1. INTRODUCTION

*Nitrous oxide (N\textsubscript{2}O), a greenhouse gas with >300 times the global warming potential of CO\textsubscript{2}, is currently increasing at a rate of ~0.26% yr\textsuperscript{-1}, mainly due to increased microbial production from fertilized agricultural systems. A better understanding of the controls over N\textsubscript{2}O production is essential to more effective mitigation policies.

Due to the complexity of microorganism processes within soil, the spatiotemporal effects of fertilizer on N\textsubscript{2}O production at a high resolution remain largely unconstrained. Advances in the use of stable isotope techniques can aid in determining the sources and mechanisms involved in soil N\textsubscript{2}O emission. Determining the intramolecular, or site-specific, position of \textsuperscript{15}N position: \textsuperscript{15}N/\textsuperscript{14}N versus a position: \textsuperscript{15}N/\textsuperscript{14}N, is a more robust tool for unraveling the physical and biological controls over atmospheric N\textsubscript{2}O. The position-specific \textsuperscript{15}N is measured as site preference (SP), which is defined as (\textsuperscript{15}N/\textsuperscript{14}N - 1)/100. Unlike total \textsuperscript{15}N/\textsuperscript{14}N, it has been shown that SP values are independent of the substrate's isotopic composition in microbial processes, with SP values of ~33‰ and ~0‰ for nitrification-derived N\textsubscript{2}O versus denitrification-derived N\textsubscript{2}O, respectively.

A subset of sites from the NOAA Global Monitoring Division (GMD) Cooperative Sampling Network is being measured using Picarro's new G5101-i analyzer capable of simultaneous N\textsubscript{2}O concentration, \textsuperscript{15}N \textsuperscript{15}N, and \textsuperscript{15}N \textsuperscript{14}N measurement in order to describe the global distribution of N\textsubscript{2}O and its isotopes on a seasonal level, and to refine current models of the global N\textsubscript{2}O cycle.

2. MEASURED SITES FROM NOAA CCGG FLASK NETWORK

3. PICARRO G5101-i Analyzer

Picarro's innovative technology employs Cavity Ring Down Spectroscopy (CRDS), where a small cavity is filled with light from a laser beam, and is then shut off, causing the light to decay exponentially. This "ring-down" is performed both with and against the laser tuned for and against N\textsubscript{2}O. The gas concentration is then calculated from the difference in these ring-down times. Since energy absorbance is a function of the size and shape of a molecule, N\textsubscript{2}O stable isotopes and isomers can both be measured using this approach. This particular analyzer employs a unique quantum cascade laser capable of the mid-infrared wavelength detection needed for N\textsubscript{2}O without the need for liquid nitrogen cooling.

Abbreviated Specs

- ~4 second sampling interval
- 0.3 to 2 ppm N\textsubscript{2}O sampling concentration
- <30 scm flow rate
- 300 to 1000 Torr sampling pressure

4. SAMPLING SYSTEM

Sampling boxes include a beveled glass water trap submerged in -47°C ethanol bath in order to remove water.

Sampling box is measured until pressure ~1013 mb; then sample is introduced and measured for 5 minutes. Samples are measured against internal standard cylinder containing ambient air filled at Niwot Ridge. Standards are measured for 10 minutes after calibration sample. A "ring-down" is performed both with and against the laser tuned for and against N\textsubscript{2}O.

"Ring-down" is performed both with and against the laser tuned for and against N\textsubscript{2}O.

5. RESULTS

* Error bars contained within datapoints
* More measurements are needed both temporally and spatially in order to detect these signals. In particular, seasonal variability of site-specific \textsuperscript{15}N \textsuperscript{15}N, and \textsuperscript{15}N \textsuperscript{14}N measurement in order to describe the global distribution of N\textsubscript{2}O and its isotopes on a seasonal level, and to refine current models of the global N\textsubscript{2}O cycle.

6. DISCUSSION

*Precision of unflagged samples averages 0.1 ppb for mole-fractions and 0.5‰ for both \textsuperscript{15}N/\textsuperscript{14}N and \textsuperscript{15}N/\textsuperscript{14}N. Precision determined by calculating standard deviation of 100 second rolling means of each sample.

\textsuperscript{15}N\textsubscript{2}O concentration measurements begin to capture northern hemisphere agricultural signal, yielding high summer N\textsubscript{2}O emissions.

We expect to see a seasonal cycle in N\textsubscript{2}O isotopomers due to stratospheric mixing in the spring of each hemisphere (causing an enrichment in total \textsuperscript{15}N/\textsuperscript{14}N and \textsuperscript{15}N/\textsuperscript{14}N) and heightened ocean and soil microbial activity in the summer and fall of each hemisphere (causing a decrease in N\textsubscript{2}O concentration as well as a depletion in total \textsuperscript{15}N/\textsuperscript{14}N).

*Antarctic data consistent in enrichment of \textsuperscript{15}N/\textsuperscript{14}N seen in the spring of each hemisphere due to stratospheric mixing.

*Data show correlation between higher N\textsubscript{2}O concentration and more depleted \textsuperscript{15}N/\textsuperscript{14}N (p<0.05), consistent with previously determined global temporal trends. However, no correlation present between N\textsubscript{2}O concentration and SP.

7. CONCLUSIONS AND FUTURE WORK

*The early stages of this project show the potential to not only better constrain the global N\textsubscript{2}O budget, but also better detect seasonal and intramural trends in N\textsubscript{2}O sources and sinks, specifically helping to partition shifts in nitification versus denitrification processes.

*More measurements are needed both temporally and spatially in order to detect these signals. In particular, seasonal variability of site-specific \textsuperscript{15}N \textsuperscript{15}N, and \textsuperscript{15}N \textsuperscript{14}N measurement in order to describe the global distribution of N\textsubscript{2}O and its isotopes on a seasonal level, and to refine current models of the global N\textsubscript{2}O cycle.

*CRDS holds several advantages over traditional IRMS methods including field deployability, ease of use, continuous/simultaneous measurement of N\textsubscript{2}O concentration and \textsuperscript{15}N isotopes, and no need for back-calculation of NO\textsuperscript{+} fragment using IRMS.

8. ABBREVIATED REFERENCES


