Development of a Spectroscopic Technique for Continuous Online Monitoring of Oxygen and Site-Specific Nitrogen Isotopic Composition of Atmospheric Nitrous Oxide*

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This reprint is one of a series intended to communicate research results and improve public understanding of global environment and energy challenges, thereby contributing to informed debate about climate change and the economic and social implications of policy alternatives.

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Nitrous oxide (N\textsubscript{2}O) is a potent, long-lived greenhouse gas\textsuperscript{4} and, as a source of reactive nitrogen to the stratosphere, the dominant contributor to catalytic ozone destruction in the 21st century.\textsuperscript{5} Since preindustrial times, N\textsubscript{2}O mixing ratio in the troposphere has increased from 270 ppb to the current level of 324.2 ± 0.1 ppb (2011) with an average growth rate of 0.2 ± 0.3% yr\textsuperscript{-1} over the past decades.\textsuperscript{3-5} This increase has been attributed to anthropogenic perturbation of the nitrogen cycle, in particular the application of inorganic fertilizers.\textsuperscript{3-8} The N\textsubscript{2}O budget, however, is poorly constrained due to the high spatial and temporal variability of fluxes, which limits our ability to develop targeted mitigation policies.\textsuperscript{9,10}

Precise measurements of isotopologues of nitrous oxide (i.e., \textsuperscript{14}\textsuperscript{N}\textsuperscript{15}\textsuperscript{N}\textsubscript{2}O, \textsuperscript{15}\textsuperscript{N}\textsuperscript{15}\textsuperscript{N}\textsubscript{2}O, and \textsuperscript{15}\textsuperscript{N}\textsuperscript{16}\textsuperscript{N}\textsubscript{2}O) provide a useful constraint to quantify contributions from different N\textsubscript{2}O sources. [Site specific \textsuperscript{15}\textsuperscript{N} composition: \textsuperscript{15}\textsuperscript{N}\textsuperscript{15}\textsuperscript{N}\textsubscript{2}O = \textsuperscript{15}\textsuperscript{N}\textsuperscript{2}O and \textsuperscript{15}\textsuperscript{N}\textsuperscript{16}\textsuperscript{N}\textsubscript{2}O = \textsuperscript{15}\textsuperscript{N}\textsuperscript{2}O. Site preference in \textsuperscript{15}\textsuperscript{N} composition: SP = \textsuperscript{14}\textsuperscript{N}\textsuperscript{15}\textsuperscript{N}\textsubscript{2}O. Bulk \textsuperscript{15}\textsuperscript{N} composition: (\textsuperscript{15}\textsuperscript{N}\textsuperscript{2}O + \textsuperscript{15}\textsuperscript{N}\textsuperscript{16}\textsuperscript{N}\textsubscript{2}O) / 2 = \textsuperscript{15}\textsuperscript{N} \textsubscript{bulk}. See Toyoda et al. (2013)\textsuperscript{8} for a detailed account of isotope notation and terminology.] The major source of N\textsubscript{2}O is microbial production in natural and agricultural soils, by both nitrifying and denitrifying bacteria. A number of studies have shown that the isotopic composition of N\textsubscript{2}O can be used to distinguish between different microbial source pathways: The bulk \textsuperscript{15}\textsuperscript{N} composition of N\textsubscript{2}O indicates the contribution of natural versus fertilized agricultural soil emissions,\textsuperscript{7,11,12} while the site preference is independent of the reaction substrate and can be used to quantify different microbial processes, i.e.,
nitrification versus denitrification. Relationships between $\delta^{15}N$, $\delta^{18}N$, and $\delta^{15}O$ indicate the relative importance of $N_2O$ reduction to $N_2$, and the oxygen isotopic composition also reflects the water in the environment where $N_2O$ was formed. In the troposphere, $N_2O$ is stable, and the major sink is transfer to stratosphere, where $N_2O$ is destroyed photolytically. UV photolysis is shown to produce a strong enrichment in $\delta^{18}O$ and $\delta^{15}N$ of the residual $N_2$, in particular, the central position $^{15}N$ ($^{15}N^\alpha$). This enrichment in $^{15}N^\alpha$ can be a particularly powerful tracer to quantify the magnitude of troposphere–stratosphere exchange, which is one of the largest uncertainties in the global $N_2O$ budget. The $\delta^{15}N$ and $\delta^{18}O$ composition of ambient $N_2O$ shows a definite decreasing trend over the past decades, reflecting the increasing contribution of anthropogenic emissions, while observed trends in site preference remain inconclusive.

Until recently, isotopic measurements of $N_2O$ have used the traditional technique of flask sampling followed by laboratory-based isotope ratio mass spectrometry (IR MS). While this technique shows excellent precision for $\delta^{18}O$ and $\delta^{15}N$, it is unsuitable for field deployment, and continuous monitoring with high time resolution is technically challenging. In addition, site preference measurements are complicated by scrambling in the ion source, non-mass-dependent oxygen isotope composition, and mass interferences such as CO$_2$. Unlike IR MS, tunable infrared laser direct absorption spectroscopy (TILDAS) measures fundamental vibrational bands of nitrous oxide isotopologues in the mid infrared regions at high precision; thus, the technique can be used to directly distinguish between $^{15}N^\alpha$ and $^{15}N^\beta$. TILDAS techniques have been applied to a number of isotopic systems such as CO$_2$, and O$_2$. Several recent studies have shown the potential of TILDAS measurement coupled to a preconcentration unit for continuous, online measurement of $N_2O$ isotopic composition.

This study presents a new instrument that will be used to conduct online, real-time measurements of $N_2O$ isotopic composition at Mace Head Atmospheric Research Station, Ireland, as part of the AGAGE network (http://agage.eas.gatech.edu). A cryogen-free preconcentration unit with no chemical traps was developed to allow continuous, long-term monitoring at this remote site with minimal maintenance. For the first time, isotopic reference gases labeled for both $\delta^{15}N$ and site-specific $^{15}N$ isotopic compositions were synthesized and measured with both IR MS and TILDAS. A comprehensive treatment of matrix dependence for TILDAS results is presented, as well as cross-calibration of site-specific isotope ratios against IR MS method, with an investigation of scrambling corrections for IR MS. Ambient air measurements and TILDAS to IR MS comparison show that TILDAS is both accurate and precise enough to observe ambient changes in $\delta^{18}O$, $^{15}N^\alpha$, and $^{15}N^\beta$ of $N_2O$ with a temporal resolution of 0.5–2 h.

**MATERIALS AND METHODS**

**Fully Automated Cryogen-Free $N_2O$ Preconcentration.** For $N_2O$ preconcentration, we use a modified Medusa system known as “Stheno II”. The “Stheno II” unit discussed here is a new unit, improving upon the principles used for the original “Stheno” preconcentration unit described in Potter et al. (2013). Medusa is a fully automated cryogen-free preconcentration unit coupled to GC/MS used to measure a number of CFCs and other non-CO$_2$ greenhouse gases at AGAGE stations; a similar system has been used previously to preconcentrate $N_2O$ for isotope measurements. The preconcentration procedure involves collecting $N_2O$ on a glass beads trap at approximately $-156 \degree C$ and is described in detail in section S1 of the Supporting Information. Our system differs from previous preconcentration units used for spectroscopic measurements in a number of ways; most notably, it uses a glass beads trap rather than a HaySep D trap to adsorb $N_2O$, and CO$_2$ is not removed from the sample air stream. These changes allow long-term operation with minimal maintenance. A basic schematic of the preconcentration/trapping routine is presented in Figure 1.

**Spectroscopic Analysis of $N_2O$ Isotopic Composition with TILDAS.** Spectroscopic measurements are made with a dual-laser TILDAS instrument (Aerodyne Research Inc.).

Figure 1. Schematic of the modified Medusa system “Stheno II”, developed for preconcentration of $N_2O$ without the use of chemical traps or liquid nitrogen. V specifies a valve, T is a trap, DP specifies a diaphragm pump, ZA = zero air, AA = ambient air, CA = compressed air. The instrument is shown with valve 3 in the “trapping” position. The system is described in detail in section S1 of the Supporting Information.
background, matrix effects, and calibration to the international isotopic standard scale. The data analysis procedure and associated corrections are described in detail in section S2 of the Supporting Information, and an example of the data analysis cycle is shown in Figure S2 in the Supporting Information.

Synthesis of Standards by NH₄NO₃ Decomposition. A range of isotopic standards were synthesized via NH₄NO₃ decomposition to compare isotopic measurements between IR MS and TILDAS. The synthesis is described in detail in section S3 of the Supporting Information, and only a brief description will be given here. NH₄NO₃ with a range of isotopic compositions was produced from recrystallizing stock NH₄NO₃ with isotopic spikes of Na¹⁸NO₃, Na¹⁵NO₃, ¹⁴NH₃Cl, and ¹⁴NH₃Cl, as well as equilibration with H₂¹⁸O. The NH₄NO₃ was flame-sealed into glass tubes and decomposed at 270 °C to form N₂O, which was purified by distillation with dry ice–ethanol and liquid nitrogen. ³⁵ Five standards were produced with varying ¹⁵N and ¹⁸O compositions, as detailed in Table S2 in the Supporting Information.

Analysis of N₂O Isotopic Composition with Isotope Ratio Mass Spectrometry. Isotopic composition of N₂O standard gases was measured with IR MS (Thermo Electron MAT 253). Pure N₂O was used for analyses; gas chromatographic analysis with a thermal conductivity detector (TCD) showed no detectable CO₂ in N₂O samples derived from NH₄NO₃ decomposition (see Figure S6 in the Supporting Information). Following Toyoda and Yoshida (1999), N/O (masses 44, 45 and 46) and NO⁺ (masses 30 and 31) ions were measured to determine position-specific ¹⁵N substitutions.²⁵,²⁷ Analysis conditions are summarized in Table S3 in the Supporting Information, and NO⁺ ion scrambling factors are discussed in the section describing Scrambling in the Ion Source in IR MS Analyses.

RESULTS AND DISCUSSION

Comparison of TILDAS and IR MS Measurements. The five N₂O standards synthesized by ammonium nitrate decomposition (Table S2 in the Supporting Information) as well as the two laboratory reference gases Ref I and Ref II were measured with IR MS and TILDAS in order to cross-calibrate the TILDAS and IR MS measured isotopologue ratios and investigate the accuracy of the two techniques considering IR MS scrambling factors and TILDAS matrix corrections. The results are presented in Table S4 in the Supporting Information and summarized in Figure 4, and show very good agreement between the IR MS and TILDAS for most samples. The instrument comparison shows that TILDAS is able to provide accurate results across a wide range of N₂O, CO₂, and bath gas compositions and N₂O isotopic compositions. TILDAS measurements at 23.5 and 45.5 ppm N₂O are not accurate; at [N₂O] < approximately 45 ppm (at 0.01 atm, 1.7 x 10¹³ molecules cm⁻³), peaks are too small for fitting (<4% absorption depth), and results are not accurate. Sufficient N₂O should be trapped to achieve at least 45 ppm in the cell at 0.01 atm, corresponding to ~1 L of air at a typical atmospheric N₂O mixing ratio of 327 ppbv.

Matrix Effects on Spectroscopic Line Shape and Measurement Accuracy. The composition and pressure of the matrix has a significant effect on line shape, and thus on data fits and measurement accuracy. Samples (trapped ambient and compressed air) and standards are therefore matrix-matched as closely as possible. Measurement accuracy was tested across a

Figure 2. Trapping routine used for N₂O preconcentration on a liquid-nitrogen-free glass beads trap, coupled to TILDAS isotope measurement. The first panel shows the cold head (red) and trap (blue) temperatures. The second panel shows the flow rate through the trap (purple; both flush and sample) and the flushing flow used to push the sample into the laser cell (orange; spikes are due to multipoint valve switching and do not affect measurement). The third panel shows the pressure (green) and temperature (red) in the laser measurement; the periods where the cell is cleaned are indicated, and Std refers to a standard while Sam refers to a sample. The fourth panel shows the concentration (molecules cm⁻³) of N₂O (major isotope; blue) and CO₂ (gray) measured in the laser cell.
A brief description of the results is given here; full details are presented in section S2.4 of the Supporting Information. The primary matrix gas in the laser cell is zero air, hereafter referred to as the "bath gas." The N$_2$O ratio of the bath gas does not have any significant effect on the peak shape (Figure S4 in the Supporting Information) or on measurement accuracy, as shown with measurements of Ref II in a bath gas of 100% N$_2$ and 100% O$_2$ (Figure 4). The total pressure of bath gas, on the other hand, has a significant effect on the results, affecting measured isotopic composition by...
The CO$_2$ partial pressure affects the measurement accuracy with the same order of magnitude as the bath gas pressure (~2.6–4 % mbar$^{-1}$; Table S1 and Figure S3 in the Supporting Information); however, it cannot be controlled in trapped samples as the ambient pressure of CO$_2$ shows significant temporal variation, for example >10% at Mace Head. A pressure correction is therefore also applied to account for differences in pressure that remain (±0.3 mbar; section S2.3 in the Supporting Information).

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The pressure dependence of isotopic measurements is most likely caused by changes in peak shape and broadening in response to different matrix gases. Peak width in the TDL Wintel software used for spectroscopic data analysis (Aerodyne Research, Inc.) is described by an approximated Voigt profile, which can be deconvolved into contributions from the Gaussian Doppler line shape function and the Lorentz line shape function due to pressure broadening. Both Gaussian and Lorentzian line widths were estimated as a function of pressure (see Figure S7 in the Supporting Information) by fitting measured spectra to a Voigt profile to find an optimum fit and exact width. The extent of pressure broadening and Dicke narrowing were estimated for comparison with literature values from the HITRAN database. The measurements and calculations are presented in section S4 of the Supporting Information; the results will be described here. [Pressure is in units of atmospheres (atm) in this section for consistency with the HITRAN database.]

The parameters describing peak shape are summarized in Table 1. For all four N$_2$O peaks, it can be seen that the derived air broadening coefficients are consistently higher than given in the HITRAN database: ~2% for $^{14}$N$^\cdot$N$^{18}$O and $^{15}$N$^\cdot$N$^{16}$O (within the uncertainty of HITRAN data), 6% for $^{14}$N$^\cdot$N$^{16}$O, and 8% for $^{15}$N$^\cdot$N$^{18}$O (significantly different to HITRAN data$^{23-44}$). The HITRAN values for N$_2$O are measured at high pressures (>0.09 atm$^{42,43}$) relative to the pressures at which these measurements were made (~0.01 atm); more importantly, while the HITRAN line widths and strengths are taken from measurements of both $^{15}$N$^\cdot$N$^{16}$O and the minor isotopes, the HITRAN broadening coefficients are taken from measurements of only $^{14}$N$^\cdot$N$^{16}$O.$^{23-44}$

Although the estimate of Dicke-narrowing factor$^{45}$ (eq S7 in the Supporting Information) is based on a parametrization and the effects of narrowing are expected to be largest at 0.006–0.07 atm$^{46}$, the results clearly show that there is significant narrowing at the low pressures used in the TILDAS cell. At measurement pressure of 10 mbar (0.01 atm), the Doppler width (2−2.3 cm$^{-1}$ for the four N$_2$O peaks; see Figure S7 in the Supporting Information) contributes a large part of the total Voigt line width (2.4–2.8 cm$^{-1}$). Dicke narrowing has a significant impact on the Doppler width and the fit, accounting for ~50% of peak width change with pressure, and thus it is an important feature needed to gain accurate and precise results. We have implemented this narrowing into our fits and find a significant improvement in precision of repeated measurements on the order of 3−4×; e.g., precision on $^{18}$O is 0.25−0.4% without the “Dicke factor” and improves to 0.07−0.15% with the “Dicke factor” included in the fit.

Scrambling in the Ion Source in IR MS Analyses. Site-specific N$_2$O isotopic composition is measured indirectly in the IR MS, by monitoring the isotopic composition of N$_2$O$^+$ ions ($m/z = 44, 45, 46$) and NO$^+$ ions ($m/z = 30, 31$). $^{15}$NO$^+$ ions result primarily from fractionation of $^{13}$N$^\cdot$N$^{16}$O; thus, the site-specific isotopic composition can be inferred.$^{24-26}$ This method is complicated by scrambling in the ion source, which means that ~8% of $^{15}$NO$^+$ is actually derived from $^{13}$N$^\cdot$N$^{16}$O and also relies on the assumption that the oxygen isotopic composition is mass-dependent.$^{53}$ This assumption is the reason why the site-specific isotopic composition for the 448-H sample, which is strongly enriched in $^{18}$O, is poorly characterized with IR MS measurements, as shown in Figure 4; the directly measured value of $^{18}$O (mass 46) is used to infer $^{16}$O according to a mass-dependent relationship (eq 9 in the Supporting Information). The inferred $^{16}$O is then used to iteratively calculate site-specific $^{15}$N isotopic composition from masses 45 ($^{15}$N$^{16}$O$^+$, $^{14}$N$^\cdot$N$^{16}$O$^+$, and $^{15}$N$^\cdot$N$^{16}$O$^+$) and 31 ($^{15}$N$^{16}$O$^+$ and $^{14}$N$^{16}$O$^+$) (see eqs 10, 11, and 13 in the Supporting Information).
Information). Thus, if the sample oxygen isotopic composition is not mass-dependent, the calculated values of $\delta^{18}O$ and thus site-specific $N_2O$ isotopic composition are incorrect. In contrast, TILDAS is able to accurately measure site-specific $^{15}N$ substitutions across a large range of $\delta^{15}O$, $\delta^{18}O$, and $\Delta^{17}O$ values.

Scrambling in the ion source was considered by comparing the measured isotopic composition of the standards (not including 448-H), which have site preference values ranging from $-1.76$ to $+15.09\%e$, between the IR MS and the TILDAS. Although the TILDAS values have an associated measurement error, the site-specific $^{15}N$ substitutions are directly measured; thus, there is no systematic relationship between site preference and error. Averaging across all the seven standards can therefore give an accurate view of IR MS measurement quality without bias from TILDAS measurement uncertainty. The calculations used for the scrambling corrections (from refs 25, 27, 47) are presented in section S5 of the Supporting Information, and the results are summarized in Figure 5. Two possible scrambling models are considered: “one-factor” scrambling, with equal yield of $^{15}NO^+$ from $^{15}N^{14}NO$ and $^{14}NO^+$ from $^{14}N^{15}NO$ described by a single scrambling factor $\gamma$, i.e., $\gamma$ of 0.08 means 8% of $^{15}NO^+$ is derived from $^{14}N^{15}NO$ and similarly for $^{14}NO^+$, and “two-factor” scrambling, where the scrambling of $^{14}N^{15}NO$ ($\gamma^o$) is not equal to the scrambling of $^{14}N^4NO$ ($\gamma^o$) (differences due to other isotopic substitution possibilities are not accounted for, e.g., clumped, $^{17}O$, $^{18}O$).

More complex scrambling models have also been considered; 2 however, the number of standards in this study is too small to consider the accuracy of models with a larger number of variables.

In agreement with the results of Westley et al., 27 scrambling is more complex than a one-factor scrambling model can account for: The IR MS and TILDAS results never agree within the measurement error (Figure S8 in the Supporting Information) with the one-factor correction. Overall, best agreement is seen for one-factor scrambling with $\gamma = 8\%$, consistent with results obtained using similar source conditions.24,25,27 However, for calculation of $\delta^{14}NO$, best agreement is obtained with a scrambling factor of 9%, highlighting the limitations of the one-factor model.

The results from comparison of IR MS and TILDAS with two-factor scrambling show $\sim 0.05\%e$ improvement in accuracy for the IR MS measurement compared to one-factor scrambling. The accuracy of results is much more sensitive to the scrambling of $^{14}N^{15}NO$ ($\gamma^o$) than $^{14}N^{15}NO$ ($\gamma^o$). From consideration of $\delta^{15}NO^+$, $\delta^{15}No$ and site preference, it is clear that the optimal value of $\gamma^o$ is $8-9\%$, in agreement with previous studies, 24,25,27 while the optimal value of $\gamma^o$ is clearly lower, between 2 and 4%. This value is much lower than reported by previous studies (e.g., single factor of 8.5% from Brenninkmeijer et al. 2009; 24 $\gamma^o$ of $\sim 9\%$ from Westley et al. 2007). This study presents the widest range of isotopic references gases yet considered and does not rely on primary calibration through techniques such as NH$_4$NO$_3$ decomposition or enriched gas mixing 24,25,27,47 which give uncertainties of $>0.2-0.3\%e$ in site preference, but instead presents the first laser spectroscopy-calibrated consideration of IR MS scrambling. The accuracy of standard site preference values in previous studies may not have been high enough to fully assess the optimum value of $\gamma^o$ considering that the calculated site preference is much less sensitive to the chosen value of $\gamma^o$ than the value of $\gamma^o$.

Even with the optimized two-factor scrambling model, correcting for scrambling in the ion source introduces an error larger than the combined IR MS and TILDAS measurement uncertainty for both $\delta^{15}NO^+$ and site preference ($\delta^{15}NO$ is accurate to within the measurement uncertainty). The error that is introduced depends on the site preference value of the $N_2O$ being considered; therefore, both measurement precision and accuracy are affected. This limits the potential of IR MS measurements for high-precision monitoring of site-specific $N_2O$ isotope ratios in lab and field studies, particularly at remote background sites like Mace Head where relevant changes in isotopic composition are very small.

**Isotopic Measurements in Preconcentrated Samples.**

**Trapping Efficiency: Trace Gas Recovery.** Quantitative recovery of $N_2O$ following trapping is critically important to prevent introduction of isotope fractionation by absorption/desorption processes. 48,49 Unlike previous instruments, 31–33 the Stheno II preconcentration unit (and the predecessor Stheno I 35) uses a glass beads trap instead of the stronger HayeSep D adsorbent. The major advantage of the glass beads trap is that no $N_2/O_2$ is trapped from the air; thus, the bath gas is added as a flush with a known composition, making the pressure and matrix easier to accurately control. The range over
which glass beads can efficiently trap N\textsubscript{2}O was investigated by trapping increasing amounts of sample and comparing the measured and expected N\textsubscript{2}O and CO\textsubscript{2} concentrations, as shown in Figure 6. N\textsubscript{2}O is efficiently trapped when the sample volume is <4 L; CO\textsubscript{2} is efficiently trapped until ~2 L. It is desirable to use the minimum trapped volume, to conserve sample when measuring flask samples and to achieve the highest possible time resolution when making continuous ambient measurements; however, at N\textsubscript{2}O mixing ratios <45 ppm (at 10 mbar total cell pressure) isotopic analysis is no longer accurate (see section describing Comparison of TILDAS and IR MS Measurements). The “optimal trapping range” is therefore 1200–1800 mL of ambient air. Within this range, N\textsubscript{2}O recovery is >99%, and therefore, the fractionation introduced by trapping is negligible.

**Measurements of N\textsubscript{2}O Isotopic Composition in Ambient Samples from Cambridge, Massachusetts.** N\textsubscript{2}O isotopic composition was measured continuously at MIT’s “Green Building” for two weeks between March 3 and 16, 2013. The sampling inlet was located on the roof of the 18-story (95 m) building and connected to sampling pumps (see Figure 1) with >50 m of Synflex 1300 tubing (Eaton Corporation). Samples were measured every 28 min, and for every 5–10 ambient air samples, one compressed air sample (medical grade, Aigars Inc.) was measured to monitor trapping efficiency and precision. The compressed air measurements and precision histograms are shown in Figure S9 in the Supporting Information; the capabilities of the instrument are summarized in Table 2. Precision is better for \( \delta^{15}N \) than \( \delta^{18}O \) due to the relatively small absorption depth of the \( ^{14}N^{16}N^{18}O \) peak (Figure 3).

Ambient air measurements over the 13-day period are shown in Figure 7. The scatter in ambient air measurements (“true” variability + measurement error; bars in Figure 7 histograms) was compared to the scatter in compressed air measurements (measurement error only; smooth line in Figure 7 histograms), to determine if the instrument precision is sufficient to see changes in isotopic composition of ambient air. \( \delta^{18}O \) values show a large amount of true variability over the measurement period; thus, although precision is lowest for this isotope, the precision is sufficient to observe ambient variations for both single measurement and four-point moving average. For \( \delta^{15}N \), there is some true variability outside the measurement error with single measurements, although the difference between frequency distributions is much clearer for the four-point average data. The true variability is smaller than the measurement error of single measurements for both \( \delta^{15}N \) and \( \delta^{18}O \); true variability of these isotopocouples can only be resolved using the four-point moving average.

The isotopic measurements were compared to weather variables to examine causes of variability in isotopic composition. The weather data is shown in Figure S10 in the Supporting Information, and correlations are summarized in Table S5 in the Supporting Information. All four isotopomers show a significant relationship to pressure: a positive correlation for \( \delta^{15}O \) and a negative correlation for all \( ^{15}N \) isotopomers. This correlation may relate to exchange of free tropospheric air. Relative humidity showed a significant correlation with all isotopocouples except \( \delta^{15}N^{18}O \). It is possible that this relates to partitioning between different microbial pathways. Wind direction showed a significant relationship to \( \delta^{15}N^{18}O \) with slightly isotopically heavier N\textsubscript{2}O originating from the continent and isotopically light N\textsubscript{2}O from the marine sector. A full investigation of the relationship between meteorological variables and measured isotopic composition is beyond the scope of this study and will be discussed in a later publication.

**CONCLUSIONS**

Measurement of N\textsubscript{2}O isotopic composition has traditionally involved the collection of flask samples, which are then purified and measured with IR MS in a laboratory. While this technique has yielded interesting results, potential for investigations of seasonal cycles or changes in sources related to meteorology is limited by the feasible number and temporal resolution of samples. Using preconcentration without CO\textsubscript{2} removal followed by TILDAS, we have obtained sufficient precision with a four-point moving average of 28-min measurements to observe ambient remote-site changes in all the isotopocouples of N\textsubscript{2}O, and we have demonstrated accuracy across a wide range of isotopic composition and site preference values. The “Stheno II” instrument is automated and remotely operated, and uses very few consumables, to be well-suited for remote deployment at sites such as Mace Head Atmospheric Research Station.

The time series in Figure 7 shows that there is significant variability in N\textsubscript{2}O isotopic composition on very short time scales. The data shows decoupling between \( ^{15}N \) and \( ^{18}O \) content of N\textsubscript{2}O. Variability in \( \delta^{18}O \) is larger than variability in \( \delta^{15}N^{18}O \), which is in turn greater than variability in \( \delta^{15}N \) and \( \delta^{15}N^{18}O \) bulk. The isotopic composition of N\textsubscript{2}O reflects sources, sinks, and transport, and the rich data set that can be obtained from “Stheno II” provides constraints on these processes. In combination with inverse modeling and analysis of other trace

| Table 2. Summary of the Precision Attainable with TILDAS Measurements of N\textsubscript{2}O Isotopic Composition |
|----------------------------------|------------------|------------------|------------------|------------------|
| \( \delta^{18}O \)              | \( \delta^{15}N \) | \( \delta^{15}N^{18}O \) | \( \delta^{15}N^{15}O \) |
| n\textsubscript{averaged}       | 0.32             | 0.17             | 0.19             | 0.16             |
| for <0.2\% precision            | 3                | no averaging required |
| temporal resolution (h)          | 1.4              | 0.5              | 0.5              | 0.5              |
| n\textsubscript{averaged}       | 11               | 3                | 4                | 3                |
| for <0.1\% precision            | 5.1              | 1.4              | 1.9              | 1.4              |

**“Precision” is the 1σ standard deviation of repeated measurements of compressed air. n\textsubscript{averaged} is the amount of measurements that need to be averaged to achieve a certain precision.**
gases and meteorological variables, the results can be used to provide new insight into N\textsubscript{2}O variability.

ASSOCIATED CONTENT

\* Supporting Information

Additional material as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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REFERENCES


