Trace gas emissions from savanna fires in northern Australia

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Abstract
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1. Introduction

Biomass burning is a global phenomenon with impacts on global atmospheric composition and chemistry. Recent inventories that utilize satellite and land cover data in conjunction with measurements of the emission factors for gases and particulates rank Australia as the third most significant source of carbon emissions from biomass burning [Ito and Penner, 2004; Kasischke and Penner, 2004; van der Werf et al., 2003, 2006] emitting approximately 8% of the global total. Despite this global significance, there are only a few previously published emission factors for many important trace gases from Australian forest and savanna fires, and there are instances of large discrepancies between studies [e.g., Holzinger et al., 1999; Hurst et al., 1994b; Shirai et al., 2003].

To determine emission factors directly, detailed field studies that include determination of the carbon content of the fuel are required. Alternatively an emission factor may be determined by measuring the emission ratio of the gas to a reference gas such as carbon monoxide (CO) or carbon dioxide (CO2) and then multiplying with a previously measured emission factor for the reference gas [Andreae and Merlet, 2001]. An example of a detailed field study is that by Hurst et al. [1994b], where prefire fuel and postfire ash samples were analyzed from an area typical of Australian savannas to give the carbon content, combustion efficiency, and the dry mass load in kilograms of dry matter per hectare (kg DM ha−1). Hurst et al. [1994b] used gas phase Fourier transform infrared (FTIR) spectroscopy, matrix isolation FTIR spectroscopy, and chemiluminescence techniques to derive excess concentrations of a large number of different trace gases in smoke samples taken from the ground and from a light aircraft. Since most of the carbon emitted by the fires was in the form of one of the carbon-containing species measured by the study, the sum of all these species could be used to estimate the total mass of carbon emitted. The fraction of the total mass of carbon emitted to the atmosphere as each species could then be used to derive emission factors for these gases by the carbon mass balance method [Radke et al., 1988]. Laboratory studies yield direct measurements of emission factors because the carbon content of the biomass and the carbon budget of the fire are readily

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determined [Andreae and Merlet, 2001; Holzinger et al., 1999; Yokelson et al., 1996]; however, it is not clear how well they simulate conditions in real wildfires.

[4] In addition to the work by Hurst et al. [1994a, 1994b] described above, two further papers report emission ratios of trace gases from Australian savanna fires measured as part of the Biomass Burning and Lightning Experiment (BIBLE) A and B in August–October 1998 and 1999 [Kondo et al., 2003; Shirai et al., 2003]. There are some other measurements from Australian savanna fires in the literature that cover a more limited range of emitted gases [Folkins et al., 1997; Sawa et al., 1999] as well as controlled laboratory-based fire experiments and many measurements from savannas fires elsewhere in the world [Andreae and Merlet, 2001; Christian et al., 2003; Yokelson et al., 1996]. For some gases, the number of measurements is particularly sparse. For instance there have been very few field studies that have measured hydrogen cyanide (HCN), and these show large discrepancies with laboratory emission measurements [Holzinger et al., 1999; Hurst et al., 1994a, 1994b]. Andreae and Merlet [2001] stressed the need for further field measurements of HCN to resolve these discrepancies.

[5] Where there are multiple estimates of the emission factor of a given trace gas from a particular ecosystem in the literature, the spread of values is often large. This is due to the natural variability of the emissions, sampling that biases the measurements to one stage of burning over another, and/or potential biases in the measurement techniques. Consequently, further measurements are useful additions to our knowledge of biomass burning emissions especially where new techniques are employed or new ecosystems sampled.

2. Measurements of Aerosol Optical Depth and Carbon Monoxide From Darwin

[6] Solar remote sensing using Fourier transform spectroscopy measurements in the near-infrared (NIR) have been made from Darwin (12.4°S, 130.9°E) since August 2005 as part of the Total Column Carbon Observing Network (TCCON) [Deutscher et al., 2010; Toon et al., 2009]. An automated system ensures that spectra are recorded whenever the weather conditions permit on two near-infrared detectors, with total coverage from 4000 to 15,500 cm⁻¹. These spectra have been analysed with the “GFIT” spectral fitting algorithm [Washenfelder et al., 2006] for total column amounts of carbon monoxide (CO), using the overtone vibrational band at 4230 cm⁻¹ (see Table 1 for details) and spectral data from the HITRAN2004 database [Rothman et al., 2005]. The automated collection of spectra results in CO data with very good temporal coverage (more than 170,000 NIR spectra were recorded between August 2005 and May 2008). The Bureau of Meteorology operate a Sun photometer that is located within 30 m of the remote sensing spectrometer and thus aerosol optical depth (AOD) measurements are also available from the site [Mitchell and Forgan, 2003; Wilson and Forgan, 2002].

[7] Figure 1 shows the time series of daily average CO total column amounts plotted alongside the time series of daily average AOD at 500 nm. Both time series show a similar annual cycle, with a steep rise in early September 2005 peaking at around 2.1 × 10¹⁸ molecules cm⁻² and 0.35 in late September and early October, respectively, before dropping off more gradually to background values of approximately 1.1 × 10¹⁸ molecules cm⁻² and 0.05 at the end March or early April 2006, respectively. These peak and minimum CO columns equate to in situ amounts of approximately 130 and 72 nmol mol⁻¹, respectively, in the lowest 1 km of the atmosphere in the a priori volume mixing ratio profile used in the analyses.

[8] A similar pattern is seen in 2007 with a very sharp rise in CO columns and AOD in early September 2007 peaking somewhat higher at around 2.3 × 10¹⁸ molecules cm⁻² and 0.6 in late September and early October, respectively, before again dropping off slowly to background values. The picture in the El Niño year of 2006 is substantially different from the other 2 years, with a more gradual rise in both AOD and column CO amounts starting in August and with peak values significantly later in late November or early December 2006. The peak amounts of column CO are substantially higher than in the other 2 years at around 2.8 × 10¹⁸ to 3.0 × 10¹⁸ molecules cm⁻² (equivalent to an in situ amount of ~200 nmol mol⁻¹), while the peak values of AOD at around 0.4–0.5 are not unusually high.

[9] During 2006 there were exceptionally severe fires in Indonesia [Chandra et al., 2009; Rinsland et al., 2008; Thampi et al., 2009] where the fire season is later than in northern Australia. Transported pollution from these fire events provides a likely explanation for the unusually high

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Table 1. Spectral Intervals, Interfering Gases Fitted, and Uncertainties in the Derived Column Amounts for Trace Gas Retrievals

<table>
<thead>
<tr>
<th>Trace Gas</th>
<th>S:N Used in Retrieval</th>
<th>Spectral Interval(s) Fitted (cm⁻¹)</th>
<th>Interfering Gases Fitted in Retrieval</th>
<th>Smoothing Uncertainty</th>
<th>Signal-to-Noise Uncertainty</th>
<th>Temperature Uncertainty</th>
<th>Total Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>700</td>
<td>4226.50–4228.30; 4231.50–4232.10; 4274.00–4275.0</td>
<td>CH₄, HDO, H₂O; CH₄, HDO, H₂O; CH₄, HDO, H₂O</td>
<td>2.4%</td>
<td>1.1%</td>
<td>2.2%</td>
<td>3.4%</td>
</tr>
<tr>
<td>H₂CO</td>
<td>500</td>
<td>2777.88–2778.92; 2780.76–2781.66; 2869.435–2870.325</td>
<td>CH₄, O₃, HDO; N₂O, O₂, CH₄, CO₂; O₃, CH₄, CO₂</td>
<td>3.1%</td>
<td>10.8%</td>
<td>1.6%</td>
<td>11.4%</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>100</td>
<td>2976.60–2977.10; 2996.70–2997.10; 3000.10–3000.60</td>
<td>H₂O, CH₄, O₂; H₂O, CH₄, O₁; CH₄, O₁</td>
<td>17.4%</td>
<td>8.4%</td>
<td>2.3%</td>
<td>19.5%</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>150</td>
<td>3304.70–3305.40</td>
<td>H₂O, CO₂</td>
<td>29.8%</td>
<td>13.4%</td>
<td>1.9%</td>
<td>32.8%</td>
</tr>
<tr>
<td>HCN</td>
<td>100</td>
<td>3268.00–3268.38; 3331.40–3331.80</td>
<td>H₂O, CO₂, N₂O</td>
<td>20.0%</td>
<td>13.9%</td>
<td>2.1%</td>
<td>24.5%</td>
</tr>
</tbody>
</table>

*Note that uncertainties for CO are for SFIT2 analysis of NIR spectra. GFIT analysis of NIR spectra uses only the first two microwindows and uncertainties are a little higher.*
CO column amounts observed in this El Niño year. Back trajectory analysis (using the British Atmospheric Data Centre online service: http://badc.nerc.ac.uk/) on each day that measurements were made at Darwin during November and December 2006 show that the typical transit time for air parcels from Indonesia to Darwin is about a week. The lifetime of smoke aerosols in the atmosphere is estimated at $3.8 \pm 0.8$ days [Chin et al., 2002; Edwards et al., 2006a; Rasch et al., 2000] compared to about 2 months for CO [Novelli et al., 1998]. Thus, the transit time is sufficient to explain why the AOD does not increase inline with the increased CO columns, because during a 1 week transit time the AOD would be expected to reduce to approximately one quarter of its original value. The 2006 peak in CO and AOD is therefore a superposition of the effects of the local fire season and the effect of transported pollution from the Indonesian fires. The later decline in CO and AOD in 2006 indicates an extended burning season in the north Australian tropical savanna region caused by a delayed wet season locally as a result of the El Niño.

The transported pollution from the unusually intense Indonesian fires of 2006 is clearly visible in the CO total column measurements made from space by the MOPITT instrument on board the NASA EOS Terra satellite in November 2006 (see Figure 2, bottom). Large enhancements in the average monthly total column CO are visible all across Indonesia and extending west far into the Indian Ocean, east into the North Pacific Ocean, north into China and south into the north and west of Australia. The monthly averaged total column amounts of CO during November 2005 (not an El Niño year) are shown for comparison in Figure 2 (top).

3. Mid-infrared Measurements of CO, H$_2$CO, HCN, C$_2$H$_2$, and C$_2$H$_6$ From Darwin

The Fourier transform spectrometer in Darwin is also capable of making mid-infrared (MIR) measurements from approximately 2000 to 6500 cm$^{-1}$. This region includes absorption features of some of the gases of interest that are emitted during biomass burning such as carbon monoxide (CO), hydrogen cyanide (HCN), formaldehyde (H$_2$CO), acetylene (C$_2$H$_2$), and ethane (C$_2$H$_6$). The instrument may be switched to MIR operation by remote access overriding its normal automatic mode that records NIR spectra. The collection of MIR data is much more sporadic than the automated collection of NIR spectra and so the time series of the extra gases that it provides (HCN, H$_2$CO, C$_2$H$_2$, and ethane C$_2$H$_6$) have a much poorer seasonal coverage than CO. Between April 2006 and May 2008 MIR spectra were recorded from Darwin on only 45 separate days, of which 20 days have been identified as affected by significant amounts of smoke pollution. Spectra are collected with an optical path difference of 45 cm and a scanner speed of 0.633 cm s$^{-1}$, resulting in high temporal resolution with a spectrum recorded every 76 s. Spectra are recorded over the whole region from 2000 to 6500 cm$^{-1}$. This has the advantage that all the gases of interest that can be retrieved from these spectra are recorded simultaneously but the disadvantage that the signal-to-noise is significantly lower than that achieved when a series of narrow band optical filters is
used. In all spectra the signal-to-noise values are substantially lower in the regions used to analyse HCN, C$_2$H$_2$, and C$_2$H$_6$ than in the regions used to analyze CO and H$_2$CO because of absorption by water vapor. For this reason, spectra were coadded to improve the signal-to-noise before analyzing for HCN, C$_2$H$_2$, and C$_2$H$_6$.

[12] All MIR spectra were analyzed for carbon monoxide and formaldehyde total column amounts using the optimal estimation algorithm SFIT2 [Hase et al., 2004; Rinsland et al., 1998] and the HITRAN2004 data base [Rothman et al., 2005]. The choice of the SFIT2 retrieval code ensures that small biases that result from an assumed concentration profile shape are avoided. This is significant when comparing smoke plumes sampled on different days that are likely to be at different altitudes [Paton-Walsh, 2009]. For CO, the overtone vibrational band at 4230 cm$^{-1}$ was used because the signal-to-noise level in the region of the fundamental band was too low. Note that there is a substantial overlap (from 2000 to 6500 cm$^{-1}$) in the spectra that we label “NIR” and the spectra that we label “MIR” in this paper and that the same spectral region is used to derive CO from both “MIR” and “NIR” spectra.

[13] The H$_2$CO absorption features are relatively weak and the signal-to-noise ratio is low, thereby reducing the precision of the measurements. For C$_2$H$_6$, C$_2$H$_2$, and HCN the situation is much worse and in many cases the absorption features were too weak to be detected above the noise level. For this reason, only spectra from days when the CO was significantly enhanced were selected and the signal-to-noise was improved (by a factor of ~3) by coadding the spectra (usually nine at a time) before analysis for these other gases. The addition of nine spectra (taking 76 s each) is equivalent to a total measurement time of approximately 11 min and no large solar zenith angles were used so that the air mass sampled is not changing greatly over the measurement time. Details of the retrievals are given in Table 1 including the uncertainties that affect the precisions of the measurements. Note that in addition to the listed uncertainties there are systematic errors in the spectral line parameters, which may bias the calculated emission ratios from true values by a further 10%–20%. In particular, it should be noted that there has been a recent revision of the infrared spectral line parameters for formaldehyde that estimates 28% stronger intensities on average across the

Figure 2. Monthly averaged CO expressed as column averaged concentrations (ppbv) retrieved from MOPITT for (top) November 2005 and (bottom) November 2006.
spectral region used in this study [Perrin et al., 2009]. Further information about spectral fitting of MIR spectra and associated uncertainties may be found in the literature [Goldman et al., 1999; Griffith et al., 2003; Hase et al., 1999; Meier et al., 2005; Paton-Walsh et al., 1997].

4. Correlations Between Carbon Monoxide and Aerosol Optical Depth

[14] Strong correlations between trace gas column amounts and aerosol optical depth (AOD) have been observed previously through smoke plumes from southeast Australian forest fires [Paton-Walsh et al., 2004, 2005, 2008] and used in conjunction with atmospheric dispersion modeling to make a total emissions estimate for a major fire event [Paton-Walsh et al., 2010]. Similarly, strong correlations have been observed between AOD and CO measurements from NASA’s Terra satellite in biomass burning plumes over South America and Africa [Edwards et al., 2006a]. For this reason, it is interesting to determine the correlations between the trace gases and AOD measured over Darwin in order to assess the possibility of using satellite measurements of AOD to map the emissions from savanna fires in northern Australia. This process is complicated around the tropical north of Australia by a strong seasonal cycle in CO caused by transport of high-CO air from the Northern Hemisphere and from biomass burning in Indonesia, Africa, and South America, especially late in the year [Hamilton et al., 2008; Staudt et al., 2001]. The fact that the aerosol component of the smoke is not as long-lived as CO in the atmosphere means that the CO to AOD ratio increases toward the end of the year as the “background levels” of column CO buildup. To minimize this effect, a linear regression may be applied to the subset of the data recorded during the local dry season from May to July each year, yielding a relationship of CO = [(1.7 ± 0.1)AOD + (1.3 ± 0.1)] × 10\(^{18}\) molecules cm\(^{-2}\), with a correlation coefficient of \(R^2 = 0.65\). (All uncertainties quoted are ±1σ.) This compares to a relationship of CO = [(1.5 ± 0.1)AOD + (1.5 ± 0.1)] × 10\(^{18}\) molecules cm\(^{-2}\), with \(R^2 = 0.87\), found for southeast Australian forest fires from measurements at Wollongong (34.5°S, 150°E) [Paton-Walsh et al., 2005]. Thus, the value of (1.3 ± 0.1) × 10\(^{18}\) molecules cm\(^{-2}\) for the dry season background CO at Darwin is slightly lower than background values at Wollongong. This is not what is expected from the latitudinal gradient [Connors et al., 1999], but both background values are supported by other measurements: ground-based NIR measurements from Darwin, MIR measurements from Wollongong, and MOPITT measurements over both sites (D. P. Edwards et al., Satellite and ground-based remote sensing of carbon monoxide over Australasia: Linking global and local scales, manuscript in preparation), implicating an unidentified local source of CO near Wollongong.

[15] The CO to AOD ratio found here for savanna fires is slightly higher than that found for forest fires [Paton-Walsh et al., 2005]. Previous measurements suggest that CO emissions per kilogram of carbon burned are lower from savanna fires than from forest fires [Andreae and Merlet, 2001], so this suggests that the aerosol loading is also lower, either as a result of lower emissions or because of greater aging of the smoke before it is sampled at Darwin.

[16] In conclusion, the relatively strong correlation that exists between CO total columns and AOD in the dry season means that in theory it would be possible to use satellite measurements of AOD to estimate emissions from Australian savanna fires in a similar manner to that done for Australian forest fires in the work of Paton-Walsh et al. [2010]. However, the complicating effects of the buildup of aged smoke and the influence of transported smoke into the region make interpretation of the measurements significantly harder than for southeast Australian forest fires. Extracting the local fire signature measured later in the year might be possible but with large associated uncertainties. On balance despite the improved sensitivity at the ground, the use of satellite measurements of AOD as a proxy for CO is not likely to lead to better estimates of biomass burning in the tropical north of Australia than the use of traditional methods or studies that use direct satellite measurements of CO such as that provided by MOPITT [Edwards et al., 2006b; Pfister et al., 2005].

5. Emissions of Formaldehyde From Tropical North Australian Savanna Fires

5.1. Correlations Between H\(_2\)CO and CO in Spectra Recorded Through Smoke Plumes

[17] Figure 3 shows the H\(_2\)CO column plotted against simultaneously measured CO column, color coded to distinguish data from different time periods in each year from 2006 to 2008. The spectra recorded during May–July (blue points) show a very strong correlation between H\(_2\)CO and CO (\(R^2 = 0.87\)). Many of the spectra from August (red points) overlap data from May to July, but a subset of the data (from a single day) has a similar value for the H\(_2\)CO to CO gradient but is shifted to the left of the plot indicating higher background H\(_2\)CO values and/or lower background CO amounts. This results in a much lower overall correlation coefficient (\(R^2 = 0.24\)) for this time of year. In comparison most spectra from September (green points, \(R^2 = 0.35\)) also show a similar H\(_2\)CO to CO gradient but are shifted to the right indicating a higher background amount of CO or depleted background amounts of H\(_2\)CO when compared to the May–July data. Finally, spectra from October and November (purple points, \(R^2 = 0.36\)) are shifted farthest to the right of the plot, indicating higher background CO, and have slightly smaller H\(_2\)CO to CO gradients.

[18] An explanation for much of the disparity between different times comes from the seasonal cycle in CO. The “background” amount of carbon monoxide in the atmosphere (being the amount of carbon monoxide not associated with local burning) can vary substantially from 1 day to the next, as high-CO air is transported into or out of the region. Higher “background” CO amounts may result if meteorological conditions cause air from the Northern Hemisphere to be located over Darwin. This is possible because Darwin is located close to the intertropical convergence zone (ITCZ) and the “chemical equator” that separates the polluted Northern Hemisphere from the more pristine Southern Hemisphere [Hamilton et al., 2008]. This effect increases later in the year and CO amounts may also be enhanced by both the build up of smoke from local fires and smoke transported from biomass burning in Indonesia, Africa, and South America.
Unlike CO (with an atmospheric lifetime of approximately 52 days [Daniel and Solomon, 1998]), H₂CO is short-lived with primary loss mechanisms being via photodissociation and reaction with the OH radical with a half-life of approximately 3 h in daylight [Warneck, 2000]. Thus, H₂CO has a much shorter atmospheric lifetime than CO and so does not build up in the same way. There are seasonal differences in the biogenic emissions of isoprene that produce a seasonal cycle in H₂CO but the vegetation around Darwin is sparse and so this is likely to be a second-order effect with regards to the H₂CO to CO ratio in this geographical region. The gradient of H₂CO to CO for local fires remains relatively constant from May to September but the “background” CO increases toward the end of the year. For this reason H₂CO to CO gradients have been calculated separately for each of the 20 individual days when MIR spectra were recorded through significant amounts of smoke. The gradients and the square of the correlation coefficients from the regression analyses for the H₂CO to CO data are shown in Table 2.

Table 2. Results of Regressions Analyses on H₂CO and CO Retrievals From Each of the 20 Individual Days When MIR Spectra Were Recorded Through Significant Amounts of Smoke From Darwin

<table>
<thead>
<tr>
<th>Date</th>
<th>Gradient</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>06 May 2008</td>
<td>0.012 ± 0.001</td>
<td>0.54</td>
</tr>
<tr>
<td>08 May 2008</td>
<td>0.033 ± 0.001</td>
<td>0.86</td>
</tr>
<tr>
<td>09 May 2008</td>
<td>0.027 ± 0.001</td>
<td>0.92</td>
</tr>
<tr>
<td>15 May 2008</td>
<td>0.022 ± 0.001</td>
<td>0.91</td>
</tr>
<tr>
<td>02 Jun 2008</td>
<td>0.012 ± 0.001</td>
<td>0.31</td>
</tr>
<tr>
<td>28 Jun 2007</td>
<td>0.019 ± 0.001</td>
<td>0.87</td>
</tr>
<tr>
<td>10 Jul 2007</td>
<td>0.032 ± 0.002</td>
<td>0.79</td>
</tr>
<tr>
<td>07 Aug 2007</td>
<td>0.018 ± 0.03</td>
<td>0.39</td>
</tr>
<tr>
<td>09 Aug 2007</td>
<td>0.033 ± 0.002</td>
<td>0.82</td>
</tr>
<tr>
<td>20 Aug 2007</td>
<td>0.016 ± 0.002</td>
<td>0.50</td>
</tr>
<tr>
<td>27 Aug 2007</td>
<td>0.024 ± 0.001</td>
<td>0.91</td>
</tr>
<tr>
<td>13 Sep 2006</td>
<td>0.025 ± 0.004</td>
<td>0.40</td>
</tr>
<tr>
<td>14 Sep 2006</td>
<td>0.016 ± 0.001</td>
<td>0.89</td>
</tr>
<tr>
<td>20 Sep 2007$^b$</td>
<td>0.003 ± 0.002</td>
<td>0.03</td>
</tr>
<tr>
<td>04 Oct 2006</td>
<td>0.012 ± 0.001</td>
<td>0.51</td>
</tr>
<tr>
<td>03 Oct 2007</td>
<td>0.007 ± 0.0003</td>
<td>0.85</td>
</tr>
<tr>
<td>10 Oct 2007$^b$</td>
<td>−0.001 ± 0.007</td>
<td>0.001</td>
</tr>
<tr>
<td>02 Nov 2006</td>
<td>0.007 ± 0.003</td>
<td>0.22</td>
</tr>
<tr>
<td>30 Nov 2006$^b$</td>
<td>−0.013 ± 0.004</td>
<td>0.63</td>
</tr>
<tr>
<td>Oct–Nov Average</td>
<td>0.009 ± 0.003</td>
<td></td>
</tr>
</tbody>
</table>

$^a$The gradient and value for the square of the correlation coefficient ($R^2$) are shown. Average values are given for spectra recorded between May and September and spectra recorded during October and November.

$^b$Note the data from 20 September 2007 give a value for the square of the correlation coefficient ($R^2$) of only 0.03 and are excluded from the May to September average values. Also the data from 10 October 2007 and 30 November 2006 show no enhancement in H₂CO columns over background values and are excluded from the October–November average values.
show diffuse smoke plumes not apparently emanating from any of the detected thermal hot spots. These may also be indicative of aged smoke because over time the smoke plumes will become more diffuse. The average and standard deviation $\text{H}_2\text{CO}$ to CO gradient for the remaining 3 days when spectra were recorded through smoke during October and November are $0.009 \pm 0.003$.

In contrast to the October and November data, the $\text{H}_2\text{CO}$ and CO retrievals from most of the days between May and September have high correlation coefficients and similar $\text{H}_2\text{CO}$ to CO gradients, with the exception being 20 September 2007. The regressions analysis of retrievals of $\text{H}_2\text{CO}$ and CO from 20 September 2007 show no significant correlation ($R^2 = 0.03$), and the data from this day were excluded before an average and standard deviation $\text{H}_2\text{CO}$ to CO gradient of $0.022 \pm 0.007$ was calculated for smoke sampled between May and September. The $\text{H}_2\text{CO}$ to CO gradients for May to September (see Table 2) are surprisingly consistent. The $\text{H}_2\text{CO}$ to CO gradient should be very sensitive to the age of the smoke sampled because of the relatively short atmospheric lifetime of $\text{H}_2\text{CO}$ compared to CO.

5.2. Estimating the Age of the Sampled Smoke Plumes

We attempted to estimate the age of the smoke sampled at Darwin by examining MODIS true color plots in conjunction with back trajectories analyses that were generated by the European Centre for Medium-Range Weather Forecasts Trajectories, via the British Atmospheric Data Centre (see http://badc.nerc.ac.uk/data/ecmwf-trj/).

In many cases, there were a large number of separate fires burning in the area, and so it was not possible to determine either the origin or the age of the smoke. However, there were 3 days when the limited number of fires burning and a combination of back trajectory analysis and visible smoke plumes in the MODIS true color images made it possible to estimate the probable age of the smoke:

1. 27 June 2007: estimated age of smoke is approximately 5 h (see Figure 4a) and $\text{H}_2\text{CO}$ to CO gradient is $0.020 \pm 0.001$.
2. 9 August 2007: estimated age of smoke is in excess of 12 h (see Figure 4b) and $\text{H}_2\text{CO}$ to CO gradient is $0.033 \pm 0.002$.
3. 20 September 2007: estimated age of smoke is in excess of 24 h (see Figure 4c) and $\text{H}_2\text{CO}$ to CO gradient is $0.003 \pm 0.002$.

The MODIS true color image from the 20 September 2007 shows widespread fires to the far east of Darwin and evidence of the build up of smoke in the region (see Figure 4c, bottom). Back trajectory analysis for 20 September 2007 suggests that the smoke is at least 24 h old and probably older (see Figure 4c, top), explaining the low amounts of $\text{H}_2\text{CO}$ detected and the poor correlation with CO on this day.

5.3. Emissions of Formaldehyde From Tropical North Australian Savanna Fires

Obviously care should be taken in trying to draw conclusions from a small data set of spectra with estimated ages for the smoke sampled. However, the smoke sampled on 9 August 2007 has both a greater estimated age and a
greater H₂CO to CO gradient than smoke from 27 June 2007. This suggests that secondary formation of H₂CO within the smoke plume may be more significant than the combined loss of H₂CO through photodissociation and oxidation via reaction with OH in the first few hours after emission. As well as being a primary emission product of biomass burning, H₂CO is produced by the oxidation of methane and non-methane volatile organic compounds (NMVOCs). The formation of H₂CO by the oxidation of CH₄ is slow with reaction times in the order of years. Similar oxidation pathways for NMVOCs will also produce H₂CO. Many of these reactions are much faster taking minutes or hours, although the degradation mechanisms of many of the NMVOCs are poorly understood, with large uncertainties in individual yields [Stavracou et al., 2009]. Since non-methane hydrocarbons are major products of biomass burning the concentrations of these trace gases that produce H₂CO will be very significantly enhanced in fresh smoke plumes making secondary production of formaldehyde an extremely significant source of H₂CO in the plumes. Stavracou et al. [2009] undertook a large scale modeling exercise using the Master Chemical Mechanism v3.1 [Saunders et al., 2003] to quantify the H₂CO production from vegetation fires and estimate the relative contributions of different NMVOCs to the total H₂CO production and the H₂CO production after a single day. Interestingly their model suggests that primary H₂CO emission accounts for only 14% of the total H₂CO produced over the course of the first day. The measurements described here support this finding at least qualitatively.

[29] In the first few hours after emission, secondary formation of formaldehyde from enhanced amounts of NMVOCs in the smoke more than compensates for H₂CO loss through photodissociation and oxidation via reaction with OH. Only when the smoke has aged sufficiently for the supply of NMVOCs to be depleted and no longer able to replenish the H₂CO does the H₂CO to CO gradient drop significantly as seen on 20 September 2007 and much of the October and November data.

[30] The average H₂CO to CO gradient from all of the smoke sampled between May and September (excluding 20 September 2007 as explained above) is 0.022 ± 0.007. This may be used as an emission ratio of H₂CO with respect to CO for local savanna fires. Using a literature value for the emission factor of CO of 65 ± 20 g kg⁻¹ dry matter (DM) burned [Andreae and Merlet, 2001], this gives an emission factor for H₂CO of 1.5 ± 0.5 g kg⁻¹ DM burned. It is possible that the effects of secondary formation of H₂CO in the smoke plumes may result in our emission ratio being biased to the high side compared to measurements made in fresh smoke. The average H₂CO to CO gradient from the 3 days with elevated H₂CO from smoke sampled in October and November is 0.009 ± 0.003. It is also possible that the emission ratio for H₂CO has some seasonality, decreasing later in the year perhaps as the savanna grasses age or due to a change in fuel moisture content. However, there is evidence from MODIS true color images suggesting that the lower values may result from significant aging of the smoke before it was sampled and that the origin of at least the smoke sampled later in the year may not be local. For this reason, the October and November data were not included in our estimate of 0.022 ± 0.007 for the emission ratio of H₂CO with respect to CO for local savanna fires.

6. Emissions of HCN, C₂H₂, and C₂H₆ From Tropical North Australian Savanna Fires

[31] Emission ratios for HCN, C₂H₂, and C₂H₆ with respect to CO could not be derived in the same manner as for H₂CO. This is because there were too few data points to reliably establish a separate regression equation for each day (after the spectra were coadded in order to improve the signal-to-noise before retrieval of HCN, C₂H₂, and C₂H₆). Instead emission ratios were derived using only the data recorded between May and July so that a consistent background column amount of CO could be determined. This limits the measured smoke plumes to those that originate from Australian savanna fires. There could be seasonal differences in these emission ratios and if this is the case these calculations will only be representative of the early dry season.

[32] The time series of CO columns derived from the NIR spectra at Darwin provides a good means of estimating background CO amounts. Minimum values are typically between January and April (at the end of the wet season) although controlled burning often takes place in predry season times and smoke from these fires could cause some higher CO column amounts. The average values from January to April for 2006, 2007, and 2008 are (1.2 ± 0.1) × 10¹⁸, (1.3 ± 0.1) × 10¹⁸, and (1.3 ± 0.1) × 10¹⁸ molecules cm⁻², respectively. Data from 2006 produced the lowest of these average values, and this was taken as a best estimate of background CO [(1.2 ± 0.1) × 10¹⁸ molecules cm⁻²], equivalent to a ground level volume mixing ratio of 78 nmol mol⁻¹ for the chosen a priori profile.

[33] Background column amounts of the other trace gases can be derived by substituting this value of CO into the simple linear regression equations derived from analyses of the column amounts of each trace gas plotted against column amounts of CO (see Figure 5). For example, the linear regression equation derived from the HCN to CO plot was:

\[
\text{HCN} = 0.0017 \text{ CO} + 1.1 \times 10¹⁵
\]

Substituting a background CO value of 1.2 ± 0.1 × 10¹⁸ molecules cm⁻² yields a background amount for HCN of 3.2 ± 0.3 × 10¹³ molecules cm⁻². Excess amounts of CO and HCN were calculated by deducting these background values from the derived column amounts for all spectra and a generalized least squares regression analysis was performed on these data taking into account uncertainties in both HCN columns and CO columns. This yielded an emission ratio for HCN of 0.0018 ± 0.0003. The simple linear regression equations relating C₂H₂ and C₂H₆ columns with CO columns are

\[
\text{C₂H₂} = 0.0025 \text{ CO} - 9.8 \times 10¹⁴
\]

and

\[
\text{C₂H₆} = 0.0020 \text{ CO} + 3.5 \times 10¹⁵
\]

yielding background amounts of 2.1 ± 0.2 × 10¹⁵ C₂H₂ molecules cm⁻² and 5.9 ± 0.5 × 10¹⁵ C₂H₆ molecules cm⁻².
respectively. Resulting emission ratios (using generalised least squares) are 0.0024 ± 0.0004 for C$_2$H$_2$ and 0.0020 ± 0.0003 for C$_2$H$_6$.

[34] Plots of the excess column amounts of each trace gas versus excess CO column are shown in Figure 5. Note that these plots are in essence the same as the plots of the whole column amounts except that they are shifted numerically by a fixed amount on both the x axis (excess CO = column CO − background CO) and the y axis (excess of gas X = column X − background X), the gradients that yield the emission ratios remain unchanged. Also note that the results of the regression analysis will depend heavily on the two points with the largest enhancements, adding to the uncertainty of the emission ratios determined. Also note that the standard deviation in the gradient is calculated during the regression analyses assuming that the uncertainty in each point is independent from the uncertainty in the other points. Since the actual uncertainties in the gradients are likely to be larger than those quoted. Converting the emission ratios to emission factors (using Andreae and Merlet’s [2001] value of using 65 ± 20 g CO kg$^{-1}$ DM burned) gives 0.11 ± 0.04 g HCN kg$^{-1}$ DM burned, 0.14 ± 0.05 g C$_2$H$_2$ kg$^{-1}$ DM burned, and 0.13 ± 0.04 g C$_2$H$_6$ kg$^{-1}$ DM burned.

[35] Also shown in Figure 5 is a plot of excess H$_2$CO column against excess CO column calculated as for the other gases using May–July data only. The lower measurement uncertainties for H$_2$CO are evident in the plot which has a high correlation coefficient ($R^2 = 0.87$). The resulting emission ratio for H$_2$CO is 0.021 ± 0.001. This is not significantly different from the emission ratio for H$_2$CO of 0.022 ± 0.007 determined using the average H$_2$CO to CO gradient found separately for each smoky day between May and September, suggesting that the emission characteristics for H$_2$CO remain constant throughout the dry season.

7. Comparison of Emission Ratios to Literature Values

[36] There have been only three previous field studies that have measured emission ratios from Australian savanna fires for any of the gases reported here [Hurst et al., 1994a, 1994b; Shirai et al., 2003]. Table 3 compares the results from these previous studies with those reported here and with measurements of laboratory fires of savanna grasses using proton transfer reaction mass spectrometry [Holzinger et al., 1999]. The H$_2$CO emission ratio calculated from this work is nearly an order of magnitude higher than the only previous field measurements from Australian savanna fires [Hurst et al., 1994b]. This might be explicable by the effects.
of secondary formation of H₂CO by oxidation of CH₄ and NMVOCs in the smoke plume. As discussed above, there is evidence that the quantity of H₂CO may reach an equilibrium value that lasts from when the smoke is just a few hours old (e.g., 5 h or less) until the reservoir of NMVOCs is depleted sufficiently to no longer be able to replenish the H₂CO lost through photodissociation and oxidation (at least 12 h or more). This equilibrium amount of H₂CO in the smoke plumes could be significantly higher than the amount of H₂CO directly emitted by the biomass burning and present in fresh smoke. The measurements by Hurst et al. [1994b] were made from the ground and in a light aircraft sampling fresh smoke very near the fires and so this theory presents one possible reason for the discrepancy between the two results. Conflicting evidence comes from the laboratory measurements of Holzinger et al. [1999] that sampled a large number of different savanna grasses when burnt. The average emission ratio found in the laboratory fires is in good agreement with that found in this study, suggesting that the measurements by Hurst et al. [1994b] may be low.

[37] Similarly, the HCN measurements described here are more than a factor of 3 higher than that found by Hurst et al. [1994a] and over 6 times higher than the value given in the work of Hurst et al. [1994b], but again in reasonable agreement with the laboratory studies of Holzinger et al. [1999]. One possible explanation for the discrepancies is that many of the measurements described in the studies by Hurst et al. [1994a, 1994b] were based upon cryogenically stored samples and gases such as H₂CO and HCN may have been subject to losses during sampling or storage. Remote sensing solar Fourier transform spectrometry measurements like those described in this paper are open-path measurements and so do not suffer from the problems associated with losses to the walls of the sampling or storage vessels.

[38] The C₂H₂ emission ratio from this work (0.0024 ± 0.0003) is in good agreement with Hurst et al. [1994a] and Shirai et al. [2003], but measurements by Hurst et al. [1994b] are more than a factor of 3 lower than all the other measurements. Using the uncertainty in the calculated gradient from the regression analyses is likely to produce an underestimate of the true uncertainties in the derived emission ratios (because of correlations between the uncertainties of points used in the regression). Thus, the emission ratio for C₂H₂ found in this study (0.0020 ± 0.0003) is broadly comparable to that found by Shirai et al. [2003] of (0.0028 ± 0.0001) but lower than that found by Hurst et al. [1994a] (0.0048 ± 0.0018).

[39] A final comment is to point out that a large spread in values for emission ratios or emission factors obtained from different studies is not uncommon in the measurement of emissions from biomass burning [Andreae and Merlet, 2001]. This underlines the contribution of studies such as this in improving the reliability of estimates of the emissions of trace gases from different fire types around the world. In particular, emission ratios are known to show discrepancies between measurements made near the ground and those measured from aircraft. This is most probably due to measurements near the ground being biased to smouldering emissions while aircraft-based measurements are biased to lofted flaming emissions [Andreae and Merlet, 2001]. Solar FTIR remote sensing measurements like those described here have the significant advantage of being vertically integrated and at a variety of distances from the origin of the smoke. For this reason, our sample is likely to be well mixed and representative of the different vegetation types and fires conditions (flaming/smoldering) within the region.

8. Summary and Conclusions

[40] Ground-based Fourier transform near-infrared solar remote sensing measurements from Darwin have been analyzed for total column amounts of CO with the resulting time series (from August 2006 and June 2008) showing a very clear annual cycle. Peak values of around 2.0 × 10¹⁸ molecules cm⁻² are typical in late September and early October toward the end of the dry season compared to minimum values of about 1.1 × 10¹⁸ molecules cm⁻² during January–March in the wet season. The peak in CO column amounts is significantly larger and later in 2006 with evidence from satellite images implicating transported pollution from Indonesia where El Niño conditions caused unusually large fires in this year. The AOD record from Darwin corroborates this hypothesis as the 2006 peak is not larger than the other years, which suggests that the extra CO comes from smoke aged sufficiently for much of the aerosol loading to have been lost through physical or chemical processes. Enhanced column amounts of CO from the savanna fires also correlate reasonably well with AOD. Despite this, the complicating influence of aged smoke on the Darwin site means that it may be difficult to use this correlation to infer CO amounts from satellite measurements of AOD in the area of savanna fires in tropical north Australia.

[41] Mid-infrared spectra have also been recorded from Darwin on 45 separate days since April 2006, with smoke plumes sampled on 20 of these days. Column amounts of CO, H₂CO, C₂H₂, C₂H₆, and HCN have been derived from these spectra, yielding emission ratios to CO for the four last gases from tropical north Australian savanna fires. Evidence from back trajectory analysis indicates that the H₂CO to CO ratio remains surprisingly consistent over several hours as the smoke ages, suggesting that the loss of H₂CO through
photodissociation and oxidation is largely compensated by secondary formation of H₂O through oxidation of other nonmethane hydrocarbons emitted by the fires. Emission ratios with respect to CO from Australian savanna fires were determined from these measurements for H₂O (0.022 ± 0.007), C₂H₂ (0.0024 ± 0.0003), C₂H₆ (0.0020 ± 0.0003), and HCN (0.0018 ± 0.0003). The values for HCN and H₂O are half and 1 order of magnitude higher, respectively, than the only previous measurements in the literature (but in agreement with laboratory studies) suggesting losses in the collection, storage, or transfer of the gases in the earlier measurements. We recommend that these revised emission ratios be incorporated into global biomass burning inventories.

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