Investigating greenhouse gases in Australia using atmospheric measurements with fourier transform spectrometry and atmospheric modeling

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NOTE

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7. Chapter 7 – Time series from FTIR trace gas analyser

7.1. In situ trace gas time series

A number of in situ FTIR trace gas analysers are deployed. Besides the instrument operating at Cape Grim, instruments operated at Darwin and Katherine in the Northern Territory, and Lauder, New Zealand, for the periods shown in Table 7.1.

<table>
<thead>
<tr>
<th>Location</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cape Grim</td>
<td>41°S</td>
<td>145°E</td>
<td>Oct 23, 2008 – Feb 16, 2009</td>
</tr>
<tr>
<td>Darwin</td>
<td>12.4°S</td>
<td>130.9°E</td>
<td>Feb, 2007 – present</td>
</tr>
<tr>
<td>Katherine</td>
<td>14.5°S</td>
<td>132.3°E</td>
<td>Oct 2, 2008 – Apr 29, 2009</td>
</tr>
<tr>
<td>Lauder</td>
<td>45.0°S</td>
<td>169.7°E</td>
<td>Jul, 2006 – present</td>
</tr>
</tbody>
</table>

The FTIR in situ gas analyser was installed in Darwin on February 28, 2007. It is co-located with the solar FTS at the ARM site adjacent to Darwin international airport. A 12m tower was installed between the solar FTS and the adjacent shipping container, and ½ inch copper tubing run to the top of the tower, where an inverted funnel with gauze filter is used as the air inlet.

At Lauder, the in situ FTIR was installed in July 2006, replacing a previous Bomem MB100 that had been in operation on site from September 2004. We only consider the data from the Bruker here. The analyser is located at the NIWA research station. A 10m standard meteorological tower fitted with ½ inch copper tubing is used to provide the sample air inlet. The instrument itself is located in a room adjacent to the solar FTS on site. The site is located in farmland in Central Otago, and is distant from populated areas.
An in situ FTIR gas analyser was installed at Katherine (Research Station on October 2, 2008. The instrument dedicated to this site is the one that was run on the Ghan Railway, as described in chapter 8. The sample inlet is ¾” Dekabon® tube, mounted to an aluminium strip that is attached to the building eaves, approximately 3m above ground level. The measurements from this instrument are discussed in Chapter 7.

Where available, standard meteorological data (temperature, pressure, humidity and wind speed and direction) have been interpolated to the same time grid as the trace gas measurements.

### 7.1.1. Cape Grim

![Graph of gas concentrations over time](image)

**Figure 7.1** Time series of $\delta^{13}$CO$_2$ (green), N$_2$O (purple), CH$_4$ (blue), CO$_2$ (black) and CO (grey) measured by FTIR at Cape Grim, from November 1, 2008 to February 16, 2009.

While the Cape Grim time series is relatively short, there are still some interesting features to examine. The full time series for CO$_2$, CO, CH$_4$, N$_2$O and $\delta^{13}$CO$_2$ are
presented in Figure 7.1. The slow decrease in methane and CO concentrations over the period is obvious. The annual cycle in CO and CH₄ decreases at this time due to the annual cycle in hydroxyl radical concentrations (see chapter 1.2.2), which is formed in greater amounts in summer. In addition to this longer term trend, there are several events which see correlated responses in trace gas concentrations.

7.1.1.1. February 7, 2009

Here we examine one event in particular around February 7, 2009 (circled in Figure 7.2), to determine the source of the airmass sampled. This period is characterised in the trace gas time series by increases in CO₂, CH₄, CO and N₂O, and a decrease in δ¹³CO₂.

![Figure 7.2 Trace gas time series measured by FTIR at Cape Grim between January 25, 2009 and February 11, 2009.](image)

The δ¹³C of the CO₂ source is calculated from the slope of the measured (δ¹³CO₂[Cₐ]) (δ₀₀₂[CO₂]) plotted against [CO₂] (C₀₀₂) for February 7 only (Figure 7.3), according to
equation 6.9, which corresponds to equation (5) from Miller and Tans [2003]. We can use this equation, because on the daily timescale we can assume the background CO₂ (Cₙ₅) is constant and has constant isotopic signature (δₙ₅).

\[
\delta_{\text{obs}} C_{\text{obs}} = \delta_{s} C_{s} - C_{\text{bg}} (\delta_{\text{bg}} - \delta_{s})
\]  

(6.9)

where:

δ = δ^{13}C

C = \([CO₂]\)

s = source

obs = observed

bg = background

---

**Figure 7.3**  Plot of δₘᵦ Cₙ₅ vs Cₙ₅ according to equation 6.9, for February 7, 2009, yielding a slope (corresponding to the δ^{13}C of the source – δₛ) of -29.9 ± 2.1 ‰.

This yields a δ^{13}CO₂ source signature of -29.9 ± 2.1 ‰, which is consistent with burning of C₃ plants with an expected signature of -28.1 ± 2.5 ‰ [O'Leary, 1981; Quay
et al., 1992]. The Victorian “Black Saturday” fires peaked in intensity on February 7, 2009. From the same day the ratio of trace gas concentration increases is used to quantify emission ratios with respect to CO₂.

\[
\text{Emission ratio} = \frac{\Delta X}{\Delta \text{CO}_2}
\]  

(6.10)

To attempt to eliminate possible background changes due to other sources and/or sinks, we narrow the period examined to between midday and 1800 local time. The resulting emission ratios are 0.71 ± 0.17 % for CH₄ and 1.05 ± 0.22 % for CO. The CH₄ emission ratio is within the range for flaming fires (0.2 – 0.7%, mean = 0.3% and 0.3 – 0.9%, mean = 0.6%) [Cofer et al., 1991], though lower than average (1.2% [Akeredolu and Isichei, 1991; Lambert et al., 1991]). One difficulty of comparing to previous emission ratio estimates is the fact that many of them have been determined for savannah or tropical vegetation. The CO emission ratio is much lower than estimates for the same flaming fires compared to for CH₄ by a factor of 5 [Cofer et al., 1991]. N₂O also shows a marked increase at the same time, with an emission ratio of 1.4 ± 0.4 x 10⁻⁴ mol mol⁻¹ relative to CO₂, well within the measured range of 1.2 – 28 x 10⁻⁵ mol mol⁻¹ measured during the flaming stage of fires [Lober et al., 1991]. The low CO ratios indicate that the source is likely to be other than the Victorian fires.
Figure 7.4  HYSPLIT back trajectory analysis for February 7, 2009. The trajectories are completed hourly from 1400 – 1900. From 1400 – 1700, the air travels south from Victoria, where the bushfires occurred. For the final 2 hours, the air has a westerly fetch. The differing panels show back trajectories landing north of and at Cape Grim. The resolution of the meteorological data used in the back trajectory model results in somewhat different trajectories for the two locations.

To further examine whether the sampled enhancements are due to the Victorian bushfires, we use back trajectory analyses using HYSPLIT with Global Data Assimilation System (GDAS) meteorological data [Derber et al., 1991; Parrish and Derber, 1992]. GDAS has 1° and 3 hourly resolution. The enhanced concentrations are noticeable until shortly after 6pm on February 7, despite the burning in Victoria continuing for several days. At Cape Grim, it appears that none of the air sampled has a source from the area burnt, but when choosing a location just north of Cape Grim (40.1°S, 144.7°E) hourly back trajectories (Figure 7.4) show that air arriving at Cape Grim changes from having a Victorian source to coming off the ocean to the west of the site somewhere between 5 and 6 pm on February 7. The different back trajectories could be a result of the coarse resolution of the meteorological data used in HYSPLIT limiting the ability to correctly predict the source of the sampled airmass. Analysis of trajectories
finishing at intermediate latitudes points to the results being derived from an interpolation between the spanning latitudinal meteorological data.

Given that even with the back trajectory analysis there is still uncertainty over the possible source of the airmass sampled at this time, we look at some of the other species sampled at Cape Grim as part of the AGAGE network to attempt to confirm the airmass source. Of those not measured by the FTIR that were available, chloroform (trichloromethane, CHCl₃), methyl chloroform (trichloroethane, CH₂CCl₃) and molecular hydrogen are known to be emitted from biomass burning [Cofer et al., 1991; Lobert et al., 1999]. The time series, measured by a multi-detector gas chromatograph (GC-MD), for each of these gases is shown in Figure 7.5. The methyl chloroform time series is dominated by a slight downward trend and no events can reliably be seen outside the level of variability. There are a significant number of episodes that see chloroform concentrations rise above the apparent background level of around 5 pmol mol⁻¹, including one that corresponds with the February 7 event. The calculated emission ratio of chloroform relative to CO₂ of 1.7 ± 0.5 x 10⁻⁶ mol mol⁻¹ is significantly higher than those previously reported (0.056 – 0.099 x 10⁻⁶ mol mol⁻¹ [Lobert et al., 1999]). Given that emission ratios for methyl chloroform reported in the same study are considerably higher than that of chloroform, and no enhancement is measured on February 7, it seems unlikely that biomass burning is the source of the air measured at Cape Grim on the afternoon of February 7. This is also supported by an apparent observed decrease in H₂ at that time. The measured increase in chloroform could be due to production at local paper mills located 100 – 200km east of the site. Paper manufacturing is the largest anthropogenic source of chloroform to the atmosphere [Aucott et al., 1999], and has previously been attributed as being the cause of measured
chloroform enhancements above background concentrations at Cape Grim [O’Doherty et al., 2001].

![Graph showing time series of CH$_3$CCl$_3$, CHCl$_3$, and H$_2$ concentrations](image)

**Figure 7.5** Measured time series of chloroform (black), methyl chloroform (blue) and molecular hydrogen (red) from Cape Grim during the time that the FTIR was in operation.

### 7.1.1.2. Other events

There are several other events measured by the FTIR that we also examine. The earlier broad peak in late January, 2009, shows a maximum in all gases in the early afternoon on January 29. Back trajectory analyses over this time period (Figure 7.6) show that air arriving at Cape Grim at this time came from directly north, over Melbourne, only at the time corresponding to the peak gas concentrations. Calculating emission ratios for urban Melbourne for this period of time yields the values summarised in Table 7.2. Previous
work has used the ratios of gases to CO measured at Cape Grim, along within an inventory estimate of total CO emissions to estimate urban trace gas emissions from Melbourne [Dunse et al., 2005]. Derived ratios of CH₄ and N₂O to CO from this work yields values of 0.7 ± 0.2 mol mol⁻¹ and 0.011 ± 0.04, respectively, in broad, but not good agreement with the values of 1.1 ± 0.1 and 0.024 ± 0.001 mol mol⁻¹ derived here. This could be because of this one event is not indicative of the same regime as sampled by Dunse et al. [2005], which showed considerably year-to-year variability, or because of a real change in the ratios of CH₄ and N₂O from Melbourne.

Table 7.2  Emission ratios calculated from air measured at Cape Grim on January 28-29, 2009, during which time air passes over the Melbourne urban area.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Emission ratio (ΔX/ΔCO₂, mol mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>3.7 ± 0.1 × 10⁻² (r=0.905)</td>
</tr>
<tr>
<td>N₂O</td>
<td>8.0 ± 0.2 × 10⁻² (r=0.886)</td>
</tr>
<tr>
<td>CO</td>
<td>3.36 ± 0.09 × 10⁻² (r=0.917)</td>
</tr>
</tbody>
</table>

Figure 7.6  Back trajectory analyses for late January, 2009. The pink trajectory corresponds to the time at which gas concentrations were at a maximum, as a result of the northerly source of air, corresponding to the urban area of Melbourne.
Table 7.3  Emission ratios calculated from air measured at Cape Grim on January 6, 2009, when a depletion of CH$_4$ is observed, and back trajectory analyses indicate a westerly ocean source.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Emission ratio ($\Delta X/\Delta CO_2$, mol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>$-3.5 \pm 0.3 \times 10^{-2}$ ($r=0.709$)</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>$4.6 \pm 0.3 \times 10^{-4}$ ($r=0.753$)</td>
</tr>
<tr>
<td>CO</td>
<td>$4.7 \pm 0.3 \times 10^{-3}$ ($r=0.813$)</td>
</tr>
</tbody>
</table>

Figure 7.7  HYSPLIT Back trajectory analyses for January 6, 2009, when a CH$_4$ depletion is measured by the FTIR at Cape Grim, along with enhancements of CO$_2$, CO and N$_2$O.

Table 7.3 and Figure 7.7 show emission ratios and back trajectories for January 6, 2009 – a period during which a negative CH$_4$ excursion is observed, correlating with enhancements in CO, CO$_2$ and N$_2$O. This depletion is also observed in the AGAGE CH$_4$ record. Also, the significantly higher N$_2$O/CO$_2$ ratio than in late January indicates that it is likely to be a source different from urban Melbourne that is being observed here. The back trajectories indicate an oceanic source for several days leading up to the event, with no obvious change in the air source that could account for the change in gas concentrations. The depletion of CH$_4$ is unexplained – the major CH$_4$ sink via reaction

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with the OH radical is common to CO₂ so a concurrent reduction in CO would be expected, though in situ production of CO resulting from CH₄ oxidation could mean that no net effect on CO is seen. The reaction of CH₄ with OH also has a time constant of around 10 years, so short term effects such as these would not be seen. Soil uptake is the other significant CH₄ sink from the atmosphere, but that would be unlikely given the apparent oceanic source of the airmass. The reduction in CH₄ could also be due to observing an older airmass in which the air has had greater time to age and the CH₄ deplete.

7.1.2. Lauder

![Figure 7.8](image)

Figure 7.8 Time series of CO₂ (top), CH₄ (2nd top), N₂O (2nd bottom) and CO (bottom) from Lauder between July 2006 and February 2009. The y-axes are not full range, but shortened to show the lower (and most frequent) mixing ratios.

Figure 7.8 shows the time series of the N₂O, CH₄, CO₂ and CO measured at Lauder between installation in July 2006 and February 2009. The seasonality in CH₄ and CO mixing ratios is obvious, with an early spring maximum and early autumn minimum. The agreement in the seasonal cycles between these gases indicates the driving factor in
their variation on seasonal timescales is dominated by a common mechanism, in this case loss via reaction with the OH radical. There is also seasonality evident in the CO$_2$ time series, with a maximum in mid-late winter, when photosynthetic loss is at a minimum. Also evident are long-term increases in N$_2$O, CO$_2$ and CH$_4$.

A “baseline” time series from Lauder is created by filtering for measurements that occurred when the average wind speed was greater than 3 ms$^{-1}$, the time was between 1300 and 1800 local time and the measured CH$_4$, CO$_2$, CO and N$_2$O are within 10 nmol mol$^{-1}$, 2 µmol mol$^{-1}$, 10 nmol mol$^{-1}$ and 1 nmol mol$^{-1}$, respectively of their daily minimum measured value. We use these data to attempt to quantify the seasonal and secular trends, with the awareness that the time series is too short to attach great significance to these results. These “baseline” data are shown in Figure 7.9.

![Figure 7.9 Baseline Lauder N$_2$O, CH$_4$, CO$_2$ and CO as measured by the in situ FTIR gas analyser. These baseline data are created by removing data collected outside the hours of 1pm – 6pm local time, when wind speed was less than 10 ms$^{-1}$ and when the wind direction is between south-east and south-west. (& when the measurements are greater than a threshold value different from the daily minimum).](image-url)
The baseline time series also reveals some seasonality in N₂O, roughly corresponding with that previously quantified in the southern hemisphere – that is, with a summer maximum, followed by an autumn minimum [Nevison et al., 2005; Nevison et al., 2007; Prinn et al., 1990]. The dominant factor causing this seasonal cycle is southern ocean ventilation [Nevison et al., 2005].

The seasonal and long-term trends in the data are quantified by fitting the baseline monthly average, shown in Figure 7.10. The fit parameters to these data are summarised in
Table 7.4. The double harmonic is not necessary to provide a good fit to the CH$_4$ and CO time series.

Figure 7.10 Monthly average baseline concentrations for CO$_2$, CO, CH$_4$ and N$_2$O. The lines show an harmonic plus linear fit for CH$_4$ and CO, and a double harmonic plus linear trend for N$_2$O and CO$_2$. Error bars are the standard deviation of the month’s baseline concentrations.
Table 7.4  Fit parameters to Lauder trace gas concentration time series. Y=a*sin(2π(x+b))+e*x+d+e*sin(4π(x+f)), where x=years since 2005. Values given as fit ± 95% confidence interval.

<table>
<thead>
<tr>
<th>Gas</th>
<th>a</th>
<th>b</th>
<th>c (yr⁻¹)</th>
<th>d</th>
<th>e</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (μmol mol⁻¹)</td>
<td>1.5±0.8</td>
<td>-23.4±0.5</td>
<td>1.8±0.7</td>
<td>375±2</td>
<td>0.5±0.8</td>
<td>0.5±1.4</td>
</tr>
<tr>
<td>CH₄ (nmol mol⁻¹)</td>
<td>-12±5</td>
<td>6.9±0.5</td>
<td>7.8±0.9</td>
<td>1724±12</td>
<td>-3±5</td>
<td>6±2</td>
</tr>
<tr>
<td>N₂O (nmol mol⁻¹)</td>
<td>0.1±0.2</td>
<td>1±2</td>
<td>0.6±0.2</td>
<td>319.9±0.6</td>
<td>0.3±0.2</td>
<td>-0.3±0.7</td>
</tr>
<tr>
<td>CO (nmol mol⁻¹)</td>
<td>-10±2</td>
<td>19.1±0.2</td>
<td>2±2</td>
<td>55±6</td>
<td>2±2</td>
<td>3.3±0.9</td>
</tr>
</tbody>
</table>

A comparison between the baseline time series derived from the FTIR measurements, and monthly mean CO₂ data from the clean air site at Baring Head is presented in Figure 7.11. Through the latter part of the record, the agreement between the series is good, with Baring Head consistently higher than Lauder, apart from during one month. During spring, when photosynthetic uptake occurs over land, Lauder concentrations are lower than those at Baring Head, because Lauder cannot avoid sampling air that has been terrestrially influenced, unlike Baring Head which can sample true baseline conditions. Through the remainder of the year, the measurements at Baring Head and Lauder are in agreement within the uncertainties.
Night-time boundary layer build-up occurs during still periods and results in gas concentration increases due to local sources [Kelliher et al., 2002]. The ratios are calculated daily, via linear fit, from days where there are more than six measurements between midnight and 6am with a corresponding wind speed of less than 1 m s\(^{-1}\). Figure 7.12 shows examples of these ratios for July 15, 2007. On this day, the CH\(_4\), N\(_2\)O and \(\delta^{13}\)CO\(_2\) x CO\(_2\) (as a means of estimating the \(\delta^{13}\)CO\(_2\) signature of the source, introduced in Chapter 6 based on work by Miller and Tans [2003]) ratios to CO\(_2\) behave in a strongly linear fashion, but CO is a more complicated picture, with earlier enhancements leading to the set of high CO outliers, and suggesting that there is at least one source different in location from CO\(_2\).
Figure 7.12  Example plots of nighttime changes in CH$_4$, N$_2$O, CO and $\delta^{13}$CO$_2$ against CO$_2$ for July 15, 2007.

Figure 7.13 shows the time series of ratios of CO, N$_2$O and CH$_4$ to CO$_2$ that occur during these events. There appears to be an increase in the ratios of CO, N$_2$O and CH$_4$ to CO$_2$ in the winter. Some common sources for N$_2$O, CH$_4$ and CO$_2$ are expected – CO$_2$ is produced by respiration of plants and animals, while methane is produced by ruminant animals, and N$_2$O in soils. All are present around the Lauder site. CO increases in winter are likely to be caused by burning of fuels for heating during winter. The increased ratios for N$_2$O and CH$_4$ could occur because of a reduction in CO$_2$ being produced via soil respiration, due to decreased temperatures. We calculate the magnitude of the change in concentration for each species during these buildup events, for each day. The maximum changes in CO$_2$ occur during the summer, suggesting a larger CO$_2$ source or contrast in PBL height in summer, while N$_2$O and CH$_4$
concentration changes do not exhibit much seasonality. CO is definitely increasing more in the winter months. Therefore the winter maxima in N₂O and CH₄ ratios to CO₂ are due to low CO₂, not high amounts of the other gases, while the increased CO/CO₂ ratio is due to a combination of increased CO emissions and decreased CO₂ production.

Figure 7.13  Ratios of (from top to bottom) CO, N₂O and CH₄ to CO₂, and δ¹³C determined from gas concentration build ups during still nights.
7.1.3. Darwin

Figure 7.14 Time series of CO$_2$ (top), CH$_4$ ($2^{nd}$ top), N$_2$O (2$^{nd}$ bottom) and CO (bottom) from Darwin between March 2007 and February 2009. The lowermost and most frequent concentrations are shown.

Figure 7.14 shows the time series of CO$_2$, CH$_4$, N$_2$O and CO measured at Darwin from March 2007 to February 2009. CO$_2$ is a minimum at the end of the monsoonal wet season from January through to March, during which time it is taken up by vigorously growing plants. For the remainder of the year, respiration dominates and the CO$_2$ gradually increases. The underlying seasonality in CH$_4$ and CO is very similar, once again because of reaction with the OH radical, but the signal is much noisier than in Lauder because of other effects, such as urban pollution and more varied surroundings, e.g. wetlands with changing spatial and temporal distribution. The late end of the record is patchy because of condensation problems that occurred when hot humid air entered the cooler container, and therefore condensed in the sample line, affecting the apparent concentrations of the other gases.
Figure 7.15 Baseline Darwin CO₂, CH₄, N₂O and CO. These baseline data include data between 1400 and 1600 local time when wind speed is greater than 5 m s⁻¹.

The baseline time series for CO₂, CH₄, N₂O and CO are shown in Figure 7.15. The monthly averages of these, and a double harmonic fit to each species is shown in Figure 7.16, and the fit parameters in Table 7.5. Seasonal amplitudes of approximately 3.8 µmol mol⁻¹ are apparent in the CO₂ time series. The increase of CH₄ in 2007-2008 seen and reported in other measurements [Rigby et al., 2008] is also captured by the in situ FTIR analysers at both Darwin and Lauder.
Figure 7.16 Monthly average baseline concentrations, and double harmonic plus linear fit to the time series. Error bars are the standard deviation of the month’s baseline mole fractions.

Table 7.5 Fit parameters to Darwin trace gas concentration time series. 

\[ Y = a \sin(2\pi(x+b)) + c \cdot x + d + e \sin(4\pi(x+f)) \]

Values given as fit \( \pm 95\% \) confidence interval.

<table>
<thead>
<tr>
<th>Gas</th>
<th>a</th>
<th>b</th>
<th>c (yr(^{-1}))</th>
<th>d</th>
<th>e</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) (μmol mol(^{-1}))</td>
<td>1.7±1.1</td>
<td>3.0±0.5</td>
<td>2.0±1.3</td>
<td>375±4</td>
<td>0.2±1.0</td>
<td>-4±4</td>
</tr>
<tr>
<td>CH(_4) (nmol mol(^{-1}))</td>
<td>8±6</td>
<td>-7.7±1.2</td>
<td>10±8</td>
<td>1728±25</td>
<td>4±7</td>
<td>-1±2</td>
</tr>
<tr>
<td>N(_2)O (nmol mol(^{-1}))</td>
<td>0.3±0.2</td>
<td>1.5±0.7</td>
<td>0.8±0.3</td>
<td>319.3±0.8</td>
<td>-0.1±0.2</td>
<td>0±3</td>
</tr>
<tr>
<td>CO (nmol mol(^{-1}))</td>
<td>26±16</td>
<td>16.1±0.7</td>
<td>-10±20</td>
<td>130±60</td>
<td>-7±16</td>
<td>-5±2</td>
</tr>
</tbody>
</table>

Figure 7.17 Monthly mean Darwin baseline CO\(_2\) concentrations, and those measured at American Samoa (14°S).
The monthly mean Darwin baseline CO₂ and that measured as part of the NOAA-ESRL surface network at American Samoa are shown in Figure 7.17. American Samoa is the site closest in latitude to Darwin, but has little influence from local sources. The two measurements agree well in the last third of each year, but those in Samoa do not capture the same magnitude of uptake in the monsoonal wet season as seen at Darwin, and exhibit a very small seasonal cycle, because of the regulatory effect of the surrounding oceans and small amount of nearby vegetation. Similar data for CH₄ and N₂O are shown in Figure 7.18 and Figure 7.19, respectively. The CH₄ at Darwin is much more variable than that at Samoa, reflecting the more complicated local sources around Darwin. Darwin CH₄ and N₂O are also consistently higher than Samoa, apart from in the late part of the year for CH₄, and in April 2007 for N₂O. The April 2007 dip is also apparent in the CO₂ concentration record. This month was highlighted by winds being consistently from the east. The CO is also low during this month, indicating that the airmasses sampled have come from a relatively clean environment. The wind consistently comes from the east at the time of year, however HYSPLIT back trajectory analyses [Draxler and Hess, 1997] indicate that in 2007 the airmasses, while crossing Cape York Peninsula, spent little time over land. In contrast, in 2008 the airmasses followed a similar path, but also crossed south-eastern Australian land and potentially polluted urban areas. Representative back trajectory examples are shown in Figure 7.20.
Figure 7.18  Monthly mean Darwin baseline CH₄ concentrations and those measured at American Samoa.

Figure 7.19  Monthly average baseline N₂O concentrations measured by FTIR at Darwin and AGAGE at Samoa.
7.1.4. Katherine

Figure 7.20 Back trajectory analyses from Darwin in April 2007 (left) and April 2008 (right). The patterns are similar, but those from 2008 spend time over south-eastern Australia, potentially picking up polluted air, while 2007 back trajectories are predominantly over ocean.

Figure 7.21 Time series of CO₂, CH₄, N₂O and CO measured by FTIR at Katherine, from September 30, 2008 to April 29, 2009. The grey shadings indicate days when there was rainfall.
The time series of CO₂, CH₄, N₂O and CO are presented in Figure 7.21, along with days on which rainfall occurred as reported by the nearby Tyndal Bureau of Meteorology site. There are a considerable number of buildup events that see large peaks in CO₂, CH₄ and N₂O mole fractions, however, applying the same treatment as for Lauder with respect to nighttime events yields poor correlations between species. Enhancements seem to be muted on days when there was rainfall compared to surrounding days, possibly because rainfall is playing a role in suppressing fluxes from soil or wetlands, but contributes to subsequent emissions. The majority of CO enhancements occur because the inlet was located next to the car park at Katherine Research Station, and thus susceptible to vehicle emissions.

7.1.5. Comparison – Lauder and Darwin

![Figure 7.22 Baseline FTIR CO₂ concentrations measured at Darwin (blue) and Lauder (black).](image)

The comparative baseline FTIR time series for CO₂ at Lauder and Darwin are presented in Figure 7.22. The variation at Darwin is greater, as is the magnitude of the apparent seasonal cycle, due to the lower land mass and consequent biospheric fluxes around...
Lauder and southern hemisphere mid-latitudes in general. The seasonal cycles are also slightly out of phase, with Darwin lagging Lauder by about 3 months, because uptake due to photosynthetic growth occurs during spring and summer in Lauder, but does not commence until summer and the monsoonal wet season in Darwin.

Similar time series for CH₄ are presented in Figure 7.23. Again the concentrations measured at Darwin are more variable, with the variation occurring predominantly in the early year wet season, due to local sources. The magnitudes of the seasonal cycles agree well, and are both driven by loss via reaction with the OH radical. The seasonal cycle in Darwin appears to slightly lead that in Lauder.

![Figure 7.23](image_url) Baseline FTIR CH₄ concentrations measured at Darwin (blue) and Lauder (black).
7.2. Conclusions

Here we have introduced an FTIR-based in situ greenhouse gas analyser, capable of high-precision and accuracy simultaneous measurements of CO$_2$, CH$_4$, N$_2$O, CO and $\delta^{13}$CO$_2$. The performance of the analyser was validated by a side-by-side comparison with existing instrumentation at Cape Grim. We also looked at measurement time series made by several of these instruments, at Lauder, Darwin, Katherine and Cape Grim.

Future work related to this but outside the scope of this project will provide further analyses of these data. This will be done by including them into atmospheric inversion modelling studies, and by making use of data mining techniques.