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The isotopic signature of nitrous oxide emitted from agricultural soils measured by FTIR spectroscopy

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The Isotopic Signature of Nitrous Oxide

Emitted from Agricultural Soils

measured by FTIR Spectroscopy

A thesis submitted in fulfilment of the requirements for the award for the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

By

Stephen Parkes, Bsc (Hons.)

School of Chemistry, 2008
Certification

I, Stephen Parkes, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Stephen Parkes
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Publications

Sections of this work described in this thesis have been reported in the following publications:


Abbreviations and Symbols

\[ 446 = \text{^{14}N}^{14}\text{N}^{16}\text{O} \]
\[ 456 = \text{^{14}N}^{15}\text{N}^{16}\text{O} \]
\[ 546 = \text{^{15}N}^{14}\text{N}^{16}\text{O} \]
\[ 448 = \text{^{14}N}^{14}\text{N}^{18}\text{O} \]
\[ 447 = \text{^{14}N}^{14}\text{N}^{17}\text{O} \]
\[ 556 = \text{^{15}N}^{15}\text{N}^{16}\text{O} \]

\[ C^{456} = \text{456 mole fraction in percent of total N}_2\text{O in a sample} \]
\[ C^{546} = \text{546 mole fraction in percent of total N}_2\text{O in a sample} \]
\[ C^{446}_{meas} = \text{measured 446 mole fraction in percent of total N}_2\text{O in a sample} \]
\[ C^{546}_{meas} = \text{measured 456 mole fraction in percent of total N}_2\text{O in a sample} \]
\[ C^{546}_{meas} = \text{measured 546 mole fraction in percent of total N}_2\text{O in a sample} \]

\[ \sum C^{N,O,meas}_\text{meas} = \text{sum of the measured mole fractions of all N}_2\text{O isotopomers and isotopologues} \]

\[ C^{446}_{\text{reference}} = \text{mole fraction of 446 in the N}_2\text{O reference used for isotopic measurements} \]
\[ C^{446}_{\text{sample}} = \text{mole fraction of 446 in a N}_2\text{O sample} \]

\[ \delta^{\text{SP}} = \text{^{15}N site preference of N}_2\text{O (‰)} \text{ (equation 1.4)} \]
\[ \delta^{456} = \text{456 composition of N}_2\text{O (‰) (equation 1.6)} \]
\[ \delta^{546} = \text{546 composition of N}_2\text{O (‰) (equation 1.7)} \]
\[ ^{15}\text{N}_{\text{bulk}} = \text{Total} \text{^{15}N composition of N}_2\text{O (atom %} \text{^{15}N) (equation 2.3)} \]
\[ \delta^{448} = \text{^{18}O composition of N}_2\text{O (‰)} \]
\[ \delta^{447} = \text{^{17}O composition of N}_2\text{O (‰)} \]
\[ R^{\text{SP}} = C^{456}/C^{546} \text{ ratio for a N}_2\text{O sample/standard} \]

\[ \text{FTIR = Fourier Transform InfraRed} \]
\[ \text{ZPD = Zero optical Path Difference} \]
\[ \text{ILS = Instrument Line Shape} \]
\[ \text{MALT = Multiple Atmospheric Layer Transmission} \]
\[ S_{\text{RS}} = \text{N}_2\text{O reference standard} \]
\[ S_{\text{WS}} = \text{N}_2\text{O working standard used as reference for isotopic measurements of N}_2\text{O} \]
\[ S_{\text{WS}2} = \text{second N}_2\text{O working standard} \]
$S_{RS}$ dilution series = a sequential dilution series where $S_{RS}$ is diluted with a N$_2$O working standard with an unknown $\delta_{SP}$ value

$S_{456}$ = near isotopically pure 456 working gas

$S_{456}$ = near isotopically pure 456 working gas

$S_{556}$ = near isotopically pure 556 working gas

$x_{RS}$ = mole fraction of the reference standard ($S_{RS}$) in a dilution series (equation 3.4/3.5)

$x_{546}$ = mole fraction of 546 derived form $S_{RS}$ in a dilution series (equation 3.10/3.13)

$S_{RS}$ dilution curve = where measured $\delta_{SP}$ values are plotted as function of $x_{546}$ for a $S_{RS}$ dilution series

$\delta_{RS}^{SP}$ = the absolute site preference value for the reference standard

$\delta_{U}^{SP}$ = the absolute site preference value for the N$_2$O diluent used for a dilution series

$\delta_{meas}^{SP}$ = raw-measured $\delta_{SP}$ value

$C^{I}$ = mole fraction of total isotopic impurities in a near-isotopically pure N$_2$O standard

$C_{meas}^{I}$ = measured mole fraction of total isotopic impurities

$C_{added}^{I}$ = mole fraction of total isotopic impurities added to a near isotopically pure N$_2$O standard.

$P^{15}N$ = average partial pressure of 456 and 546 in a measurement of N$_2$O (equation 3.21)

$P^{14}N$ = partial pressure of 446 in a measurement of N$_2$O

WFPS = Water Filled Pore Space (WFPS)

$^{15}$NH$_4^{+}$ = $^{15}$N composition of soil NH$_4^{+}$ (atom % $^{15}$N)

$^{15}$NO$_3^{-}$ = $^{15}$N composition of soil NO$_3^{-}$ (atom % $^{15}$N)

$^{15}$N$_2$O = N$_2$O emissions derived from denitrification

$^{15}$N$_2$O = N$_2$O emissions derived from nitrification

High NH$_4^{+}$ = 100kg-N.ha$^{-1}$ NH$_4^{+}$ treatment

Low NH$_4^{+}$ = 50kg-N.ha$^{-1}$ NH$_4^{+}$ treatment

High NO$_3^{-}$ = 100kg-N.ha$^{-1}$ NH$_4^{+}$ treatment

Low NO$_3^{-}$ = 50kg-N.ha$^{-1}$ NH$_4^{+}$ treatment

$F^{N,O}$ = flux of N$_2$O (kg-N.ha$^{-1}$.day$^{-1}$)

$\sum F^{N,O}$ = mean cumulative N$_2$O emissions for flux chambers receiving the same
single treatment

EF = N$_2$O emission factor

$N_{\text{applied}}$ = Nitrogen application rate (kg-N.ha$^{-1}$)

$F_{\text{ert}}^{N_2O}$ = mean daily N$_2$O emissions derived from fertiliser nitrogen pool

$F_{\text{soil}}^{N_2O}$ = mean daily N$_2$O emissions derived from existing soil nitrogen pool

$\delta_N^{SP}$ = $\delta^{SP}$ of N$_2$O emitted from nitrification

$\delta_D^{SP}$ = $\delta^{SP}$ of N$_2$O emitted from denitrification

($\delta_D^{SP}$)$_{\text{prod}}$ = $\delta^{SP}$ of N$_2$O emitted from denitrification with no reduction of N$_2$O to N$_2$

($\delta_D^{SP}$)$_{\text{obs}}$ = the observed $\delta^{SP}$ of the N$_2$O emitted from denitrification

$x_N$ = fraction of the total N$_2$O emissions produced from nitrification

$x_D$ = fraction of total N$_2$O emissions produced from denitrification

$x_{N,D}^{N_2O}$ = fraction of N$_2$O emissions derived from the applied nitrogen

$F_{\text{ert}}^{N_2O}$ = N$_2$O emissions derived from denitrification

$F_D^{N_2}$ = N$_2$ emissions derived from denitrification

$F_D^N$ = Total denitrification emissions ($F_D^{N_2O}$ + $F_D^{N_2}$)

$^{15}N_N$ = $^{15}N_{\text{bulk}}$ of N$_2$O emitted from nitrification

$^{15}N_D$ = $^{15}N_{\text{bulk}}$ of N$_2$O emitted from denitrification

$\varepsilon$ = isotopic enrichment factor

$\alpha$ = isotopic fractionation factor
Abstract

Agriculture contributes 16% to Australia’s greenhouse gas emissions, of which 23% are the result of nitrous oxide (N\textsubscript{2}O) emissions. Global N\textsubscript{2}O emissions from agricultural activities have increased substantially since the beginning of the industrial revolution. This has been driven by the increase in the amount of nitrogen added to agricultural soils, stimulating the N\textsubscript{2}O-producing nitrification and denitrification processes.

Currently there is a poor quantitative understanding of N\textsubscript{2}O emissions from nitrification and denitrification and their controlling parameters. This is difficult to quantify since N\textsubscript{2}O emissions from nitrification and denitrification occur simultaneously. As N\textsubscript{2}O produced from these microbial processes have different stable isotopic signatures, stable isotope measurements have shown promise as a method to partition N\textsubscript{2}O emissions. Additionally, the intramolecular \textsuperscript{15}N site preference of N\textsubscript{2}O presents a further stable isotopic measurement which can be used for studies of N\textsubscript{2}O emissions from nitrification and denitrification.

In this thesis, the absolute intramolecular \textsuperscript{15}N site preference of N\textsubscript{2}O measured using high resolution FTIR. The FTIR system was fully calibrated for site preference measurements of \textsuperscript{15}N enriched N\textsubscript{2}O sample. In addition, using the FTIR system the absolute site preference value for the N\textsubscript{2}O working standard used as a reference for isotopic measurements was determined. Using this absolute site preference value, it was possible to determine a value of 19.9 (±2.1)‰ for the absolute site preference of tropospheric N\textsubscript{2}O. The absolute site preference value of the N\textsubscript{2}O working standard was used to report measurements of field collected N\textsubscript{2}O samples on the absolute scale.

To determine the intramolecular site preference of N\textsubscript{2}O produced from nitrification and denitrification, a 2 week field campaign was completed at a dairy farm in south eastern Australia. Soil plots were treated with \textsuperscript{15}N-labelled NH\textsubscript{4}\textsuperscript{+} or NO\textsubscript{3}\textsuperscript{-}, either at application rates of 100 or 50 kg-N.ha\textsuperscript{-1}, followed by irrigation. Following treatment, daily measurements were made of the N\textsubscript{2}O emissions, isotopic composition of N\textsubscript{2}O, soil mineral nitrogen concentrations and \textsuperscript{15}N composition, as well as soil moisture. From the interpretation of the collected data, intramolecular site preference signatures of -17 (±5)‰ was determined for nitrification and a range of 0.5 to 12.3‰ was attributed to denitrification. Using the \textsuperscript{15}N measurements of N\textsubscript{2}O, it was possible to estimate the N\textsubscript{2}O emissions produced from nitrification and denitrification. For all treatments, emissions produced from denitrification far outweighed those from nitrification. These measurements indicated that the reduction of N\textsubscript{2}O to N\textsubscript{2} was a key process controlling N\textsubscript{2}O emissions. Additionally, there was a clear relationship between the intramolecular site preference of N\textsubscript{2}O, and the amount of N\textsubscript{2}O reduced to N\textsubscript{2}. This relationship was used to estimate that for treatments receiving NH\textsubscript{4}\textsuperscript{+}, 5 – 22% of the applied nitrogen was emitted as N\textsubscript{2}.
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