Calibration of the total carbon column observing network using aircraft profile data


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TCCON calibration

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Abstract

The Total Carbon Column Observing Network (TCCON) produces precise measurements of the column average dry-air mole fractions of CO$_2$, CO, CH$_4$, N$_2$O and H$_2$O at a variety of sites worldwide. These observations rely on spectroscopic parameters that are not known with sufficient accuracy to compute total columns that can be used in combination with in situ measurements. The TCCON must therefore be calibrated to World Meteorological Organization (WMO) in situ trace gas measurement scales. We present a calibration of TCCON data using WMO-scale instrumentation aboard aircraft that measured profiles over four TCCON stations during 2008 and 2009. The aircraft campaigns are the Stratosphere-Troposphere Analyses of Regional Transport 2008 (START-08), which included a profile over the Park Falls site, the HIAPER Pole-to-Pole Observations (HIPPO-1) campaign, which included profiles over the Lamont and Lauder sites, a series of Learjet profiles over the Lamont site, and a Beechcraft King Air profile over the Tsukuba site. These calibrations are compared with similar observations made during the INTEX-NA (2004), COBRA-ME (2004) and TWP-ICE (2006) campaigns. A single, global calibration factor for each gas accurately captures the TCCON total column data within error.

1 Introduction

The Total Carbon Column Observing Network (TCCON) is a ground-based network of Fourier transform spectrometers that precisely measure total columns of CO$_2$, CO, CH$_4$, N$_2$O, H$_2$O, HF and other gases (Wunch et al., 2010). The TCCON instruments measure the absorption of direct sunlight by atmospheric gases in the near infrared (NIR) spectral region. To derive a total column measurement of the gases from these spectra, external information about the atmosphere (e.g. temperature, pressure, a priori mixing ratio) and NIR spectroscopy is required. A significant effort is put into minimizing errors in this external information, and the resulting total columns are precise.
(<0.25% in CO₂).

Due to systematic biases in the spectroscopy, the absolute accuracy of the column measurements is ~1% which is inadequate for use in combination with in situ measurements for carbon cycle science. In order to make TCCON column measurements useful for these combined analyses, they must be calibrated to the World Meteorological Organization (WMO) in situ trace gas measurement scales. To do this, we use profiles obtained with in situ instrumentation flown on aircraft over TCCON sites. A set of profiles were measured over the Park Falls, Wisconsin TCCON site in 2004–2005 (Washenfelder et al., 2006) during the Intercontinental Chemical Transport Experiment–North America campaign (INTEX-NA, Singh et al., 2006) and the CO₂ Budget and Rectification Airborne – Maine experiment (COBRA-ME, Gerbig et al., 2003; Lin et al., 2006). A single profile was measured coincidently with the Darwin, Australia site in 2006 as part of the Tropical Warm Pool International Cloud Experiment (TWP-ICE, Deutscher et al., 2010; May et al., 2008). Since then, other TCCON sites have begun operational measurements. In this paper, we describe the first global calibration of five TCCON sites (Park Falls, Lamont, Darwin, Lauder and Tsukuba), using instrumentation calibrated to WMO scales aboard the HIAPER aircraft, during the START-08 and HIPPO overpasses in 2008 and 2009, Learjet overflights of Lamont during summer of 2009, and a Beechcraft King Air 200T aircraft profile over Tsukuba, Japan in January 2009 (Tanaka et al., 2009). We present the calibration of CO₂, CO, CH₄, N₂O and H₂O.

2 TCCON

The TCCON was developed to provide a long, nearly continuous, time series to serve as a transfer standard between in situ networks and satellite measurements, and to provide insights into the carbon cycle (e.g., Yang et al., 2007; Keppel-Aleks et al., 2008; Wunch et al., 2009; Deutscher et al., 2010). TCCON sites are located worldwide (Fig. 1). The first TCCON site, located in Park Falls, is described by Washenfelder et al.
Total column abundances are retrieved from spectra measured with the TCCON instruments using a nonlinear least-squares spectral fitting algorithm (GFIT), which scales an a priori profile to produce a synthetic spectrum that achieves the best fit to the measured spectrum. We use spectral windows and spectroscopic data listed in Table 1.

Column-averaged dry-air mole fractions (DMF), denoted $X_G$ for gas G, are computed using the retrieved $O_2$ columns as a measure of the dry air column.

$$X_G = 0.2095 \frac{\text{column}_G}{\text{column}_{O_2}}.$$  

Dividing by $O_2$ improves the precision of the measurement by significantly reducing the effects of instrumental or measurement errors that are common to both the gases (e.g. solar tracker pointing errors, zero level offsets, instrument line shape errors, etc. described in Wunch et al., 2010). However, any errors specific to either $\text{column}_G$ or $\text{column}_{O_2}$ will create errors in the DMFs of each gas. The $O_2$ dry-air mole fraction decreased by about 0.01% since the start of the TCCON record in 2004 (Tohjima et al., 2005), which leads to a 0.04 ppm error in $X_{CO_2}$.

All TCCON $X_{CO_2}$ data have an airmass-dependent artifact, which causes the retrievals to be $\sim 1\%$ larger at noon than at sunrise or sunset (Wunch et al., 2010). This artifact is caused primarily by spectroscopic inadequacies which are common to all TCCON instruments (e.g. line widths, neglect of line-mixing, inconsistencies in the relative strengths of weak and strong lines). The airmass-dependent artifact is removed from the TCCON data with a single empirical correction factor before calibration. Airmass dependent artifacts have not been seen in $X_{CH_4}$, $X_{CO}$, $X_{N_2O}$ or $X_{H_2O}$.


3 Aircraft campaigns

Three independent aircraft campaigns were held in 2008 and 2009 that included profiles over four TCCON stations. The instrumentation on each aircraft used for the calibration are listed in Table 2. The WMO calibration scales used for the aircraft instrumentation are described for CO$_2$ in Zhao and Tans (2006) and Keeling et al. (2002), for N$_2$O in Hall et al. (2007), for CH$_4$ in Dlugokencky et al. (2005) and for CO in Novelli et al. (1994).

3.1 START-08/pre-HIPPO and HIPPO-1

The NCAR/NSF High-performance Instrumented Airborne Platform for Environmental Research (HIAPER), is a modified Gulfstream V (GV) jet which hosted the Stratosphere-Troposphere Analyses of Regional Transport 2008 (START-08) campaign (Pan et al., 2010) and the preliminary HIAPER Pole-to-Pole Observations (pre-HIPPO) campaign during 2008. The two experiments shared flight time and instrumentation and made observations across North America, including a vertical profile above the Park Falls site. The HIAPER Pole-to-Pole Observations (HIPPO-1) campaign (Wofsy et al., 2010) covered a cross-section of the globe that spanned the Arctic to the Antarctic (Fig. 1) with profiles over Lamont and Lauder. The START-08/pre-HIPPO and HIPPO-1 missions used similar in situ instrumentation (Table 2). The water profiles are from the available H$_2$O measurements on board the aircraft, with additional stratospheric information supplied by the noontime NCEP/NCAR specific humidity profile for that day. The HIPPO-1 profiles used in this analysis over Lamont are shown in Fig. 2.

3.2 Learjet

The NASA Glenn Lear-25 aircraft performed three profiles from 5–13 km altitude over the Southern Great Plains (SGP) Atmospheric Radiation Measurement (ARM) Lam-
ont site during a campaign from 31 July 2009 to 5 August 2009 (Abshire et al., 2010). Lower altitude (0.3–5 km) profiles were measured with a Cessna 210 at essentially the same times and locations. On both aircraft, the CO₂, CH₄, N₂O and CO measurements were made by flask samplers, which were analysed at the National Oceanic and Atmospheric Administration’s Earth System Research Laboratory (NOAA’s ESRL). Water profiles were obtained from on-site sonde measurements taken at 11:30 a.m. LT.

Many years of bi-weekly Cessna 0–5 km flights are available over Park Falls and Lamont and will be used in a future analysis to assess possible calibration drifts for those sites. The ceiling of these flights is insufficiently high for use in this analysis.

### 3.3 Beechcraft King Air

The Beechcraft King Air 200T aircraft measures CO₂ continuously with a Li-COR (Li-840) non-dispersive infrared analyzer. CH₄ and other gases are measured using hand-operated flask samplers, which are analysed at the National Institute for Environmental Studies (NIES). The aircraft overpasses of the Tsukuba FTS instrument were carried out on 7 and 15 January 2009 over Tsukuba (36.1° N, 140.1° E) and Kumagaya (36.15° N, 139.38° E). Due to air traffic control restrictions, the higher part of the profile (2 to 7 km) was observed over Kumagaya, and the lower altitude range (0.5 to 2 km) was observed over Tsukuba. For the purposes of the FTS calibration, only data from the 15 January overflight is used, because of heavy cloud cover on 7 January. Water profiles were obtained from nearby radiosonde measurements taken at the Tateno Aerological Observatory near the time of the overpass.

### 4 Numerical integration of aircraft in situ profiles

To calibrate the total column measurements of the TCCON network, the aircraft in situ profiles must be integrated with respect to altitude. In order to properly compare the ground-based FTS measurements with the in situ aircraft measurement, which we
consider the best measure of the true state of the atmosphere, the averaging kernels of the FTS measurements ($A$) must be taken into account. From the aircraft profiles ($x_h$), an averaging kernel-smoothed profile ($x_s$) can be computed that, when integrated, can be directly compared with the FTS retrieved total columns. The smoothed profile represents the profile the FTS would retrieve, if it were measuring perfectly (i.e. without spectroscopic errors), given the GFIT a priori profile ($x_a$) and retrieved profile scale factor ($\gamma$). We use Eq. (4) of Rodgers and Connor (2003),

$$x_s = \gamma x_a + A(x_h - \gamma x_a).$$

(2)

Note that for a GFIT scaling retrieval, the kernels are calculated for the solution mole fraction profile, not the a priori profile, so the point of linearization of the Taylor expansion producing Eq. (2) is $\gamma x_a$ and not $x_a$.

For column measurement calibration, Eq. (2) is integrated vertically:

$$\hat{c}_s = \gamma c_a + a^T(x_h - \gamma x_a)$$

(3)

where $\hat{c}_s$ is the smoothed column-averaged DMF, $c_a$ is the column-averaged DMF from integrating the a priori profile and $a$ is the FTS dry pressure-weighted column averaging kernel. The $a^T(x_h - \gamma x_a)$ term represents the column averaging kernel-weighted vertical integration of the difference between the in situ profile and the scaled a priori profile. Column averaging kernels vary as a function of pressure and solar zenith angle.

Integrating these profiles is done most accurately on a pressure grid, under the assumption that the atmosphere is in hydrostatic balance. The total vertical column for gas G ($VC_G$) is then defined in the following manner:

$$VC_G = \int_{0}^{P_s} \frac{f_G(p)}{g \cdot m} dp$$

(4)

where $f_G = f_G^{\text{dry}} \cdot (1 - f_{H_2O})$ is the mole fraction of gas G, $P_s$ is the surface pressure, and $g$ is the gravitational acceleration, which is a function of altitude ($z$) and latitude ($\phi$). We distinguish between the true mole fraction ($f_G$), and the dry mole fraction ($f_G^{\text{dry}}$),
which is what the aircraft in situ instrumentation measures. The mean molecular weight of air, $m$, can be expressed in terms of its wet and dry components as well:

$$m = m_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}} + m_{\text{air}} (1 - f_{\text{H}_2\text{O}}).$$

Substituting these into Eq. (4) and rearranging yields a useful, numerically integrable relationship to compute $V_{C_G}$.

$$V_{C_G} = \int_{0}^{P_s} \frac{f_{G}^{\text{dry}}(p)}{g(z(p), \phi) \cdot m_{\text{air}} \cdot \left[ 1 + f_{\text{H}_2\text{O}}^{\text{dry}}(p) \cdot (m_{\text{H}_2\text{O}} / m_{\text{air}}) \right]} dp$$

(5)

where $f_{G}^{\text{dry}}$ is the aircraft profile of gas $G$, $f_{\text{H}_2\text{O}}^{\text{dry}} \equiv f_{\text{H}_2\text{O}}$, where $f_{\text{H}_2\text{O}}$ is the $\text{H}_2\text{O}$ aircraft or sonde profile, $m_{\text{H}_2\text{O}} = 18.02 \times 10^{-3} / N_A \text{ kg/molecule}$, $m_{\text{air}} = 28.964 \times 10^{-3} / N_A \text{ kg/molecule}$, and $N_A$ is Avogadro’s constant. To compute the column averaging kernel-weighted vertical column (to satisfy the right-hand term in Eq. 3), the column averaging kernel ($a(p)$) must be included at every level in the integral.

$$V_{C_G,ak} = \int_{0}^{P_s} \frac{f_{G}^{\text{dry}}(p) \cdot a(p)}{g(z(p), \phi) \cdot m_{\text{air}} \cdot \left[ 1 + f_{\text{H}_2\text{O}}^{\text{dry}}(p) \cdot (m_{\text{H}_2\text{O}} / m_{\text{air}}) \right]} dp$$

(6)

The column of dry air ($V_{\text{Cair}}$) is computed by setting the numerator in Eq. (6) to 1. The column-averaged DMF is computed by dividing the appropriate vertical columns by the column of dry air. Hence, Eq. (3) becomes:

$$\hat{c}_s = \gamma c_a + \left( \frac{V_{\text{Cair}}^{\text{aircraft}} - \gamma V_{\text{Cair}}^{\text{a priori}}}{V_{\text{Cair}}} \right)$$

(7)

Aircraft measurements have good accuracy, but are limited in altitude floor and ceiling, and so we must use additional information for the surface and the stratosphere. When multiple instruments aboard the aircraft measure the same species, a running
mean is applied. There is one instance where two CO measurements on HIPPO-1 disagree over Lauder in the upper troposphere (RAF and QCLS): in this case, QCLS is used.

For surface measurements, most TCCON sites are co-located with tower or surface in situ measurements. In the event that there were no surface or tower measurements available, and the aircraft did not measure to the surface, the lowest measured value was assumed to be the surface value (e.g. Park Falls on 14 July 2004).

For stratospheric CO\textsubscript{2}, the mole fractions are predictable at the 0.3% level, as described in more detail below. For N\textsubscript{2}O and CH\textsubscript{4}, the stratospheric mole fractions are more difficult to estimate because they decrease rapidly with altitude, causing transport-driven variations in the stratospheric column. In general, the unknown state of the atmosphere above the aircraft ceiling is the largest source of uncertainty in the total integrated column.

The CO\textsubscript{2} profiles in the stratosphere are empirically derived from in situ measurements on high-altitude balloons and include realistic latitude and time-dependencies. The stratosphere is set by an exponential decrease above the tropopause, based on the age of air measurements of Andrews et al. (2001). The tropopause pressure comes from the NCEP/NCAR four-times daily analysis, which is interpolated to local noon at the latitude and longitude of the site. A generous error of ±1 ppm is assumed for the GFIT stratospheric a priori. These stratospheric profiles are used as a prioris for all TCCON retrievals. A prioris for the troposphere are derived from GLOBALVIEW (GLOBALVIEW-CO\textsubscript{2}, 2006).

The GFIT CH\textsubscript{4}, N\textsubscript{2}O, CO and HF a prioris are generated from MkIV FTS balloon profiles (Toon, 1991). The profiles are shifted up or down in altitude depending on the tropopause pressure for local noon on that day. The CH\textsubscript{4}-HF and N\textsubscript{2}O-HF correlations in the a priori profiles are consistent with those observed by Luo et al. (1995) and Washenfelder et al. (2003) and are preserved under the vertical shifting. Due to a complete absence of HF in the troposphere, HF is a sensitive indicator of ascent and descent in the stratosphere. Indeed, a 1 km vertical shift in the HF profile produces
a \sim 15\% \text{change in the total column, which is easily measureable. Since HF is a long-lived, stable stratospheric tracer, we assume that any difference in the retrieved HF column from the a priori value is due to the stratospheric dynamics and will be anti-correlated with the stratospheric N}_2\text{O and CH}_4. The magnitude of the deviation of the HF column from the a priori HF column is used to adjust the CH}_4 and N}_2\text{O stratospheric profiles to generate our best estimate of the “true” stratospheric profile for a given overpass. An illustration of this is in Fig. 3. Note that even small errors in the stratospheric a priori profile of N}_2\text{O will be very important in this analysis, because the N}_2\text{O column averaging kernels increase significantly in the stratosphere. The stratospheric error contribution for both CH}_4 and N}_2\text{O is estimated by shifting the stratospheric profile up and down by 1 km and integrating the results, giving upper and lower bounds on the column due to errors in the stratospheric profile.}

Unlike CH}_4 and N}_2\text{O, stratospheric CO is highly variable and does not have a simple relationship to HF. To estimate the CO stratospheric contributions, v2.2 profiles from the low-Earth orbiting ACE-FTS instrument (Bernath et al., 2005) were averaged within one month of the overpass and \pm 5 degrees latitude of the site. The work by Clerbaux et al. (2008) has shown that the ACE-FTS CO values are accurate to 30\% in the upper troposphere/lower stratosphere, and 25\% above. For our stratospheric error budget, we have taken the larger of the standard deviation of the ACE profiles, and the estimated error by Clerbaux et al. (2008).

If water vapor profiles are not available from the aircraft in situ data (Tsukuba, Darwin and during the Learjet overpasses of Lamont), radiosonde measurements of H}_2\text{O are used. Any additional stratospheric information is provided from GFIT a prioris, which are derived from NCEP profiles, and extended upwards using a model based on MkIV balloon profiles. Because most of the water column is located at altitudes below \sim 5 km, errors in the upper altitude water profile do not significantly affect the total column. The errors on the H}_2\text{O columns are estimated to be 10\% of the total column.}

To estimate the H}_2\text{O calibration curve for the TCCON, the radiosonde profiles over Tsukuba, Darwin, Lamont, Lauder and Park Falls are used, which tend to reach higher
altitudes than the aircraft (generally well above the tropopause). Water profiles are available from daily sonde measurements at Lamont and Darwin.

Once full profiles of the gas of interest and H$_2$O are generated on a fine altitude or pressure grid, the profiles are integrated via Eqs. (5) or (6), and the smoothed profile is computed via Eq. (7).

5 Results

Aircraft overflights of the Park Falls, Darwin, Lamont, Lauder and Tsukuba TCCON stations are listed in Table 3, including their dates and which molecules were measured on the aircraft. Sample profiles from the HIPPO aircraft over Lamont are shown in Fig. 2 and the derived column-average calibration data are shown in Figs. 4–8. Errors on the FTS measurements are quoted as the 1–σ standard deviations during the duration of the overflight for CO$_2$, CO, CH$_4$ and N$_2$O, and 2–σ standard deviations for H$_2$O, because the atmospheric variability of H$_2$O over the course of a day can be much greater than for the other molecules. Errors computed for the smoothed, integrated aircraft measurements are the sum in quadrature of estimated stratospheric uncertainties and the estimated error on the aircraft or sonde profiles in the troposphere. In all cases (except H$_2$O), the stratospheric uncertainty is a significant component of the total error. The slopes of the calibration curves are listed in Table 4. Errors on the slopes are quoted as standard errors on the best fit, calculated using the errors in both the x and y axis (York et al., 2004) and as 2 standard deviations of the individual measurement ratios.

Our retrieval method is predicted to be both linear and have no intercept. We thus fit the data with a linear least-squares and force a zero intercept. When the least-squares fits are allowed a nonzero y-intercept, all but H$_2$O have a y-intercept that is zero within the uncertainty. To attempt to remove any biases added from errors in the GFIT a priori, the aircraft profile with our best estimate of the stratospheric profile was input as the a priori profile. The same spectra were processed using the standard GFIT
a priori as well. The calibration coefficient for both cases have identical slopes within standard error, suggesting that the GFIT a priori does not add a significant bias to the retrievals. Figures 4–8 show the calibration curves calculated using the aircraft profile as the a priori.

For all molecules, there is excellent consistency between the TCCON calibrations obtained from different sites and seasons. Within measurement error, all stations can be described by a single regression line and hence single calibration factor, with variations around the regression line being explicable by instrumental and site differences. Hence, the reported TCCON columns are produced by dividing the retrieved columns by the values listed in Table 4. The largest uncertainties in the calibration coefficients are for H$_2$O. The H$_2$O calibration curve shows that over a large range of humidities, the FTS instruments are capable of measuring water columns to a good degree of accuracy, but due to the high variability of tropospheric H$_2$O, we do not expect calibration errors as small as for CO$_2$, CH$_4$, CO or N$_2$O.

The uncertainties on the slopes, listed in Table 4, are used to compute the species uncertainty of each molecule, and can be compared with the WMO-recommended intercomparability for the molecules (WMO, 2007). The calibrated TCCON data, though less precise and accurate than the in situ data, provide long time series of precise and accurate total column measurements of atmospheric CO$_2$, CH$_4$, CO and N$_2$O.

6 Conclusions

The TCCON column-averaged dry-air mole fractions of CO$_2$, CO, CH$_4$ and N$_2$O have been calibrated to the WMO scale using aircraft profiles measured between 2004 and 2009. The TCCON H$_2$O columns have been calibrated using radiosonde measurements. The calibration curves show excellent consistency between the different TCCON sites and seasons, and can be described by a single calibration factor for each molecule. Future plans include extending this calibration set using additional HIPPO campaigns and other aircraft programs. We expect that all TCCON sites will eventually
be calibrated using WMO-scale in situ measurements.

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Table 1. TCCON spectral windows and spectroscopy.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Central wavenumber (cm(^{-1}))</th>
<th>Spectral width (cm(^{-1}))</th>
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<td>CO(_2)</td>
<td>6220.00</td>
<td>80.00</td>
<td>Rothman et al. (2009);</td>
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<td>6339.50</td>
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<td>CO</td>
<td>4233.00</td>
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<td></td>
<td>4290.40</td>
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<td>5938.00</td>
<td>116.00</td>
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<td>6002.00</td>
<td>11.10</td>
<td>Frankenberg et al. (2008)</td>
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<td></td>
<td>6076.00</td>
<td>138.00</td>
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<td>N(_2)O</td>
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<td>37.70</td>
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<td>4429.80</td>
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<td>O(_2)</td>
<td>7885.00</td>
<td>240.00</td>
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<td></td>
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### Table 2. Aircraft instrumentation used in this study.

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<th>Instrument</th>
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<td>NCAR Airborne Oxygen (AO₂) Li-840</td>
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<td>HAIS/SWS Vertical Cavity Surface Emitting Laser</td>
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<td>Hygrometer (VCSEL, Zondlo et al., 2010)</td>
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<td>CO</td>
</tr>
<tr>
<td></td>
<td>HAIS/SWS Vertical Cavity Surface Emitting Laser</td>
<td>H₂O</td>
</tr>
<tr>
<td></td>
<td>Hygrometer (VCSEL, Zondlo et al., 2010)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NOAA Unmanned Aircraft Systems Chromatograph for Atmospheric Trace Species (UCATS)</td>
<td>CH₄, H₂O</td>
</tr>
<tr>
<td>Learjet</td>
<td>NOAA Flask Samplers</td>
<td>CO₂, CH₄, CO, N₂O</td>
</tr>
<tr>
<td>Beechcraft King Air 200T</td>
<td>CO₂ Continuous Measurement Equipment (CME)</td>
<td>CO₂</td>
</tr>
<tr>
<td></td>
<td>Li-COR 840 non-dispersive infrared analyser</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hand-operated Flask Sampling Equipment (HSE)</td>
<td>CH₄</td>
</tr>
</tbody>
</table>
Table 3. Aircraft overflights. The TCCON site of the overpass, aircraft campaign name, dates and molecules measured are listed in columns 1–4. In many cases, H₂O sonde profiles were measured along with the aircraft campaign, and those are listed separately in column 4, along with the sonde type.

<table>
<thead>
<tr>
<th>Site</th>
<th>Aircraft campaign</th>
<th>Dates</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Park Falls</td>
<td>INTEX-NA and COBRA-ME</td>
<td>12 Jul–15 Aug 2004</td>
<td>CO₂, CO</td>
</tr>
<tr>
<td></td>
<td>START-08/pre-HIPPO</td>
<td>12 May 2008</td>
<td>CO₂, CO, CH₄, N₂O, H₂O</td>
</tr>
<tr>
<td>Darwin</td>
<td>TWP-ICE</td>
<td>20 Jan–14 Feb 2006</td>
<td>CO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O (RS92-15 Vaisala radiosonde)</td>
</tr>
<tr>
<td>Lamont</td>
<td>HIPPO</td>
<td>30 Jan 2009</td>
<td>CO₂, CO, CH₄, N₂O, H₂O</td>
</tr>
<tr>
<td>Lear</td>
<td></td>
<td>31 Jul–5 Aug 2009</td>
<td>CO₂, CO, CH₄, N₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O (RS92-KL Vaisala radiosonde)</td>
</tr>
<tr>
<td>Lauder</td>
<td>HIPPO</td>
<td>21 Jan 2009</td>
<td>CO₂, CO, CH₄, N₂O, H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O (RS92 Vaisala radiosonde)</td>
</tr>
<tr>
<td>Tsukuba</td>
<td>Beechcraft King Air 200T</td>
<td>7 and 15 Jan 2009</td>
<td>CO₂, CH₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O (RS2-91 Meisei Electric Co., Ltd. radiosonde)</td>
</tr>
</tbody>
</table>
Table 4. TCCON scale factors. The TCCON data are divided by the scale factors to calibrate to the WMO scale. Columns 5 and 6 describe the uncertainties associated with each species, and the WMO-recommended inter-network comparabilities. There are no WMO recommendations on H₂O.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Scale factor (TCCON/Aircraft)</th>
<th>Best fit standard error</th>
<th>TCCON:Aircraft ratio uncertainty (2σ)</th>
<th>Species uncertainty (2σ)</th>
<th>WMO recommendation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.989</td>
<td>0.001</td>
<td>0.002</td>
<td>0.8 ppm</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>0.99</td>
<td>0.02</td>
<td>0.04</td>
<td>4 ppb</td>
<td>2 ppb</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.978</td>
<td>0.002</td>
<td>0.004</td>
<td>7 ppb</td>
<td>2 ppb</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.958</td>
<td>0.005</td>
<td>0.01</td>
<td>3 ppb</td>
<td>0.1 ppb</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.024</td>
<td>0.004</td>
<td>0.1</td>
<td>0.4 ppth</td>
<td>—</td>
</tr>
</tbody>
</table>
Fig. 1. TCCON site locations. The HIPPO flight path is overlaid in solid black, START-08 in solid green, the King Air in black stars (*) and the Lear in black plusses (+).
Fig. 2. Lamont profiles from the 30 January 2009 HIPPO overpass. The colored dots show the aircraft data. The thick grey line in the CO panel shows the mean ACE-FTS CO profile. The thin black lines show the GFIT a priori profile for 30 January 2009 over Lamont. The thick black line is the profile that is integrated.
Fig. 3. An illustration of the HF correction used to determine the best stratospheric profiles. Panel (a) shows the MkIV FTS balloon profiles before correcting with the NCEP tropopause pressure. The tropopause height for the balloon profiles is indicated with the horizontal dotted line. Panel (b) shows the standard GFIT a priori profiles, which uses the NCEP tropopause height (indicated by the horizontal dashed line), pressure, temperature and altitude to scale the gas profiles. Panel (c) shows the adjusted GFIT a priori profiles, using the scale factors from the retrieved HF columns. The thick black dash-dot line shows the altitude shift (0.8 km) from an HF scale factor of 0.9. The correlation between HF and CH$_4$ is preserved for all panels.
Fig. 4. The TCCON calibration curve for CO$_2$. The smoothed aircraft value is $\hat{c}_s$ from Eq. (7).
Fig. 5. As in Fig. 4, but for CO.
Fig. 6. As in Fig. 4, but for CH₄.
Fig. 7. As in Fig. 4, but for N$_2$O.
Fig. 8. As in Fig. 4, but for H_2O.