Faculty of Science - Papers (Archive)

Faculty of Science, Medicine and Health

2008

Measurement of methanol emissions from Australian wildfires by ground-based solar fourier transform spectroscopy

Clare Paton-Walsh
University of Wollongong, clarem@uow.edu.au

Stephen R. Wilson
University of Wollongong, swilson@uow.edu.au

N. B. Jones
University of Wollongong, njones@uow.edu.au

D. W. T. Griffith
University of Wollongong, griffith@uow.edu.au

Measurement of methanol emissions from Australian wildfires by ground-based solar fourier transform spectroscopy

Abstract

We report the first atmospheric column measurements of methanol made by ground-based solar Fourier transform infrared spectroscopy. The measurements were made through smoke plumes over South Eastern Australia during the Austral summers of 2001/2002 and 2002/2003. There is a strong correlation between the measured column amounts of methanol and simultaneous and co-located measurements of aerosol optical depth. An emission factor for methanol from Australian forest fires of 2.3 ± 0.8 grams per kilogram of dry fuel consumed is estimated by use of the correlations of methanol and carbon monoxide with aerosol optical depth and literature values for the emission factor of carbon monoxide. This agrees well with literature values for emissions measured from extra-tropical forest fires elsewhere in the world. Methanol is clearly an important volatile organic product of forest fires with an emission factor similar to formaldehyde's and approximately half that of methane.

Keywords

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

Publication Details

Measurement of Methanol Emissions from Australian Wildfires by Ground-based Solar Fourier Transform Spectroscopy

Clare Paton-Walsh, Stephen R. Wilson, Nicholas B. Jones and David W. T. Griffith
Department of Chemistry, University of Wollongong, Australia.

Abstract

We report the first atmospheric column measurements of methanol made by ground-based solar Fourier transform infrared spectroscopy. The measurements were made through smoke plumes over South Eastern Australia during the Austral summers of 2001/2002 and 2002/2003. There is a strong correlation between the measured column amounts of methanol and simultaneous and co-located measurements of aerosol optical depth. An emission factor for methanol from Australian forest fires of 2.3 ± 0.8 grams per kilogram of dry fuel consumed is estimated by use of the correlations of methanol and carbon monoxide with aerosol optical depth and literature values for the emission factor of carbon monoxide. This agrees well with literature values for emissions measured from extra-tropical forest fires elsewhere in the world. Methanol is clearly an important volatile organic product of forest fires with an emission factor similar to formaldehyde's and approximately half that of methane.

Keywords : Biomass burning, Methanol, Aerosol Optical Depth, Atmosphere, emissions, FTIR spectroscopy.

1. Introduction

Methanol is the second most abundant volatile organic compound in the atmosphere after methane [*Jacob, et al.*, 2005] with a lifetime in the surface boundary layer of 3-6 days [*Heikes, et al.*, 2002]. Despite being present in typical mixing ratios of a few parts per billion (ppb) in the continental boundary layer and up to 1 ppb in the free troposphere [*Heikes, et al.*, 2002], it is a difficult species to measure by Fourier transform infrared spectrometry because its broad infrared absorption cross-section means that background absorption depths are within the spectral noise. Biomass burning is a known source of methanol to the atmosphere [*Andreae and Merlet*, 2001] and so enhanced concentrations of methanol are to be expected in smoke plumes, simplifying the measurement task. The burning of large amounts of biomass releases significant amounts of particulates and different trace gases into the atmosphere [*Crutzen and Andreae*, 1990]. In order to assess the impact of these emissions, we need reliable quantitative estimates for inclusion in atmospheric chemical transport models. The amounts of trace gases emitted by fires depends upon the severity of the fire, the composition of the fuel and the chemical and physical processes occurring whilst the fuel is burning. The amount of a trace gas such as methanol emitted into the atmosphere from a fire episode may be estimated by multiplying the amount of biomass burnt with an emission factor for the fuel type, (the amount of methanol emitted per mass of biomass burned). Since the amount of a particular gas emitted during flaming combustion will often be different from the amount emitted during smouldering combustion, this emission factor should encompass both stages of combustion in their typical ratios for the material being burnt. During the course of a fire the emissions of many different traces gases occur simultaneously. For this reason enhancements in the mixing ratios of emitted

trace gases within the plume will correlate well until their different atmospheric lifetimes cause the correlations to break down. In our case the smoke plumes are sampled within hours from their sources and so methanol (lifetime 3-6 days) should correlate well with carbon monoxide (lifetime 1-3 months). Emission factors from different fire types for common combustion products such as carbon monoxide can be found in the literature, and used in conjunction with a whole-fire emission ratio, (the measured excess amount of the gas of interest (methanol) divided by coincident measurements of the reference gas excess (carbon monoxide)) [*Hurst, et al.*, 1994]. Since emission factors can vary enormously from one fuel source to another, these measurements for Australian temperate forest fires (where the fuel source is pre-dominantly varieties of Eucalyptus trees and associated litter) form a useful addition to the knowledge required to make accurate estimates of the sources of methanol from biomass burning.

2. Measurements

Several fire episodes in South Eastern Australia during the 2001/2002 and 2002/2003 austral summers resulted in smoke plumes passing over Wollongong NSW, Australia (34.4°S, 150.9°E). More than seventeen hundred infrared solar atmospheric absorption spectra were recorded on 30 separate days through these smoke plumes using a Bomem DA8 high-resolution Fourier transform infrared spectrometer coupled to a solar tracker. The spectra were recorded in a series of different frequencies ranges from 700 cm^{-1} to 4500 cm^{-1} by use of Mercury Cadmium Telluride and Indium Antimonide detectors and a set of optical filters that only pass a relatively narrow band of frequencies [*Griffith, et al.*, 1998].

Simultaneous and co-located direct solar spectral irradiance measurements spanning the visible wavelengths were also made using an Ocean Optics OD2000 grating spectrometer with a

3

2048 pixel CCD detector array spanning the visible wavelengths. The measurements were calibrated using the Langley technique to derive the top of the atmosphere signal in volts from data collected on clear days before and after the smoke measurements [*Wilson and Forgan*, 2002]. Individual estimates of aerosol optical depth (AOD) at 500 nm were derived from each measurement of irradiance through subtraction of the Rayleigh scattering component, and the mean value calculated for the period of time taken to record each of the infrared spectra, so that the optical depth of the atmosphere during the time of the infrared measurements could be determined. Although our measurements span the visible spectrum, maximum signal intensity and minimum interference by molecular absorbance is obtained at 500nm. The original dataset was reduced by removing spectra with coincident AOD values less than 0.1 or unusually low signal-to-noise values typically caused by clouds. AOD values greater than 0.1 can result from cloud cover as well as smoke, however since only cloud strongly attenuates the mid-infrared signal, the strength of the infrared signal in the retained spectra confirms the qualitative evidence of the presence of smoke.

3. Analysis of Infrared Spectra for Methanol Column Amounts

Previous studies have reported the analysis of these spectra for carbon monoxide (CO), hydrogen cyanide (HCN), formaldehyde (H_2CO), ammonia (NH_3), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), and formic acid (HCOOH)[*Paton-Walsh, et al.*, 2004; *Paton-Walsh, et al.*, 2005; *Rinsland, et al.*, 2005]. Methanol (CH_3OH) was not included in the original analyses because its line parameters have only recently become available in the HITRAN database [*Rothman, et al.*, 2005].

In this current study the spectral fitting algorithm known as GFIT [G. Toon, Jet Propulsion Laboratories - see [*Washenfelder, et al.*, 2006]] was used to determine the vertical column amount of CH_3OH (the number of molecules of methanol per square centimetre above the measurement site) from each spectrum recorded using the optical filter that transmitted in the region from $900cm^{-1}$ to $1350 \ cm^{-1}$, a total of 166 spectra. A spectrum is simulated using a layered model of the atmosphere, with the pressure, temperature and an initial mixing ratio for each gas assigned for 70 layers. Pressure and temperature dependent atmospheric absorption coefficients for each gas in each layer are then calculated line-by-line in the chosen spectral window using the HITRAN04 database [*Rothman, et al.*, 2005]. In this study the spectra were analysed for methanol within smoke plumes of unknown altitudes and vertical extent, so the initial mixing ratio profile for methanol was chosen to be 900 parts per trillion (ppt) from the ground to 9 km with the mixing ratio decreasing linearly with altitude to 100 ppt at 17 km and then decreasing rapidly to 0.001 ppt at 23 km and remaining at this value to the top of the atmosphere. Daily NCEP (National Centre for Environmental Prediction) temperature and pressure data were used. The simulated spectrum is compared with the measured spectrum and a best fit is obtained by iteratively scaling the mixing ratio profile of methanol by a single multiplicative factor (and independently scaling each interfering trace gas) until the root-mean-square difference between measured and simulated spectrum is minimised.
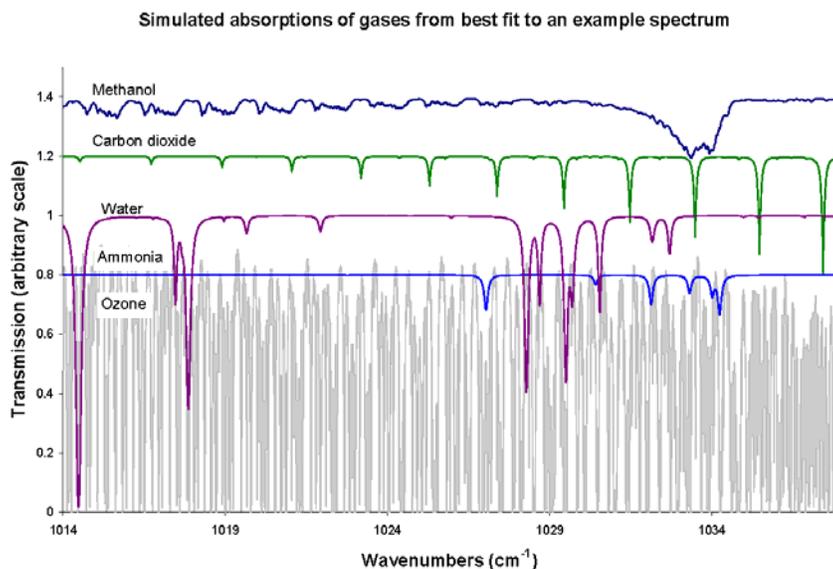
Simulated absorptions of gases from best fit to an example spectrum

Figure 1: Simulated absorptions of methanol, carbon dioxide, water, ammonia and ozone produced by the GFIT algorithm's best fit to an example spectrum for the 1014 cm^{-1} to 1038 cm^{-1} region. The simulations have been offset vertically for clarity.

Figure 1 shows the simulated absorptions of methanol, carbon dioxide, water, ammonia and ozone produced by the GFIT algorithms best fit to an example spectrum for the 1014 cm^{-1} to 1038 cm^{-1} region. The simulations have been offset vertically for clarity. Figure 2 shows two sets of residuals: firstly the residuals from the analysis shown in figure 1, and secondly the residuals from the best fit that resulted when methanol was fixed at assumed background levels in the analysis (and ammonia was fixed at the enhanced amount found from the original GFIT analysis). Also plotted in Figure 2 is a methanol spectrum that has been scaled and offset for comparison. The enhanced methanol amounts in this example spectrum can clearly be seen in figure 2.
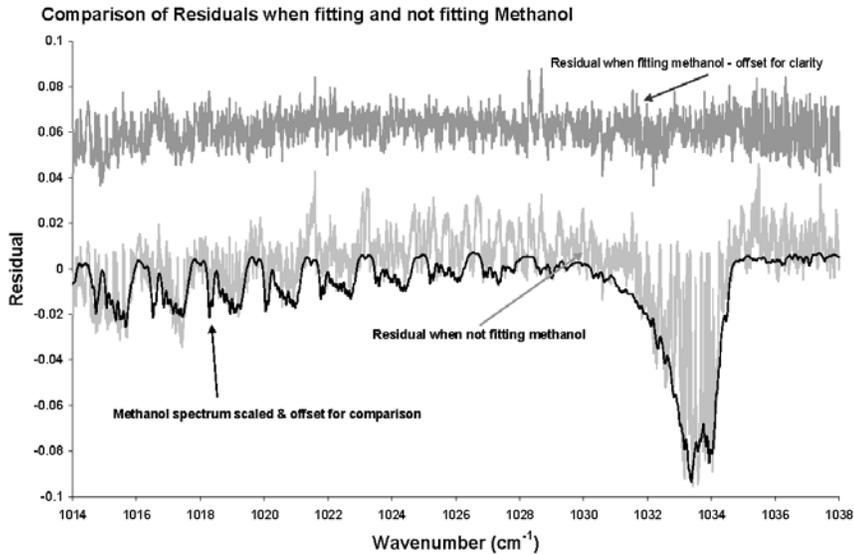
Figure 2 Residuals of the best fits that resulted (1) from the analysis described in the text and illustrated in figure 1 and (2) when the methanol was not adjusted in the analysis but left at background levels whilst the ammonia was fixed at the enhanced amount found from the original GFIT analysis. Also plotted in this figure is a methanol spectrum scaled and offset for comparison.

In GFIT, for each absorbing gas the whole mixing ratio profile is scaled by a single factor and thus no information about the altitude of the absorber is obtained from the spectra. Altitude information can be obtained by the pressure broadening of some trace gases' absorption lines [*Jones*, 2007] but methanol has sufficiently broad absorption features that the altitude information is lost. This lack of altitude information results in a large uncertainty in the temperature of the methanol because the smoke plume could be dispersed or it could be located in a narrow altitude region anywhere within the troposphere or in extreme cases even penetrate into the lower stratosphere [Fromm, 2006]. Evidence from the retrieval of other gases from these smoke plumes (eg CO) suggests that plumes from the January 2003 fires typically peaked at an altitude of around 4km, whilst many other smoke plumes extended to the ground [Paton-Walsh,

7

2005]. The actual vertical distribution differs from day to day and so this uncertainty adds to the imprecision of the dataset as a whole.

Temperature differences of around 80 – 90 K are typical between the ground and the tropopause, and our analysis assumes that methanol's mixing ratio is constant across the lowest 9km of the troposphere. We estimate that this assumption results in a temperature uncertainty of 20 K at one sigma and a subsequent uncertainty in the methanol absorption line strengths and derived column amounts of 4.4%. This is a significant contribution to the uncertainty of the measurements and can manifest itself as a reduction in the precision of the measurements, a systematic bias or a combination of the two. This temperature uncertainty is the dominant uncertainty when the sampled smoke plumes are thick and the concentration of methanol is large. The other main contribution to the precision of the measurements is the signal-to-noise uncertainty. This is the column amount of each trace gas that would produce the equivalent area of absorption feature as the noise in each spectrum. This uncertainty dominates when the smoke is thin and the absorption feature being fitted is weak. These two components are added in quadrature to give an estimate of the overall precision for each spectrum. Inaccuracies in the HITRAN line parameters will also contribute to the overall uncertainty of the retrievals. Further details of uncertainties inherent in determining total column amounts from infrared solar atmospheric absorption spectra can be found elsewhere [*Griffith, et al.*, 2003; *Meier, et al.*, 2005; *Walsh, et al.*, 1997].

4. Methanol Emissions using Aerosol Optical Depth as a Proxy for Carbon Monoxide

Emission ratios are used to extract useful information from measurements of gases within smoke plumes. The amount of a given trace gas measured at a particular time depends upon plume

thickness as well as the amount of that gas emitted by the fire. For this reason, the measured gas is often divided by coincident measurements of a reference gas, usually CO_2 or CO [*Hurst, et al.*, 1994]. In this case the excess column amount of CO_2 caused by the presence of smoke is difficult to measure with sufficient accuracy against its large background amount and there are no coincident measurements of CO with CH_3OH (because the column amounts are derived from spectra recorded at different times using different optical filters). Instead we can use the coincident measurements of aerosol optical depth (AOD) as a proxy since previous studies [*Edwards, et al.*, 2004; *Paton-Walsh, et al.*, 2004; *Paton-Walsh, et al.*, 2005] have shown that AOD is highly correlated with CO. The regression equation relating CO to AOD from the measurements described here is: CO column = [(1.5 ± 0.1)AOD + (1.5 ± 0.1)] x 10^{18} [*Paton-Walsh, et al.*, 2005].
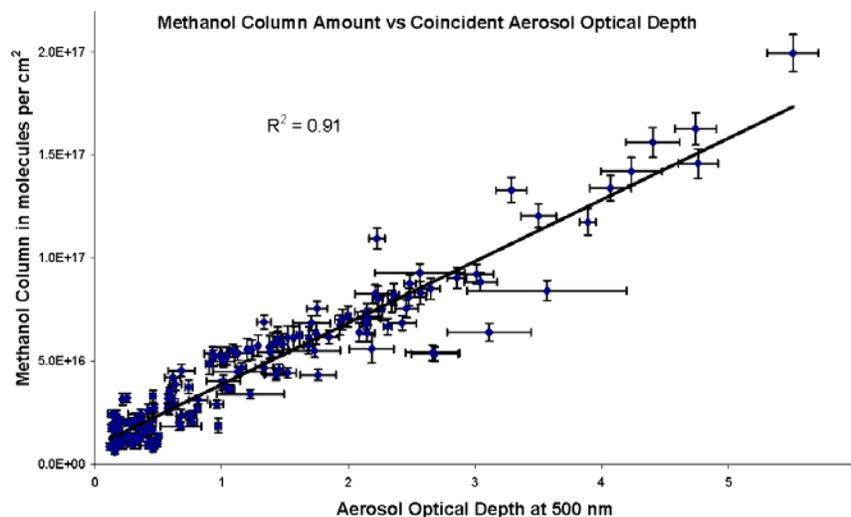

Figure 3 Vertical column amounts of CH_3OH plotted against simultaneous, co-located measurements of AOD at 500nm. The error-bars are the total uncertainty (precision) for each spectrum and the one sigma standard deviation of the aerosol optical depth measurements during the time taken to record each infrared spectrum. The column amounts of CH_3OH are highly correlated with AOD at 500 nm with an R^2 value of 0.91.

Figure 3 shows the vertical column amounts of CH_3OH plotted against simultaneous, co-located measurements of AOD at 500nm. Data from the first of January 2002 have been

9

excluded because these data have been shown previously to be unrepresentative [Paton-Walsh, 2005], with anomalously low AOD values, probably due to the close proximity of the fires on that day meaning that secondary aerosol production had not yet started in these fresh, local smoke plumes. The error-bars are the total uncertainty (precision) for each spectrum calculated as described above and the one sigma standard deviation of the aerosol optical depth measurements during the time taken to record each infrared spectrum. It is apparent from figure 3 that the column amounts of CH_3OH are highly correlated with AOD at 500 nm, and using a linear generalised least squares regression analysis (http://www.eurometros.org/distributions: "xgenline") that accounts for uncertainties in the "x-axis" (AOD) as well as the "y-axis" (CH_3OH column), we find the relationship between the column amounts of methanol and the coincident AOD measurements to be

CH_3OH column = $[(2.9 \pm 0.1)AOD + (0.7 \pm 0.1)]x10^{16}$ molecules per square centimetre. Using 0.03 as a typical background value for AOD at Wollongong [*Phillips*, 2001], this regression equation was used to determine that $(0.8\pm 0.2) \times 10^{16}$ molecules per square centimetre was a suitable value to use as a background level for CH_3OH. This is equivalent to a tropospheric mixing ratio of 0.4 ± 0.1 ppb methanol throughout the bottom 9 kilometres, but in reality background mixing ratios are likely to be higher near the ground than at greater altitudes.

An emission ratio of 0.019 ± 0.001 was derived from the slope of a linear generalised least squares regression to all 166 measured methanol column amounts and the carbon monoxide columns calculated from coincident AOD measurements. This compares to a mean emission ratio of 0.024 ± 0.015 calculated by dividing the enhanced CH_3OH (above $8x10^{15}$) by the enhanced CO (above 1.5×10^{18}) from each of the 166 spectra. The generalised least squares

regression is a more reliable method because it does not rely on assumptions about background amounts of either gas and each value is weighted by its own individual uncertainties.

Another parameter frequently used to characterise emissions from fires is the emission factor, which is defined as the amount of a compound released per amount of dry fuel consumed, expressed in units of g kg^{-1}. To convert our data from an emission ratio with respect to CO, we use a literature value for the mean emission factor from extra-tropical forests for CO, (EF$_{CO}$), and calculate the emission factor for CH$_3$OH as

$$\mathbf{EF_{CH3OH} = ER_{(CH3OH/CO)}.(MW_{CH3OH}/MW_{CO}).EF_{CO}}$$

(where EF$_{CH3OH}$ = the emission factor for methanol; ER$_{(CH3OH/CO)}$ = the emission ratio of methanol with respect to CO; MW$_{CH3OH}$ = the molecular weight of methanol (32.04); MW$_{CO}$ = the molecular weight of CO (28.01) and EF$_{CO}$ = the emission factor for CO).

Using an emission factor for CO for extra-tropical forests of 107 ± 37 g kg^{-1} [*Andreae and Merlet*, 2001] and our emission ratio 0.019 ± 0.001 we calculate an emission factor of 2.3 ± 0.8 grams of methanol emitted per kilogram of dry fuel consumed in combustion. The uncertainty quoted is derived from the uncertainty in the literature emission factor for CO, (35%), combined in quadrature with the one-sigma standard deviation in our measured emission ratio to CO, (5%). This emission factor from fires in Australian temperate forests, where the fuel source is pre-dominantly varieties of Eucalyptus trees, agrees within the uncertainties with the mean emission factor from all extra-tropical forest measurements given in the literature of 2.0 ± 1.4 grams of methanol emitted per kilogram of dry fuel consumed [*Andreae and Merlet*, 2001]. Methanol is thus as significant an emission product as formaldehyde (since the emission factor from these fires has been determined as 2.6 ± 1.2 grams of formaldehyde emitted per kilogram of dry fuel

consumed in combustion) [*Paton-Walsh, et al.*, 2005]. In comparison the emission factor for methane (the most abundant volatile organic compound in the atmosphere) from all extra-tropical forest fires is roughly double this at 4.7 ± 1.9 grams of methane emitted per kilogram of dry fuel consumed [*Andreae and Merlet*, 2001].

5. Summary

The first reported measurements of column amounts of methanol by ground-based solar Fourier transform infrared spectroscopy have been made from Wollongong, NSW, Australia, (34.4°S, 150.9°E). The derived column amounts of methanol are highly correlated with coincident measurements of aerosol optical depth. Analysis yielded an estimate of the background column amount of methanol over Wollongong of (0.8 ± 0.2) x10^{16} molecules per square centimetre. The regression equations relating both methanol and carbon monoxide to coincident measurements of aerosol optical depth have been used (with an emission factor for carbon monoxide from the literature) to determine an emission factor from Australian temperate forest fires of 2.3 ± 0.8 grams of methanol per kilogram of dry fuel consumed. This value indicates that methanol is an important emission product from the burning of Eucalptus forests with an emission factor similar to previously published emission factors from other extra-tropical forest fires.

References and Notes

Andreae, M. O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning, *Global Biogeochemical Cycles*, *15*, 955-966.

Crutzen, P. J., and M. O. Andreae (1990), Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, *250*.

Edwards, D. P., et al. (2004), Observations of carbon monoxide and aerosols from the Terra satellite: Northern Hemisphere variability, *Journal Of Geophysical Research-Atmospheres*, *109*.

Griffith, D. W. T., et al. (1998), Interhemispheric ratio and annual cycle of carbonyl sulfide (OCS) total column from ground-based solar FTIR spectra, *Journal of Geophysical Research*, *103*, 8447-8454.

Griffith, D. W. T., et al. (2003), Intercomparison of NDSC ground-based solar FTIR measurements of atmospheric gases at Lauder, New Zealand, *Journal of Atmospheric and Oceanic Technology*, *20*, 1138-1153.

Heikes, B. G., et al. (2002), Atmospheric methanol budget and ocean implication, *Global Biogeochem Cy*, *16*.

Hurst, D. F., et al. (1994), Trace Gas Emissions from Biomass Burning in Tropical Australian Savannas, *Journal of Geophysical Research-Atmospheres*, *99*, 16441-16456.

Jacob, D. J., et al. (2005), Global budget of methanol: Constraints from atmospheric observations, *Journal Of Geophysical Research-Atmospheres*, *110*.

Jones, N. B., Y. Kasai, E. Dupuy, Y Murayama, B. Barret, M. Sinnhuber, A. Kagawa, T. Koshiro, J. Urban, P. Racaud, and D. Murtagh (2007), Annual Variability of Mesopheric CO as measured by a ground based FT Spectrometer; comparisons with Odin/SMR and a 2-D model, *J. Geophys. Res.*, DOI: 10.1029/2006JD007916.

Meier, A., et al. (2005), Evidence of reduced measurement uncertainties from an FTIR instrument intercomparison at Kiruna, Sweden, *Journal of Quantitative Spectroscopy and Radiative Transfer*, *96*, 75.

Paton-Walsh, C., et al. (2004), Trace gas emissions from biomass burning inferred from aerosol optical depth, *Geophysical Research Letters*, *31*, -.

Paton-Walsh, C., et al. (2005), Measurements of trace gas emissions from Australian forest fires and correlations with coincident measurements of aerosol optical depth, *Journal Of Geophysical Research-Atmospheres*, *110*.

Phillips, F. A. (2001), Determination of atmospheric ozone by solar infrared, ultraviolet and visible spectroscopy, University of Wollongong, Wollongong.

Rinsland, C. P., et al. (2005), High spectral resolution solar absorption measurements of ethylene (C2H4) in a forest fire smoke plume using HITRAN parameters: Tropospheric vertical profile retrieval, *Journal of Quantitative Spectroscopy and Radiative Transfer*, *96*, 301.

Rothman, L. S., et al. (2005), The HITRAN 2004 molecular spectroscopic database, *Journal Of Quantitative Spectroscopy & Radiative Transfer*, *96*, 139-204.

Walsh, C. P., et al. (1997), An uncertainty budget for ground-based Fourier transform infrared column measurements of HCl, HF, N2O, and HNO3, deduced from results of side-by-side instrument intercomparisons, *Journal of Geophysical Research-Atmospheres*, *102*, 8867-8873.

Washenfelder, R. A., et al. (2006), Carbon dioxide column abundances at the Wisconsin Tall Tower site, *Journal Of Geophysical Research-Atmospheres*, *111*.

Wilson, S. R., and B. W. Forgan (2002), Aerosol optical depth at Cape Grim, Tasmania, 1986 - 1999, *Journal of Geophysical Research*, *107*.