project was the first deployment of an N_2O isotope monitor at a remote station. The instrument can now be remotely accessed and operated for data analysis at Utrecht University and MIT. Over the coming months, the instrument will provide data that will enhance our understanding of N_2O sources and sinks and facilitate mitigation of N_2O emissions. A paper detailing the development of the instrument is currently in preparation for publication. We anticipate further publications about the first results from Mace Head, observable seasonal cycles, incorporation into models, and other topics over the coming two years. A second Stheno system is currently being developed at MIT for future deployment at another AGAGE station, most likely Cape Grim, which will provide a dataset for comparison with the Mace Head instrument.

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