

2001

## Isotopic characterisation of atmospheric nitrous oxide fourier transform infrared spectroscopy

Federico Turatti  
*University of Wollongong*

Follow this and additional works at: <https://ro.uow.edu.au/theses>

### University of Wollongong

#### Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

### Recommended Citation

Turatti, Federico, Isotopic characterisation of atmospheric nitrous oxide fourier transform infrared spectroscopy, Doctor of Philosophy thesis, Department of Chemistry, University of Wollongong, 2001.  
<https://ro.uow.edu.au/theses/1160>

## **NOTE**

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

## **UNIVERSITY OF WOLLONGONG**

### **COPYRIGHT WARNING**

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

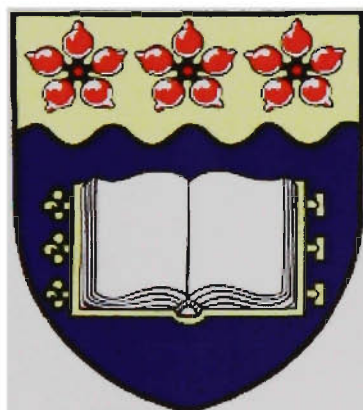
Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

# **Isotopic Characterisation of Atmospheric Nitrous Oxide by Fourier Transform Infrared Spectroscopy**

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

DOCTOR OF PHILOSOPHY

from



UNIVERSITY OF WOLLONGONG

by

**FEDERICO TURATTI, BSc (Hons.)**

Department of Chemistry, 2001

### ***Certification***

I, Federico Turatti, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Department 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.

Federico Turatti

## **Acknowledgments**

*Many people have helped me complete this work and all deserve my sincere thanks and acknowledgement:*

- My academic supervisors, Associate Professor David Griffith, Dr Stephen Wilson and Dr Paul Steele, for their many suggestions, their scientific encouragement and for their constructive advice and criticisms.*
- The University of Wollongong and CSIRO Atmospheric Research for financial and scientific support, and CSIRO Land and Water for scientific support.*
- Fellow team members of the Atmospheric Chemistry and Spectroscopy Group for their companionship, especially David Hsu for many cups of tea and many absorbing discussions about politics, current affairs and authentic Szechwan food. Joanne Menegazzo and Jerker Samuelsson also deserve my thanks for their invaluable help in the atrocious and unforgettable conditions of the Corowa field trip.*
- Steve Cooper, Geoffrey Hurt and John Bourke of the Faculty of Science Workshop for constructing crucial pieces of hardware used in this work.*

*I reserve my deepest and most heartfelt gratitude for my wife Justine, for my dearest friends and for my family, whose support made progress through a painful journey possible. Those who complete works of substance inevitably face doubts, but courage is found in the support of one's closest confidants.*

## ***Publications***

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

- Turatti, F., D.W.T. Griffith, S.R. Wilson, M.B. Esler, T. Rahn, H. Zhang, and G.A. Blake, Positionally dependent  $^{15}\text{N}$  fractionation factors in the photolysis of  $\text{N}_2\text{O}$  determined by high resolution FTIR spectroscopy, *Geophysical Research Letters*, 27 (16), 2489-2492, 2000.
- Turatti, F., D.W.T. Griffith, S.R. Wilson, M.B. Esler, L.P. Steele, T. Rahn, and H. Zhang, Isotopic analysis of atmospheric  $\text{N}_2\text{O}$  by FTIR spectroscopy:  $^{15}\text{N}$ ,  $^{18}\text{O}$  and  $^{15}\text{N}$  positional dependence, in *Cape Grim Baseline Air Pollution Station Annual Meeting*, edited by N. Tindale, CSIRO Atmospheric Research, Aspendale, 1999.
- Esler, M.B., D.W.T. Griffith, F. Turatti, S.R. Wilson, and T. Rahn,  $\text{N}_2\text{O}$  concentration and flux measurements and complete isotope analysis using FTIR spectroscopy, *Chemosphere: Global Change Science*, 2, 445-454, 2000.
- Griffith, D.W.T., S.R. Wilson, F. Turatti, M.B. Esler, and I.M. Jamie, Isotopomeric Analysis of Environmental Trace Gases by FTIR spectrometry:  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , in *1st International Symposium on Isotopomers*, edited by N. Yoshida, Yokohama, Japan, 2001.
- Wilson, S.R., D.W. Griffith, F. Turatti, and J. Menegazzo, Characterisation of agricultural  $\text{N}_2\text{O}$  emission sources using isotopic labelling studies, in *Cape Grim Baseline Air Pollution Station Annual Scientific Meeting*, edited by N. Tindale, and N. Derek, Aspendale, Vic, Australia, 2000.

## ***Abstract***

Nitrous oxide is the third most important anthropogenic greenhouse gas after CO<sub>2</sub> and CH<sub>4</sub> and contributes 6% of the total terrestrial radiative forcing due to greenhouse gases. It is closely involved in the depletion of stratospheric ozone by providing one of the main sources of NO radicals. Biological processes such as nitrification and denitrification are primarily responsible for N<sub>2</sub>O production. Despite its importance and years of research, the estimates of the global size of N<sub>2</sub>O sources and sinks remain highly uncertain, and its budget is not yet fully balanced.

Analysis of N<sub>2</sub>O isotopes can aid in reducing the large uncertainties in source and sink estimates by providing information that is complementary to the N<sub>2</sub>O mixing ratio. Analysis of the mean  $\delta^{15}\text{N}$  and mean  $\delta^{18}\text{O}$  has already lead to some insight on the N<sub>2</sub>O budget. Until very recently the intramolecular <sup>15</sup>N positional isotopes <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O were not measurable by any analytical technique. The intramolecular difference  $\delta^{14}\text{N}^{15}\text{N}^{16}\text{O} - \delta^{15}\text{N}^{14}\text{N}^{16}\text{O}$  is an additional isotopic discriminator than the mean  $\delta^{15}\text{N}$  alone, as it directly describes the processes forming the N-N bond in N<sub>2</sub>O production processes such as nitrification and denitrification.

This thesis describes the development of a high resolution Fourier transform infrared technique for the measurement of the N<sub>2</sub>O isotopomers <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O, <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>14</sup>N<sup>18</sup>O and <sup>14</sup>N<sup>14</sup>N<sup>17</sup>O. The FTIR technique utilises 0.012 cm<sup>-1</sup> resolution FTIR spectroscopy, a 2.4 m optical pathlength, 120 mL sample cell, with precise control of sample temperature and pressure. The typical analytical precision of the <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O isotopomers is of the order of 1-2 ‰, and approximately 3-4 ‰ for the oxygen isotopomers <sup>14</sup>N<sup>14</sup>N<sup>18</sup>O and <sup>14</sup>N<sup>14</sup>N<sup>17</sup>O. Two independent chemometric multivariate analytical methods were developed for determination of high resolution N<sub>2</sub>O spectra: multi-micro-window classical least squares, and non-linear least squares. The strengths and limitations of the FTIR technique are analysed and compared to those of the complementary isotope ratio mass spectrometry technique. The FTIR technique is analytically robust and serves as an independent and complementary technique to N<sub>2</sub>O analysis by isotope ratio mass spectrometry.

The FTIR technique was used to analyse N<sub>2</sub>O from several contexts. The isotopic fractionation factors in the laboratory photolysis of N<sub>2</sub>O at three wavelengths were determined by analysis of the unphotolysed N<sub>2</sub>O fraction. Samples of nitrous oxide were extracted from whole air at an urban location over the period of approximately one year and isotopically characterised. The emissions of N<sub>2</sub>O from a pig effluent fertilised crop field have been isotopically characterised. In each of the three contexts, results are interpreted in relation to the processes involved.

TABLE OF CONTENTS

<i>CERTIFICATION .....</i>	<i>II</i>
<i>ACKNOWLEDGMENTS.....</i>	<i>III</i>
<i>PUBLICATIONS.....</i>	<i>IV</i>
<i>ABSTRACT.....</i>	<i>V</i>
<b>CHAPTER 1 INTRODUCTION .....</b>	<b>1</b>
<b>1.1 THE SIGNIFICANCE OF ATMOSPHERIC N<sub>2</sub>O .....</b>	<b>2</b>
<i>1.1.1 THE ATMOSPHERIC RADIATIVE BALANCE.....</i>	<i>2</i>
<i>1.1.2 THE N<sub>2</sub>O STRATOSPHERIC CHEMISTRY .....</i>	<i>5</i>
<b>1.2 THE N<sub>2</sub>O BUDGET .....</b>	<b>6</b>
<i>1.2.1 NATURAL SOURCES.....</i>	<i>9</i>
<i>1.2.1.1 Oceans .....</i>	<i>9</i>
<i>1.2.1.2 Soils under natural vegetation.....</i>	<i>10</i>
<i>1.2.2 ANTHROPOGENIC SOURCES.....</i>	<i>10</i>
<i>1.2.2.1 Arable land .....</i>	<i>10</i>
<i>1.2.2.2 Animal excreta.....</i>	<i>11</i>
<i>1.2.2.3 Biomass burning.....</i>	<i>11</i>
<i>1.2.2.4 Industrial sources of N<sub>2</sub>O .....</i>	<i>11</i>
<i>1.2.2.5 Tropical forest conversion.....</i>	<i>12</i>
<i>1.2.2.6 Other potential N<sub>2</sub>O sources.....</i>	<i>12</i>
<i>1.2.3 SINKS .....</i>	<i>13</i>
<b>1.3 THE ISOTOPOMERS OF N<sub>2</sub>O.....</b>	<b>15</b>
<i>1.3.1 BUDGET IMPLICATIONS OF N<sub>2</sub>O ISOTOPOMER ANALYSIS .....</i>	<i>17</i>
<i>1.3.2 ISOTOPOMER EFFECTS OF NITRIFICATION AND DENITRIFICATION.....</i>	<i>18</i>
<i>1.3.2.1 The denitrification mechanism .....</i>	<i>20</i>
<i>1.3.2.2 Nitrification.....</i>	<i>22</i>
<i>1.3.2.3 Isotopic fractionation during sink processes.....</i>	<i>23</i>
<b>1.4 GAS ISOTOPOMER MEASUREMENT METHODS.....</b>	<b>26</b>
<i>1.4.1 ISOTOPE RATIO MASS SPECTROMETRY .....</i>	<i>26</i>
<i>1.4.2 OPTICAL EMISSION SPECTROSCOPY.....</i>	<i>29</i>
<i>1.4.3 TUNABLE DIODE LASER SPECTROSCOPY.....</i>	<i>31</i>
<i>1.4.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY .....</i>	<i>32</i>
<b>1.5 INTRODUCTION TO THIS WORK .....</b>	<b>33</b>
<b>1.6 REFERENCES.....</b>	<b>35</b>
<b>CHAPTER 2 EXPERIMENTAL I: INFRARED SPECTROSCOPY AND QUANTITATIVE SPECTRAL ANALYSIS.....</b>	<b>40</b>



<b>2.1 THE INFRARED SPECTRUM OF THE NITROUS OXIDE MOLECULE .....</b>	<b>40</b>
2.1.1 THE ROTATIONAL ENERGY LEVELS OF $N_2O$ .....	40
2.1.2 THE VIBRATIONAL SPECTRUM OF $N_2O$ .....	41
2.1.3 THE INFRARED SPECTRUM OF $N_2O$ .....	42
<b>2.2 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY .....</b>	<b>44</b>
2.2.1 BASIC FTIR THEORY.....	46
2.2.2 SPECTRAL SIGNAL TO NOISE RATIO (SNR).....	49
<b>2.3 CALCULATING SPECTRA FROM FIRST PRINCIPLES .....</b>	<b>50</b>
<b>2.4 CALCULATION OF SYNTHETIC SPECTRA WITH MALT.....</b>	<b>53</b>
<b>2.5 CLASSICAL LEAST SQUARES (CLS).....</b>	<b>56</b>
2.5.1 THEORY.....	56
2.5.2 WINDOWS AND REGIONS .....	59
2.5.3 THE WEIGHTS FOR EACH MICRO-WINDOW .....	63
2.5.4 EFFECT OF THE WEIGHTS ON DETERMINATION PRECISION .....	66
2.5.5 THE CAUSES OF WEIGHT VARIATION AND SPECTRUM TO SPECTRUM VARIABILITY.....	69
<b>2.6 NON-LINEAR LEAST SQUARES (NLLS).....</b>	<b>69</b>
2.6.1 THEORY.....	70
2.6.2 THE NON-LINEAR LEAST SQUARES ALGORITHM.....	71
2.6.3 OPTIMUM FITTING REGIONS.....	73
2.6.4 THE ADVANTAGES OF NON-LINEAR LEAST SQUARES OVER CLASSICAL LEAST SQUARES .....	80
<b>2.7 REFERENCES .....</b>	<b>82</b>
 <b>CHAPTER 3 EXPERIMENTAL II: HARDWARE, SAMPLE HANDLING AND MEASUREMENT PROCEDURES .....</b>	 <b>84</b>
<b>3.1 THE FTIR SPECTROMETER AND OPTICAL CONFIGURATION .....</b>	<b>84</b>
<b>3.2 SAMPLE HANDLING AND TEMPERATURE CONTROL .....</b>	<b>85</b>
<b>3.3 SAMPLE MEASUREMENT PROCEDURES .....</b>	<b>92</b>
3.3.1 SAMPLE INTRODUCTION AND MEASUREMENT.....	92
3.3.2 MEASURING $N_2O$ WORKING STANDARD AND EVACUATED CELL REFERENCE SPECTRA .....	93
<b>3.4 SELECTION OF AN <math>N_2O</math> WORKING STANDARD .....</b>	<b>94</b>
<b>3.5 EXTRACTING <math>N_2O</math> FROM SOURCES .....</b>	<b>99</b>

3.5.1 $N_2O$ EXTRACTION .....	100
<b>3.6 REFERENCES.....</b>	<b>101</b>
<b>CHAPTER 4 EXPERIMENTAL III: OPTIMAL SPECTROSCOPIC CONDITIONS, TECHNIQUE PRECISION AND LIMITATIONS .....</b>	<b>102</b>
4.1 ESTIMATING THE OPTIMAL $N_2O$ AMOUNT AND SPECTROSCOPIC CONDITIONS	102
4.2 VALIDATION OF THE THEORETICAL IDEAL CONDITIONS .....	106
4.3 THE THEORETICAL PRECISION LIMITS.....	107
4.4 EFFECT OF TEMPERATURE CHANGES ON $\delta$ DETERMINATION.....	110
4.5 EFFECT OF SAMPLE PRESSURE ON $\delta$ DETERMINATION .....	114
4.6 EFFECT OF LINE SHAPE VARIABILITY ON $\delta$ DETERMINATION .....	117
4.7 WHAT LIMITS THE ISOTOPOMER PRECISION? .....	120
4.8 A SUMMARY OF THE HIGH RESOLUTION FTIR METHOD CONDITIONS .....	121
4.9 REFERENCES.....	122
<b>CHAPTER 5 RESULTS I: ISOTOPIC ENRICHMENT FACTORS FOR <math>^{14}N^{15}N^{16}O</math>, <math>^{15}N^{14}N^{16}O</math>, <math>^{14}N^{14}N^{18}O</math> AND <math>^{14}N^{14}N^{17}O</math> IN THE LABORATORY PHOTOLYSIS OF <math>N_2O</math>.....</b>	<b>123</b>
5.1 INTRODUCTION .....	123
5.2 EXPERIMENTAL .....	125
5.3 RESULTS AND DISCUSSION .....	126
5.4 CONCLUSIONS.....	139

<b>5.5 REFERENCES.....</b>	<b>139</b>
 <b>CHAPTER 6 RESULTS II: ISOTOPOMERIC CHARACTERISATION OF TROPOSPHERIC N<sub>2</sub>O .....</b>	
<b>6.1 INTRODUCTION .....</b>	<b>141</b>
<b>6.2 EXPERIMENTAL .....</b>	<b>142</b>
<b>6.3 RESULTS AND INTERPRETATIONS.....</b>	<b>143</b>
6.3.1 LOCAL AND LARGE SCALE WEATHER CONDITIONS .....	143
6.3.2 THE N <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> AND CO MIXING RATIOS.....	145
6.3.3 THE MEAN $\delta^{15}\text{N}$ RELATIVE TO ATMOSPHERIC N <sub>2</sub> .....	146
6.3.4 INDIVIDUAL <sup>15</sup> N ISOTOPOMERS AND THE INTRAMOLECULAR <sup>15</sup> N DIFFERENCE, $\delta^{456}$ - $\delta^{546}$ .....	153
6.3.5 THE OXYGEN ISOTOPOMERS, <sup>14</sup> N <sup>14</sup> N <sup>18</sup> O AND <sup>14</sup> N <sup>14</sup> N <sup>17</sup> O.....	157
6.3.6 ISOTOPOMER CORRELATION WITH LOCAL SCALE WEATHER CONDITIONS.....	159
<b>6.4 SUMMARY AND CONCLUSIONS.....</b>	<b>160</b>
<b>6.5 REFERENCES.....</b>	<b>161</b>
 <b>CHAPTER 7 RESULTS III: ISOTOPIC CHARACTERISATION OF N<sub>2</sub>O FROM PIG EFFLUENT FERTILISED CROP SOILS.....</b>	
<b>7.1 THE ROLE OF SOILS IN GLOBAL N<sub>2</sub>O EMISSIONS .....</b>	<b>163</b>
<b>7.2 EXPERIMENTAL .....</b>	<b>164</b>
7.2.1 SITE AND EXPERIMENT DESCRIPTION.....	164
7.2.2 EXTRACTION OF N <sub>2</sub> O FROM SOIL GAS EMISSIONS.....	165
7.2.3 MEASURING THE N <sub>2</sub> O FLUX AND ISOTOPIC COMPOSITION .....	170
<b>7.3 RESULTS.....</b>	<b>172</b>
7.3.1 FLUXES OF N <sub>2</sub> O AND CO <sub>2</sub> .....	172
7.3.2 N <sub>2</sub> O ISOTOPIC COMPOSITION.....	173
<b>7.4 RESULT INTERPRETATION AND DISCUSSION .....</b>	<b>174</b>
7.4.1 N <sub>2</sub> O FLUXES .....	174
7.4.2 $\delta^{15}\text{N}$ OF N <sub>2</sub> O FROM EXPERIMENT SITES .....	180
7.4.3 THE INTRAMOLECULAR <sup>15</sup> N DIFFERENCE: $\delta^{456}$ - $\delta^{546}$ AND THE INDIVIDUAL $\delta^{456}$ AND $\delta^{546}$ .....	185
7.4.4 THE OXYGEN ISOTOPOMERS.....	187

7.5 CONCLUSIONS .....	193
7.6 REFERENCES .....	195
 CHAPTER 8 CONCLUSIONS.....	198
8.1 FURTHER WORK ALREADY IN PROGRESS .....	201
8.2 FURTHER WORK.....	203
8.3 OVERALL CONCLUSION .....	204
8.4 REFERENCES .....	205
 APPENDIX A PROCEDURES AND PUBLICATIONS .....	206
A.1 PROCEDURE FOR DISMANTLING THE VACUUM LINE AND WHITE CELL .....	206
A.2 PROCEDURE FOR WASHING THE WHITE CELL.....	207
A.3 PROCEDURE FOR ATTACHING CaF <sub>2</sub> WINDOW TO THE WHITE CELL .....	208
A.4 REASSEMBLY PROCEDURE.....	209
A.5 PUBLICATIONS .....	209

LIST OF FIGURES

FIGURE 1.1 A CONCEPTUAL MODEL OF NITRIFICATION AND DENITRIFICATION.....19

FIGURE 1.2 THE PARALLEL MECHANISM FOR DENITRIFICATION.....21

FIGURE 1.3 THE SEQUENTIAL MECHANISM FOR DENITRIFICATION .....21

FIGURE 1.4 SCHEMATIC DIAGRAM OF THE NITRIFICATION MECHANISM.....23

FIGURE 1.5 VERTICAL PROFILES OF  $\delta^{546}$ - $\delta^{456}$  OF N<sub>2</sub>O FROM FTIR BALLOON FLIGHTS AS DESCRIBED BY GRIFFITH ET AL. [2000] .....25

FIGURE 1.6 SCHEMATIC DIAGRAM OF AN ISOTOPE RATIO MASS SPECTROMETER OPTIMISED FOR MEASURING  $\delta^{15}\text{N}$  [MULVANEY, 1993].....27

FIGURE 1.7 BASIC COMPONENTS OF AN OPTICAL EMISSION  $^{15}\text{N}$  ANALYSER [PRESTON, 1993] .....30

FIGURE 1.8 SCHEMATIC DIAGRAM OF AN FTIR INSTRUMENT FOR ANALYSIS OF  $\delta^{13}\text{C}$  AND TRACE GASES [ESLER ET AL., 2000A].....33

FIGURE 2.1 NORMAL VIBRATIONS AND THEIR FUNDAMENTAL FREQUENCIES FOR THE N<sub>2</sub>O MOLECULE.41

FIGURE 2.2 SYNTHETICALLY CALCULATED FTIR SPECTRA BETWEEN 2120 AND 2280 cm<sup>-1</sup> OF THE SIX MOST NATURALLY ABUNDANT N<sub>2</sub>O ISOTOPOMERS.....44

FIGURE 2.3 SCHEMATIC DIAGRAM OF THE MICHELSON INTERFEROMETER .....45

FIGURE 2.4 FUNCTIONS  $e^{-\alpha x}$  (SYM1) AND  $x e^{-\alpha x}$  (SYM2).....56

FIGURE 2.5 MEASURED, FITTED AND RESIDUAL SPECTRUM FOR N<sub>2</sub>O BETWEEN 2130 AND 2160 cm<sup>-1</sup>, MICRO-WINDOW 1. ....62

FIGURE 2.6 MEASURED, FITTED AND RESIDUAL SPECTRUM FOR N<sub>2</sub>O BETWEEN 2190.65 AND 2191.25 cm<sup>-1</sup>, MICRO-WINDOW 38. ....62

FIGURE 2.7 WEIGHTS AS A FUNCTION OF MICRO-WINDOW FOR EACH N<sub>2</sub>O ISOTOPOMER.....64

FIGURE 2.8  $\delta^{14}\text{N}^{15}\text{N}^{16}\text{O}$  DETERMINATIONS FOR CONSECUTIVE N<sub>2</sub>O SPECTRA SERIES SE25033M DETERMINED WITH DIFFERENT SETS OF WEIGHTS. ....68

FIGURE 2.9 FLOWCHART FOR SPECTRAL ANALYSIS BY NON-LINEAR LEAST SQUARES BY THE PROGRAM NLM3. ....72

FIGURE 2.10 STANDARD ERROR SURFACE FOR  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  ISOTOPOMER A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW.....74

FIGURE 2.11 STANDARD ERROR SURFACE FOR  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  ISOTOPOMER A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW.....76

FIGURE 2.12 STANDARD ERROR SURFACE FOR  $^{14}\text{N}^{14}\text{N}^{18}\text{O}$  ISOTOPOMER AS A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW.....76

FIGURE 2.13 STANDARD ERROR SURFACE FOR  $^{14}\text{N}^{14}\text{N}^{17}\text{O}$  ISOTOPOMER AS A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW.....77

FIGURE 2.14 STANDARD ERROR SURFACE FOR PARENT  $^{14}\text{N}^{14}\text{N}^{16}\text{O}$  ISOTOPOMER AS A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW .....79

FIGURE 2.15	NON-LINEAR LEAST SQUARES FIT TO THE 2120 – 2270 $\text{cm}^{-1}$ (LEFT) AND 2172.1–2172.6 $\text{cm}^{-1}$ (RIGHT) REGIONS OF THE $\text{N}_2\text{O}$ SPECTRUM.....	80
FIGURE 3.1	THE INFRARED OPTICAL CONFIGURATION.....	87
FIGURE 3.2	ENGINEERING DRAWING OF THE TEMPERATURE CONTROL SYSTEM AND WHITE CELL .....	88
FIGURE 3.3	SCHEMATIC DIAGRAM OF THE SAMPLE HANDLING MANIFOLD AND WHITE CELL .....	89
FIGURE 3.4	THE SAMPLE HANDLING MANIFOLD ATTACHED TO THE DA8 SPECTROMETER .....	90
FIGURE 3.5	DIFFERENCE BETWEEN FTIR AND IRMS MEASUREMENT OF THREE $\text{N}_2\text{O}$ WORKING STANDARDS RELATIVE TO BOC GASES $\text{N}_2\text{O}$ . .....	98
FIGURE 4.1	PRECISION SURFACE FOR $\delta^{456}$ WITH VARIABLE $\text{N}_2\text{O}$ AMOUNT AND SPECTRAL RESOLUTION FOR A CONSTANT 30 MINUTE ACQUISITION TIME AND VARIABLE SIGNAL TO NOISE RATIO. ....	105
FIGURE 4.2	CROSS SECTION OF PRECISION SURFACE (FIGURE 4.1) FOR 0.8 TORR $\text{N}_2\text{O}$ . ....	105
FIGURE 4.3	THEORETICAL DETERMINATION PRECISION FOR $\text{N}_2\text{O}$ ISOTOPOMERS BY NON-LINEAR AND CLASSICAL LEAST SQUARES TECHNIQUES. ....	108
FIGURE 4.4	THE EFFECT OF A TEMPERATURE CHANGE ON PARTIAL PRESSURE DETERMINATION (LEFT) AND $\delta$ DETERMINATION (RIGHT) AS DETERMINED BY CLS .....	111
FIGURE 4.5	THE EFFECT OF A TEMPERATURE CHANGE ON PRESSURE DETERMINATION (LEFT) AND $\delta$ DETERMINATION (RIGHT) AS DETERMINED BY NLLS .....	112
FIGURE 4.6	THE EFFECT OF A PRESSURE CHANGE ON PRESSURE DETERMINATION (LEFT) AND $\delta$ DETERMINATION (RIGHT) AS DETERMINED BY CLS.....	115
FIGURE 4.7	THE EFFECT OF A PRESSURE CHANGE ON PRESSURE DETERMINATION (LEFT) AND $\delta$ DETERMINATION (RIGHT) AS DETERMINED BY NLLS .....	116
FIGURE 4.8	SINGLE SCAN REPRODUCIBILITY FOR HIGH RESOLUTION SPECTRA DETERMINED ON 25 SEPTEMBER 2000. ....	118
FIGURE 4.9	LINE SHAPE OF 25 CONSECUTIVE 30-SCAN SPECTRA. ....	119
FIGURE 5.1	RAYLEIGH DISTILLATION PLOTS FOR $\text{N}_2\text{O}$ PHOTOLYSIS AT 211.5 NM, 207.6 NM AND 193 NM FOR $^{15}\text{N}$ ISOTOPOMERS.....	129
FIGURE 5.2	RAYLEIGH DISTILLATION PLOTS FOR $\text{N}_2\text{O}$ PHOTOLYSIS AT 211.5 NM, 207.6 NM AND 193 NM FOR $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ AND $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ ISOTOPOMERS.....	130
FIGURE 5.3	COMPARISON OF $\epsilon^{456}$ AND $\epsilon^{546}$ ENRICHMENT FACTORS PREDICTED BY TWO $\text{N}_2\text{O}$ PHOTOLYSIS THEORIES .....	134
FIGURE 5.4	ENRICHMENT FACTORS $\epsilon^{15}\text{N}$ AND $\epsilon^{456-546}$ FOR THE LABORATORY PHOTOLYSIS OF $\text{N}_2\text{O}$ .....	135
FIGURE 5.5	ENRICHMENT FACTORS $\epsilon^{448}$ AND $\epsilon^{447}$ FOR THE LABORATORY PHOTOLYSIS OF $\text{N}_2\text{O}$ . ....	136
FIGURE 5.6	ENRICHMENT FACTOR RATIOS $\epsilon^{456}/\epsilon^{546}$ AND $\epsilon^{448}/\epsilon^{447}$ FOR THIS WORK AND TWO THEORIES	137
FIGURE 6.1	$\delta^{15}\text{N}$ AS A FUNCTION OF $\text{N}_2\text{O}$ MIXING RATIO FOR THE COLLECTED TROPOSPHERIC $\text{N}_2\text{O}$ SAMPLES .....	148
FIGURE 6.2	PERTURBATION OF AN $\text{N}_2\text{O}$ RESERVOIR OF CONSTANT CONCENTRATION AND $\delta$ BY AN $\text{N}_2\text{O}$ SOURCE (SCHEMATIC) .....	149
FIGURE 6.3	KEELING PLOT FOR $\delta^{15}\text{N}$ FOR COLLECTED TROPOSPHERIC $\text{N}_2\text{O}$ SAMPLES .....	151

FIGURE 6.4	$\delta^{456}$ , $\delta^{546}$ AND $\delta^{456}$ - $\delta^{546}$ AS A FUNCTION OF $N_2O$ MIXING RATIO .....	154
FIGURE 6.5	$\delta^{456}$ - $\delta^{546}$ AS A FUNCTION OF $\delta^{15}N$ (LEFT) AND $\delta^{546}$ (RIGHT) FOR THIS WORK AND <i>YOSHIDA AND TOYODA</i> [2000] .....	158
FIGURE 6.6	$\delta^{15}N$ (RIGHT) AND $\delta^{448}$ (LEFT) AS A FUNCTION OF RAIN FALL, 24 HOURS TO 0900.....	158
FIGURE 7.1	LOCATION OF COROWA, NSW.....	166
FIGURE 7.2	SCHEMATIC DIAGRAM OF THE COROWA EXPERIMENT SITE. ....	166
FIGURE 7.3	THE COROWA FIELD SITE, LOOKING EAST TOWARDS THE ACCESS ROAD .....	168
FIGURE 7.4	THE BOOM IRRIGATOR .....	168
FIGURE 7.5	THE WATERLOGGED REGION OF THE CROP FIELD SITE .....	169
FIGURE 7.6	THE $N_2O$ EXTRACTION LINE MOUNTED INSIDE THE 4WD VEHICLE .....	169
FIGURE 7.7	RELATIVE RATES OF NITRIFICATION AND DENITRIFICATION AS A FUNCTION OF WATER FILLED PORE SPACE. ....	177
FIGURE 7.8	FLUX $N_2O$ AS A FUNCTION OF TIME POST-IRRIGATION.....	179
FIGURE 7.9	$\delta^{15}N$ OF $N_2O$ SOIL EMISSIONS AS A FUNCTION OF $N_2O$ FLUX FOR COROWA FIELD SITES ....	179
FIGURE 7.10	$\delta^{15}N$ OF $N_2O$ SOIL EMISSIONS AS A FUNCTION OF TIME POST-IRRIGATION FOR COROWA FIELD SITES .....	180
FIGURE 7.11	INTRAMOLECULAR $^{15}N$ DIFFERENCE ( $\delta^{456}$ - $\delta^{546}$ ) OF $N_2O$ SOIL EMISSIONS AS A FUNCTION OF $N_2O$ FLUX FOR COROWA FIELD SITES .....	184
FIGURE 7.12	$\delta^{546}$ AS A FUNCTION OF $\delta^{456}$ FOR THE COROWA FIELD SITES. ....	184
FIGURE 7.13	$\delta^{456}$ - $\delta^{546}$ AS A FUNCTION OF $\delta^{15}N$ FOR THIS WORK, <i>PEREZ ET AL.</i> [2001] AND <i>MENEGAZZO</i> [2000]. ....	187
FIGURE 7.14	$\delta^{448}$ RELATIVE TO ATMOSPHERIC $O_2$ FOR $N_2O$ SOIL EMISSIONS AS A FUNCTION OF $N_2O$ FLUX (LEFT) AND TIME POST-IRRIGATION (RIGHT) FOR COROWA FIELD SITES.....	189
FIGURE 7.15	$\delta^{447}$ FOR $N_2O$ SOIL EMISSIONS AS A FUNCTION OF $N_2O$ FLUX (LEFT) AND TIME POST-IRRIGATION (RIGHT) FOR COROWA FIELD SITES.....	189
FIGURE 7.16	$\delta^{448}$ (REL. ATM. $O_2$ ) AS A FUNCTION OF $\delta^{15}N$ (REL. ATM. $N_2$ ) FOR THIS WORK, <i>PEREZ ET AL.</i> [2001] AND <i>MENEGAZZO</i> [2000]. ....	190
FIGURE 7.17	$\delta^{447}$ AS A FUNCTION OF $\delta^{448}$ FOR COROWA FIELD SITES .....	191
FIGURE 7.18	$\Delta^{17}O$ FOR $N_2O$ SOIL EMISSIONS AS A FUNCTION OF $N_2O$ FLUX (LEFT) AND TIME POST-IRRIGATION (RIGHT) FOR COROWA FIELD SITES.....	192

LIST OF TABLES

TABLE 1.1	GLOBAL WARMING POTENTIALS FOR SEVERAL GREENHOUSE GASES <sup>(A)</sup> .....	4
TABLE 1.2	SOURCE AND SINK ESTIMATES FOR N <sub>2</sub> O .....	8
TABLE 1.3	ISOTOPOMERS OF N <sub>2</sub> O AND THEIR NATURAL ABUNDANCES .....	15
TABLE 2.1	MICRO-WINDOWS USED IN CLS ANALYSIS OF HIGH RESOLUTION N <sub>2</sub> O SPECTRA .....	60
TABLE 2.2	NUMBER OF MICRO-WINDOWS CONTRIBUTING 90% OF TOTAL WEIGHT IN MICRO-WINDOW CLS ANALYSIS.....	63
TABLE 2.3	STANDARD DEVIATION OF ISOTOPOMER DETERMINATION FOR A SERIES OF SPECTRA <sup>(A)</sup> DETERMINED BY NLLS AND CLS TECHNIQUES.....	81
TABLE 3.1	RELATIVE ISOTOPIC SIGNATURES OF VARIOUS N <sub>2</sub> O WORKING STANDARDS DETERMINED BY THE FTIR METHOD .....	97
TABLE 3.2	δ <sup>15</sup> N AND δ <sup>18</sup> O OF N <sub>2</sub> O WORKING STANDARDS RELATIVE TO ATMOSPHERIC N <sub>2</sub> AND O <sub>2</sub> , RESPECTIVELY * .....	99
TABLE 4.1	CONDITIONS USED FOR ESTIMATING THE ISOTOPOMER PRECISION SURFACE .....	104
TABLE 4.2	THEORETICAL DETERMINATION PRECISION AT RMS-SNR 1000 AND BEST EXPERIMENTAL PRECISION. ....	109
TABLE 4.3	COMPARATIVE ISOTOPIC DETERMINATION PRECISIONS (± 1 σ) FOR TWO FTIR SPECTROMETERS .....	120
TABLE 4.4	THE STANDARD SPECTROSCOPIC CONDITIONS .....	121
TABLE 4.5	THE STANDARD SPECTRAL ANALYSIS CONDITIONS .....	122
TABLE 4.6	PERFORMANCE SUMMARY FOR THE FTIR METHOD.....	122
TABLE 5.1	ISOTOPOMER DETERMINATIONS IN PER MILLE RELATIVE TO SNOW <sup>(A)</sup> FOR LABORATORY PHOTOLYSED N <sub>2</sub> O BY NON-LINEAR LEAST SQUARES .....	128
TABLE 5.2	PHOTOLYSIS ENRICHMENT FACTORS OF N <sub>2</sub> O DETERMINED BY NON-LINEAR LEAST SQUARES .....	131
TABLE 5.3	PHOTOLYSIS ENRICHMENT ACTORS OF N <sub>2</sub> O DETERMINED BY CLS FOR THIS EXPERIMENT AND PREVIOUSLY PUBLISHED BY <i>TURATTI ET AL.</i> [2000].....	131
TABLE 6.1	LOCAL SCALE WEATHER CONDITIONS FOR EACH N <sub>2</sub> O SAMPLE COLLECTION.....	144
TABLE 6.2	MIXING RATIOS OF N <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> AND CO FOR COLLECTED TROPOSPHERIC AIR SAMPLES .....	145
TABLE 6.3	ISOTOPOMER RESULTS <sup>(A)</sup> FOR TROPOSPHERIC N <sub>2</sub> O SAMPLES COLLECTED FROM WOLLONGONG, AUSTRALIA .....	147
TABLE 6.4	ANALYSIS OF CLEAN BACKGROUND AIR FROM CAPE SHANK, VICTORIA .....	152
TABLE 7.1	FLUXES OF N <sub>2</sub> O AND CO <sub>2</sub> FOR THE COROWA FIELD EXPERIMENT SITES.....	173
TABLE 7.2	N <sub>2</sub> O ISOTOPIC SIGNATURES FOR COROWA FIELD EXPERIMENT SITES <sup>(A)</sup> .....	174