

Calibration of the Total Carbon Column Observing Network using Aircraft Profile Data

Debra Wunch¹, Geoffrey C. Toon^{2,1}, Paul O. Wennberg^{2,1}, Steven C. Wofsy³, Britton B. Stephens⁴, Marc L. Fischer¹⁰, Osamu Uchino¹⁴, James B. Abshire¹², Peter Bernath^{8,9}, Sebastien C. Biraud¹⁰, Jean-François L. Blavier^{2,1}, Chris Boone⁸, Kenneth P. Bowman¹³, Edward V. Browell¹¹, Teresa Campos⁴, Brian J. Connor⁷, Bruce C. Daube³, Nicholas M. Deutscher⁵, Minghui Diao¹⁵, James W. Elkins¹⁷, Christoph Gerbig¹⁶, Elaine Gottlieb³, David W. T. Griffith⁵, Dale F. Hurst^{18,17}, Rodrigo Jiménez³, Gretchen Keppel-Aleks¹, Eric Kort³, Ronald Macatangay⁵, Toshinobu Machida¹⁴, Hidekazu Matsueda¹⁹, Fred Moore¹⁸, Isamu Morino¹⁴, Sunyoung Park³, John Robinson²⁰, Coleen M. Roehl¹, Yusuke Sawa¹⁹, Vanessa Sherlock⁶, Colm Sweeney¹⁸, Tomoaki Tanaka¹⁴, and Mark A. Zondlo¹⁵

¹California Institute of Technology, Pasadena, CA, USA.

²Jet Propulsion Laboratory, Pasadena, CA, USA.

³Harvard University, Cambridge, MA, USA.

⁴National Center for Atmospheric Research, Boulder, CO, USA.

⁵Center for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia.

⁶National Institute of Water & Atmospheric Research, Wellington, New Zealand.

⁷BC Consulting Limited, Alexandra, New Zealand.

⁸University of Waterloo, Waterloo, ON, Canada.

⁹York University, York, UK.

¹⁰Lawrence Berkeley National Laboratories, Berkeley, CA, USA.

¹¹NASA Langley Research Center, Hampton, VA, USA.

¹²NASA Goddard Space Flight Center, Greenbelt, MD, USA.

¹³Texas A&M University, College Station, TX, USA.

¹⁴National Institute for Environmental Studies, Tsukuba, Japan.

¹⁵Princeton University, Princeton, NJ, USA.

¹⁶Max-Planck-Institut für Biogeochemie, Jena, Germany.

¹⁷National Oceanic and Atmospheric Administration, Boulder, CO, USA.

¹⁸Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA.

¹⁹Meteorological Research Institute, Tsukuba, Japan.

²⁰National Institute of Water & Atmospheric Research, Lauder, New Zealand.

Correspondence to: Debra Wunch (dwunch@gps.caltech.edu)

Abstract. The Total Carbon Column Observing Network (TCCON) produces precise measurements of the column average dry-air mole fractions of CO₂, CO, CH₄, N₂O and H₂O 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 Ob-
servations (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.

15 1 Introduction

The Total Carbon Column Observing Network (TCCON) is a ground-based network of Fourier
transform spectrometers that precisely measure total columns of CO₂, CO, CH₄, N₂O, H₂O, 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 measure-
ment 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 coincidentally 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 (Figure 1). The first TCCON site, located in Park Falls, is described by Washenfelder et al. (2006).

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.

$$X_G = 0.2094 \frac{\text{column}_G}{\text{column}_{O_2}}. \quad (1)$$

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. (Wunch et al., 2010)). However, any errors specific to either column_G or column_{O_2} will create errors in the DMFs of each gas.

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_2O 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 HI-

APER 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 (Figure 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 H₂O measurements on board the aircraft, with additional stratospheric information supplied by the noon-time NCEP/NCAR specific humidity profile for that day. The HIPPO-1 profiles used in this analysis over Lamont are shown in Figure 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) Lamont site during a campaign from July 31, 2009 to August 5, 2009 (Abshire et al., 2010). Lower altitude (0.3 km – 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 am local time.

Many years of bi-weekly Cessna 0-5km 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 January 15 overflight is used, because of heavy cloud cover on January 7. Water profiles were obtained from nearby radiosonde measurements taken 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 ($\mathbf{A}$) must be taken into account. From the aircraft profiles ($\mathbf{x}_h$), an averaging kernel-smoothed profile ($\mathbf{x}_s$) can be computed that, when integrated, can be directly compared with the FTS retrieved total columns. The smoothed
110 profile represents the profile the FTS would retrieve, if it were measuring perfectly (i.e. without spectroscopic errors), given the GFIT a priori profile ($\mathbf{x}_a$) and retrieved profile scale factor (γ). We use equation 4 of Rodgers and Connor (2003),

$$\mathbf{x}_s = \gamma \mathbf{x}_a + \mathbf{A}(\mathbf{x}_h - \gamma \mathbf{x}_a). \quad (2)$$

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 equation 2 is
115 $\gamma \mathbf{x}_a$ and not $\mathbf{x}_a$.

For column measurement calibration, equation 2 is integrated vertically:

$$\hat{c}_s = \gamma c_a + \mathbf{a}^T(\mathbf{x}_h - \gamma \mathbf{x}_a) \quad (3)$$

where $\hat{c}_s$ is the smoothed column-averaged DMF, c_a is the column-averaged DMF from integrating the a priori profile and $\mathbf{a}$ is the FTS dry pressure-weighted column averaging kernel. The $\mathbf{a}^T(\mathbf{x}_h - \gamma \mathbf{x}_a)$ term represents the column averaging kernel-weighted vertical integration of the
120 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:

$$VC_G = \int_0^{P_s} \frac{f_G(p)}{g \cdot m} dp \quad (4)$$

125 where $f_G = f_G^{dry} \cdot (1 - f_{H_2O})$ 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 (ϕ). We distinguish between the true mole fraction (f_G), and the dry mole fraction (f_G^{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: $m = m_{H_2O} \cdot f_{H_2O} + m_{air}^{dry} \cdot (1 - f_{H_2O})$. Substituting these into
130 equation 4 and rearranging yields a useful, numerically integrable relationship to compute VC_G .

$$VC_G = \int_0^{P_s} \frac{f_G^{dry}(p)}{g(z(p), \phi) \cdot m_{air}^{dry} \cdot [1 + f_{H_2O}^{dry}(p) \cdot (m_{H_2O}/m_{air}^{dry})]} dp \quad (5)$$

where f_G^{dry} is the aircraft profile of gas G, $f_{H_2O}^{dry} \equiv \frac{f_{H_2O}}{1 - f_{H_2O}}$, where f_{H_2O} is the H_2O aircraft or sonde profile, $m_{H_2O} = 18.02 \times 10^{-3}/N_A$ kg/molecule, $m_{air}^{dry} = 28.964 \times 10^{-3}/N_A$ 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 equation 3), the column averaging kernel ($a(p)$) must be included
 135 at every level in the integral.

$$VC_{G,ak} = \int_0^{P_s} \frac{f_G^{dry}(p) \cdot a(p)}{g(z(p), \phi) \cdot m_{air}^{dry} \cdot \left[1 + f_{H_2O}^{dry}(p) \cdot (m_{H_2O}/m_{air}^{dry})\right]} dp \quad (6)$$

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

$$\hat{c}_s = \gamma c_a + \left(\frac{VC_{G,ak}^{aircraft} - \gamma VC_{G,ak}^{apriori}}{VC_{air}} \right) \quad (7)$$

Aircraft measurements have good accuracy, but are limited in altitude floor and ceiling, and so
 140 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 mea-
 145 surements. 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 July 14, 2004).

For stratospheric CO_2 , the mole fractions are predictable at the 0.3% level, as described in more detail below. For N_2O and CH_4 , the stratospheric mole fractions are more difficult to estimate
 150 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_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
 155 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-
 160 CO_2 , 2006).

The GFIT CH_4 , N_2O , 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_4 -HF and N_2O -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
 165 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 ~15% 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 N₂O and CH₄.

170 The magnitude of the deviation of the HF column from the a priori HF column is used to adjust the CH₄ and N₂O stratospheric profiles to generate our best estimate of the “true” stratospheric profile for a given overpass. An illustration of this is in Figure 3. Note that even small errors in the stratospheric a priori profile of N₂O will be very important in this analysis, because the N₂O column averaging kernels increase significantly in the stratosphere. The stratospheric error contribution
175 for both CH₄ and N₂O 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 CH₄ and N₂O, 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
180 ACE-FTS instrument (Bernath et al., 2005) were averaged within one month of the overpass and ± 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).

185 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 H₂O 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 ~5 km, errors in the upper altitude water profile do not significantly affect the total column. The errors on the H₂O columns are estimated to be 10% of the total
190 column.

To estimate the H₂O 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
195 at Lamont and Darwin.

Once full profiles of the gas of interest and H₂O are generated on a fine altitude or pressure grid, the profiles are integrated via equation 5 or 6, and the smoothed profile is computed via equation 7.

5 Results

Aircraft overflights of the Park Falls, Darwin, Lamont, Lauder and Tsukuba TCCON stations are
200 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 Figure 2 and the derived column-average calibration data are shown in Figures 4–8. Errors on the FTS measurements are quoted as the 1- σ standard deviations during the duration of the overflight for CO₂, CO, CH₄ and N₂O, and 2- σ standard deviations for H₂O, because the atmospheric variability of H₂O 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 H₂O), 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 H₂O 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 H₂O. The H₂O 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 H₂O, we do not expect calibration errors as small as for CO₂, CH₄, CO or N₂O.

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 CO₂, CH₄, CO and N₂O.

6 Conclusions

235 The TCCON column-averaged dry-air mole fractions of CO₂, CO, CH₄ and N₂O have been calibrated to the WMO scale using aircraft profiles measured between 2004 and 2009. The TCCON H₂O 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.

Acknowledgements. NCEP Reanalysis data is provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at <http://www.cdc.noaa.gov/>. Data were obtained through the Atmospheric Radiation Measurement (ARM) Program sponsored by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research under contract DE-AC02-05CH11231. Data were generated by the National Oceanic and Atmospheric Administration (NOAA), Earth System Research Laboratory (ESRL), Carbon Cycle Greenhouse Gases Group, including flask data from Andrews et al. (2009). US funding for TCCON comes from NASA's Terrestrial Ecology Program, the Orbiting Carbon Observatory project and the DOE/ARM Program. ACE is funded primarily by the Canadian Space Agency. Support for the Learjet-25 measurements was provided by the NASA ASCENDS development and ESTO IIP programs. We acknowledge funding for Darwin and Wollongong from the Australian Research Council, Projects DP0879468 and LP0562346 with the Australian Greenhouse Office. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

References

- Abshire, J. B., Riris, H., Allan, G. R., Weaver, C., Mao, J., Sun, X., and Hasselbrack, W.: Pulsed Airborne Lidar
255 Measurements of Atmospheric CO₂ Column Absorption from 3-13 km Altitudes, in: 25th International Laser
Radar Conference, 2010.
- Andrews, A., Boering, K., Daube, B., Wofsy, S., Loewenstein, M., Jost, H., Podolske, J., Webster, C., Herman,
R., Scott, D., et al.: Mean ages of stratospheric air derived from in situ observations of CO₂, CH₄, and N₂O,
Journal of Geophysical Research-Atmospheres, 106, 2001.
- 260 Andrews, A., Kofler, J., Bakwin, P., Zhao, C., and Tans, P.: Carbon Dioxide and Carbon Monoxide Dry
Air Mole Fractions from the NOAA ESRL Tall Tower Network, 1992-2009, Version: 2010-03-29, ftp:
//ftp.cmdl.noaa.gov/ccg/towers/, 2009.
- Bernath, P., McElroy, C., Abrams, M., Boone, C., Butler, M., Camy-Peyret, C., Carleer, M., Clerbaux, C.,
Coheur, P., Colin, R., et al.: Atmospheric chemistry experiment (ACE): mission overview, Geophys. Res.
265 Lett, 32, 2005.
- Clerbaux, C., George, M., Turquety, S., Walker, K. A., Barret, B., Bernath, P., Boone, C., Borsdorff, T., Cam-
mas, J. P., Catoire, V., Coffey, M., Coheur, P.-F., Deeter, M., De Mazire, M., Drummond, J., Duchatelet, P.,
Dupuy, E., de Zafra, R., Eddounia, F., Edwards, D. P., Emmons, L., Funke, B., Gille, J., Griffith, D. W. T.,
Hannigan, J., Hase, F., Hpfner, M., Jones, N., Kagawa, A., Kasai, Y., Kramer, I., Le Flochmon, E., Livesey,
270 N. J., Lopez-Puertas, M., Luo, M., Mahieu, E., Murtagh, D., Ndlec, P., Pazmino, A., Pumphrey, H., Ricaud,
P., Rinsland, C. P., Robert, C., Schneider, M., Senten, C., Stiller, G., Strandberg, A., Strong, K., Sussmann,
R., Thouret, V., Urban, J., and Wiacek, A.: CO measurements from the ACE-FTS satellite instrument: data
analysis and validation using ground-based, airborne and spaceborne observations, Atmospheric Chemistry
and Physics, 8, 2569–2594, <http://www.atmos-chem-phys.net/8/2569/2008/>, 2008.
- 275 Deutscher, N. M., Griffith, D. W. T., Bryant, G. W., Wennberg, P. O., Toon, G. C., Washenfelder, R. A., Keppel-
Aleks, G., Wunch, D., Yavin, Y., Allen, N. T., Blavier, J.-F., Jimnez, R., Daube, B. C., Bright, A. V., Matross,
D. M., Wofsy, S. C., and Park, S.: Total column CO₂ measurements at Darwin, Australia – site description
and calibration against in situ aircraft profiles, Atmospheric Measurement Techniques Discussions, 3, 989–
1021, doi:10.5194/amtd-3-989-2010, <http://www.atmos-meas-tech-discuss.net/3/989/2010/>, 2010.
- 280 Dlugokencky, E., Myers, R., Lang, P., Masarie, K., Crotwell, A., Thoning, K., Hall, B., Elkins, J., and Steele,
L.: Conversion of NOAA atmospheric dry air CH₄ mole fractions to a gravimetrically prepared standard
scale, J. Geophys. Res, 110, 2005.
- Frankenberg, C., Warneke, T., Butz, A., Aben, I., Hase, F., Spietz, P., and Brown, L.: Pressure broadening in
the 2ν₃ band of methane and its implication on atmospheric retrievals, Atmos. Chem. Phys, 8, 5061–5075,
285 2008.
- Gerbig, C., Lin, J., Wofsy, S., Daube, B., Andrews, A., Stephens, B., Bakwin, P., and Grainger, C.: Toward
constraining regional-scale fluxes of CO₂ with atmospheric observations over a continent: 2. Analysis of
COBRA data using a receptor-oriented framework, J. Geophys. Res, 108, 10–1029, 2003.
- GLOBALVIEW-CO₂: Cooperative Atmospheric Data Integration Project - Carbon Dioxide, CD-ROM, NOAA
290 GMD, Boulder, Colorado, 2006.
- Gordon, I. E., Kass, S., Campargue, A., and Toon, G. C.: First identification of the $a^1\Delta_g - X^3\Sigma_g^-$ electric
quadrupole transitions of oxygen in solar and laboratory spectra, Journal of Quantitative Spectroscopy &

Radiative Transfer, in press, 2010.

- 295 Hall, B., Dutton, G., and Elkins, J.: The NOAA nitrous oxide standard scale for atmospheric observations, *J. Geophys. Res.*, 112, 2007.
- Jenouvrier, A., Daumont, L., Régalia-Jarlot, L., Tyuterev, V. G., Carleer, M., Vandaele, A. C., Mikhailenko, S., and Fally, S.: Fourier transform measurements of water vapor line parameters in the 4200-6600 cm^{-1} region, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 105, 326 – 355, 2007.
- 300 Keeling, C., Guenther, P., Emanuele III, G., Bollenbacher, A., and Moss, D.: Scripps reference gas calibration system for carbon dioxide-in-nitrogen and carbon dioxide-in-air standards: Revision of 1999 (with addendum), Tech. rep., SIO Reference Series No. 01-11, http://scrippsco2.ucsd.edu/publications/refgas_report_2002.pdf, 2002.
- Keppel-Aleks, G., Wennberg, P., Schneider, T., Honsowetz, N., and Vay, S.: Total column constraints on Northern Hemisphere carbon dioxide surface exchange, in: American Geophysical Union, Fall Meeting 2008, abstract #A43F-03, 2008.
- 305 Lin, J. C., Gerbig, C., Wofsy, S. C., Daube, B. C., Matross, D. M., Chow, V. Y., Gottlieb, E., Andrews, A. E., Pathmathevan, M., and Munger, J. W.: What have we learned from intensive atmospheric sampling field programs of CO_2 ?, *Tellus Series B-Chemical and Physical Meteorology*, 58, 331–343, 2006.
- Luo, M., Cicerone, R., and Russell, J.: Analysis of Halogen Occultation Experiment HF versus CH_4 correlation plots: chemistry and transport implications, *Journal of geophysical research*, 100, 13 927–13 937, 1995.
- 310 May, P., Mather, J., Vaughan, G., Jakob, C., McFarquhar, G., Bower, K., and Mace, G.: The tropical warm pool international cloud experiment, *Bulletin of the American Meteorological Society*, 89, 629–645, 2008.
- Novelli, P., Collins, Jr., J., Myers, R., Sachse, G., and Scheel, H.: Reevaluation of the NOAA/CMDL carbon monoxide reference scale and comparisons with CO reference gases at NASA-Langley and the Fraunhofer Institut, *Journal of Geophysical Research*, 99, 12–833, 1994.
- 315 Pan, L. L., Bowman, K. P., Atlas, E. L., Wofsy, S. C., Zhang, F., Bresch, J. F., Ridley, B. A., Pittman, J. V., Homeyer, C. R., Romashkin, P., and Cooper, W. A.: The Stratosphere-Troposphere Analyses of Regional Transport 2008 Experiment, *Bulletin of the American Meteorological Society*, 91, 327–342, doi:10.1175/2009BAMS2865.1, 2010.
- 320 Rodgers, C. and Connor, B.: Intercomparison of remote sounding instruments, *J. Geophys. Res.*, 108, 4116–4229, 2003.
- Rothman, L., Gordon, I., Barbe, A., Benner, D., Bernath, P., Birk, M., Boudon, V., Brown, L., Campargue, A., Champion, J., et al.: The HITRAN 2008 molecular spectroscopic database, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2009.
- 325 Singh, H., Brune, W., Crawford, J., Jacob, D., and Russell, P.: Overview of the summer 2004 Intercontinental Chemical Transport Experiment-North America (INTEX-NA), *Journal of Geophysical Research (Atmospheres)*, 111, 2006.
- Tanaka, T., Morino, I., Machida, T., Kojima, H., Yamaguchi, K., and Emi Ota, T. K., Oyama, H., Oguma, H., Uchino, O., and Yokota, T.: Aircraft Measurement of Carbon Dioxide for Calibration of Ground-Based High-Resolution Fourier Transform Spectrometer at Tsukuba, in: 8th International Carbon Dioxide Conference, September 13-19, Jena, Germany, 2009.
- 330 Toon, G.: The JPL MkIV interferometer, *Optics & Photonics News*, 2, 19–21, 1991.

- Toth, R.: Measurements of positions, strengths and self-broadened widths of H₂O from 2900 to 8000 cm⁻¹: line strength analysis of the 2nd triad bands, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 94, 51–107, 2005.
- Toth, R., Brown, L., Miller, C., Malathy Devi, V., and Benner, D.: Spectroscopic database of CO₂ line parameters: 4300–7000cm⁻¹, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 109, 906–921, 2008.
- Washenfelter, R., Wennberg, P., and Toon, G.: Tropospheric methane retrieved from ground-based near-IR solar absorption spectra, *Geophys. Res. Lett.*, 30, 2226, 2003.
- Washenfelter, R., Toon, G., Blavier, J., Yang, Z., Allen, N., Wennberg, P., Vay, S., Matross, D., and Daube, B.: Carbon dioxide column abundances at the Wisconsin Tall Tower site, *J. Geophys. Res.*, 111, D22305, doi:10.1029/2006JD007154, 2006.
- WMO: 14th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, Tech. rep., WMO/IAEA, Helsinki, Finland, <http://www.fmi.fi/kuvat/14thExpertsRecom.pdf>, 2007.
- Wofsy, S. C., Daube, B. C., Jimenez, R., Kort, E., Pittman, J. V., Park, S., Commene, R., Xiang, B., Santoni, G., Jacob, D., Fisher, J., Pickett-Heaps, C., Wang, H., Wecht, K., Wang, Q.-Q., Stephens, B. B., Schertz, S., Romashkin, P., Campos, T., Haggerty, J., Cooper, W. A., Rogers, D., Beaton, S., Elkins, J. W., Fahey, D., Gao, R., Moore, F., Montzka, S. A., Schwartz, J. P., Hurst, D., Miller, B., Sweeney, C., Oltmans, S., Nance, D., Hints, E., Dutton, G., Watts, L. A., Spackman, R., Rosenlof, K., Ray, E., Zondlo, M., Diao, M., Mahoney, M. J., Chahine, M., Olsen, E., Keeling, R., Bent, J., Atlas, E. A., Lueb, R., Patra, P., Ishijima, K., Engelen, R., Nassar, R., Jones, D. B., and Mikaloff-Fletcher, S.: HIPPO: Fine grained, global scale measurements for determining rates for transport, surface emissions, and removal of climatically important atmospheric gases and aerosols, *Philosophical Transactions of the Royal Society A*, under review, 2010.
- Wunch, D., Wennberg, P., Toon, G., Keppel-Aleks, G., and Yavin, Y.: Emissions of greenhouse gases from a North American megacity, *Geophys. Res. Lett.*, 36, L15810, doi:10.1029/2009GL039825, 2009.
- Wunch, D., Toon, G. C., Blavier, J.-F. L., Washenfelter, R., Notholt, J., Connor, B. J., Griffith, D. W. T., Sherlock, V., and Wennberg, P. O.: The Total Carbon Column Observing Network (TCCON), *Philosophical Transactions of the Royal Society A*, accepted, 2010.
- Yang, Z., Wennberg, P., Cageao, R., Pongetti, T., Toon, G., and Sander, S.: Ground-based photon path measurements from solar absorption spectra of the O₂ A-band, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 90, 309–321, 2005.
- Yang, Z., Washenfelter, R., Keppel-Aleks, G., Krakauer, N., Randerson, J., Tans, P., Sweeney, C., and Wennberg, P.: New constraints on Northern Hemisphere growing season net flux, *Geophysical Research Letters*, 34, L12 807, 2007.
- York, D., Evensen, N., Martínez, M., and Delgado, J.: Unified equations for the slope, intercept, and standard errors of the best straight line, *American Journal of Physics*, 72, 367, 2004.
- Zhao, C. and Tans, P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, *Journal of Geophysical Research*, 111, D08S09, 2006.
- Zondlo, M. A., Paige, M., Massick, S., and Silver, J.: Vertical Cavity Laser Hygrometer for the National Science Foundation Gulfstream-V Aircraft, *J. Geophys. Res.-Atmos.*, submitted, 2010.

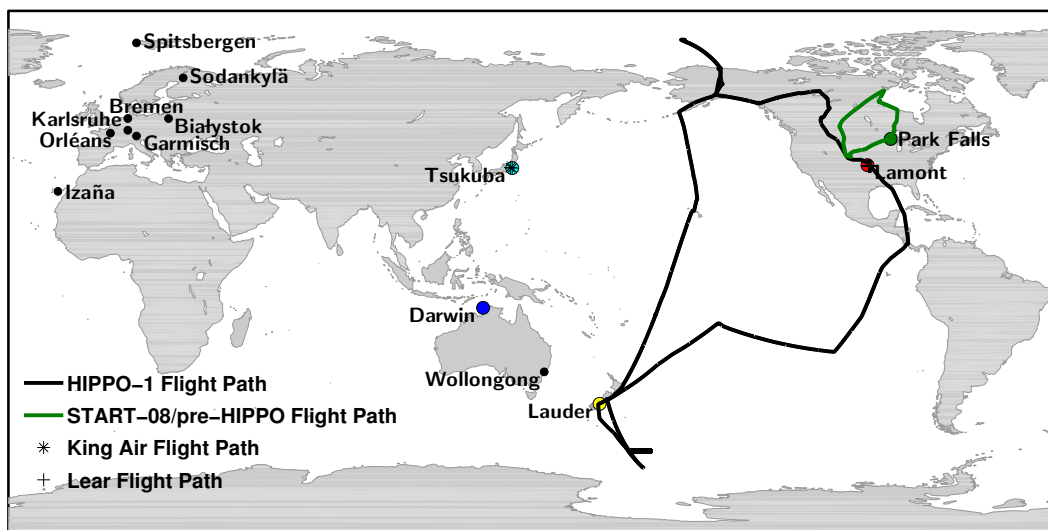


Fig. 1. TCCON Site Locations. The HIPPO flight path is overlaid in solid black, START-08 in solid green, the King Air in black stars (*) and the Lear in black plusses (+).

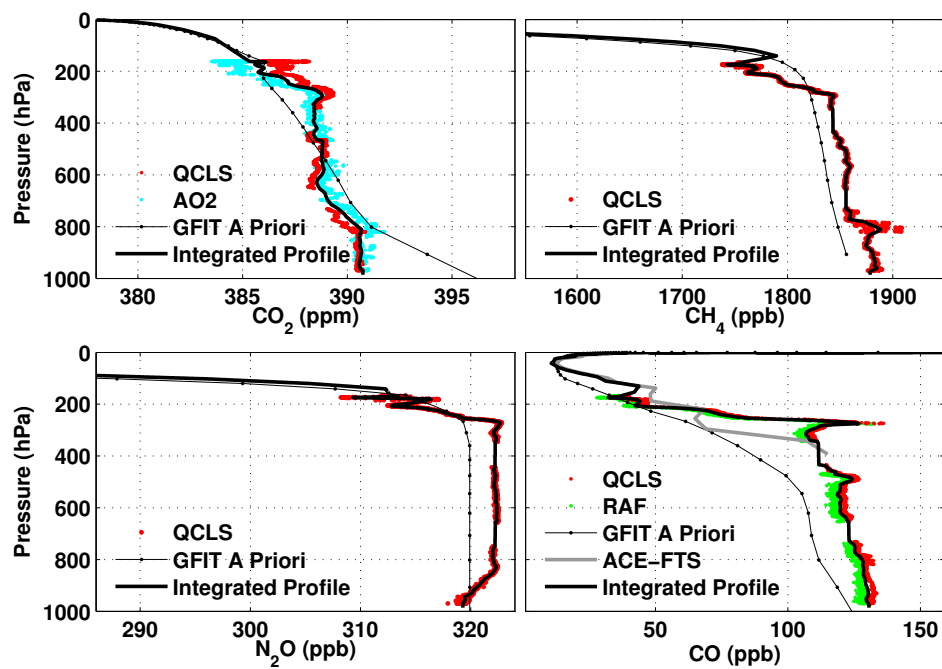


Fig. 2. Lamont profiles from the January 30, 2009 HIPPO overpass. The colored dots show the aircraft data. The thick grey line in the CO panel shows the mean ACE-FTS CO profile. The thin black lines show the GFIT a priori profile for January 30, 2009 over Lamont. The thick black line is the profile that is integrated.

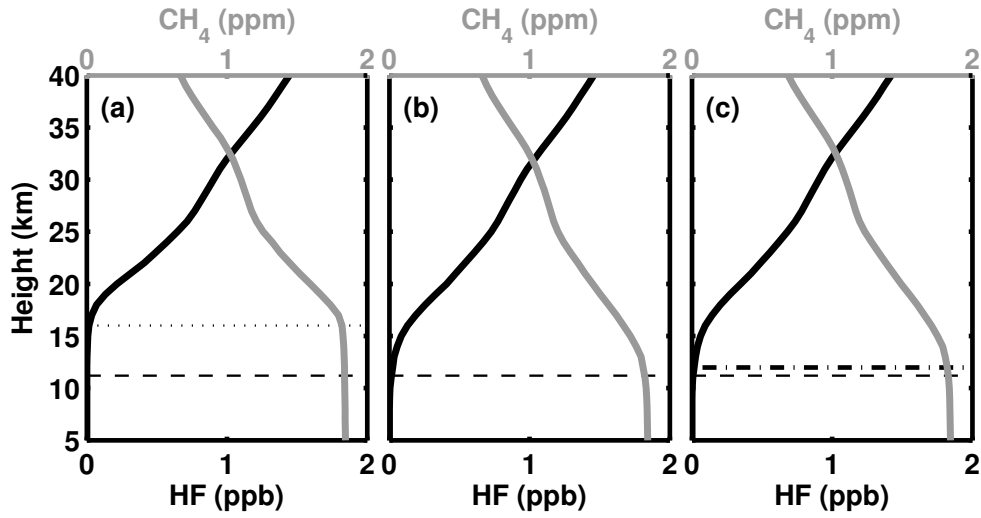


Fig. 3. An illustration of the HF correction used to determine the best stratospheric profiles. Panel (a) shows the MkIV FTS balloon profiles before correcting with the NCEP tropopause pressure. The tropopause height for the balloon profiles is indicated with the horizontal dotted line. Panel (b) shows 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.

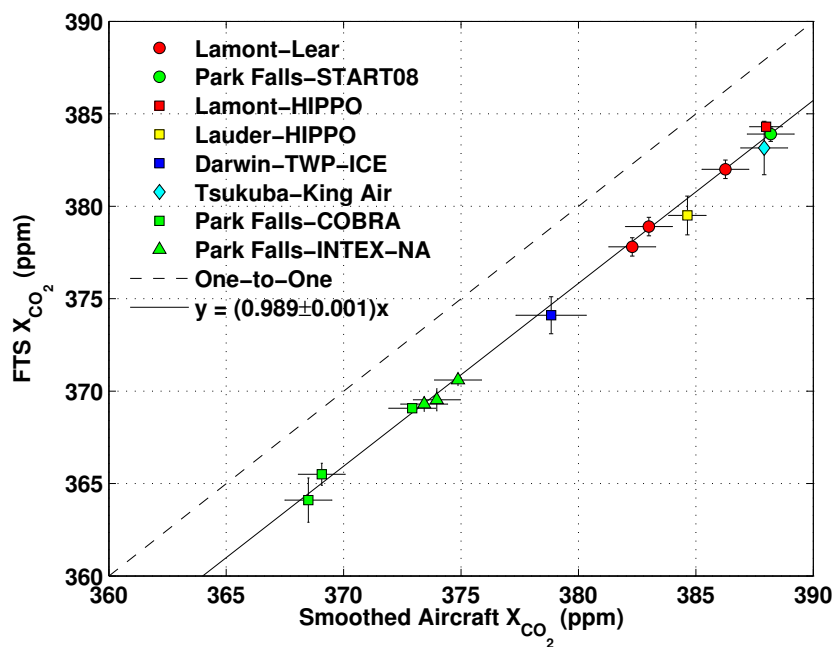


Fig. 4. The TCCON calibration curve for CO₂. The smoothed aircraft value is $\hat{c}_s$ from equation 7.

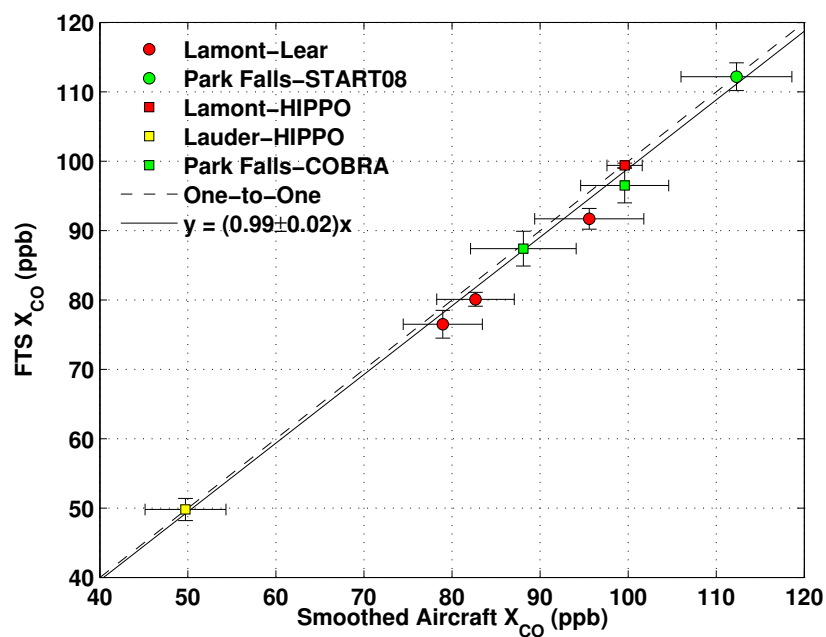


Fig. 5. As in Fig. 4, but for CO.

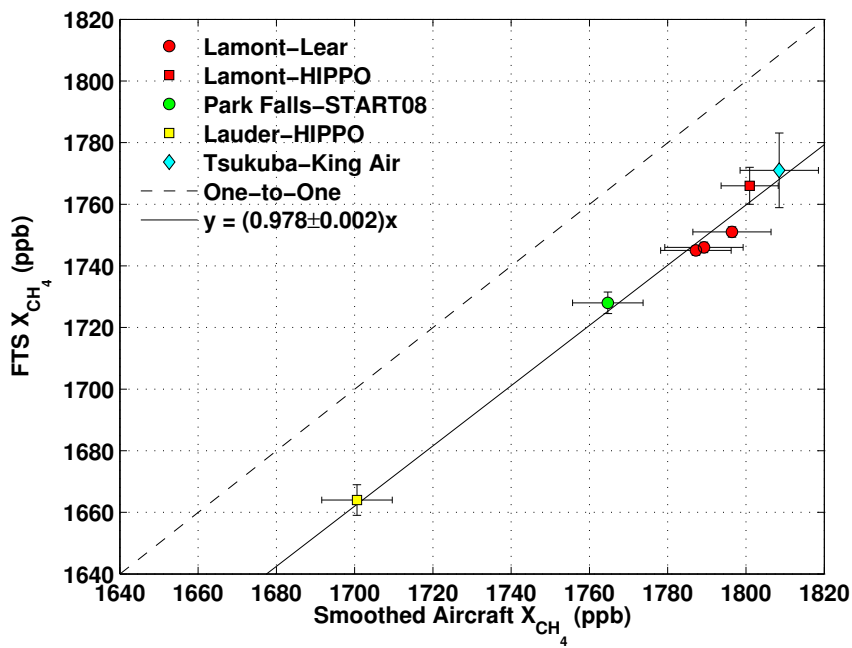


Fig. 6. As in Fig. 4, but for CH_4 .

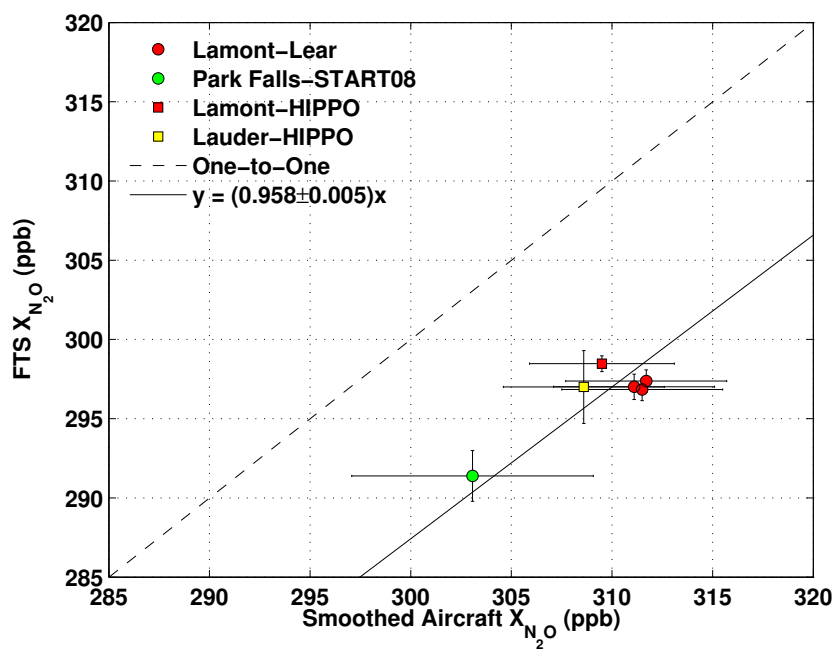


Fig. 7. As in Fig. 4, but for N_2O .

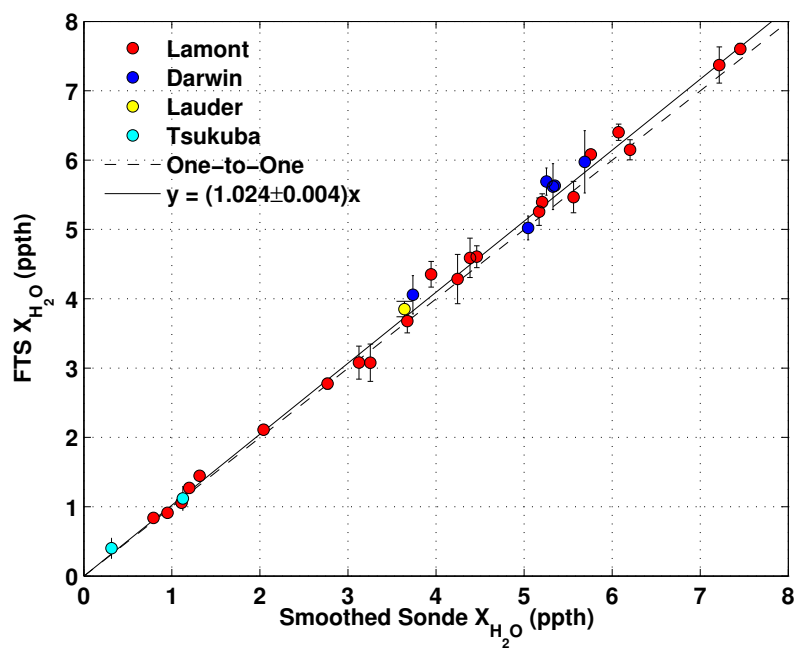


Fig. 8. As in Fig. 4, but for H_2O .

Table 1. TCCON spectral windows and spectroscopy.

Molecules	Central Wavenumber (cm^{-1})	Spectral Width (cm^{-1})	Spectroscopic Line List
CO ₂	6220.00	80.00	Rothman et al. (2009)
	6339.50	85.00	Toth et al. (2008)
CO	4233.00	48.60	Rothman et al. (2009)
	4290.40	56.80	
CH ₄	5938.00	116.00	Rothman et al. (2009) Frankenberg et al. (2008)
	6002.00	11.10	
	6076.00	138.00	
N ₂ O	4395.50	37.70	Rothman et al. (2009)
	4429.80	23.60	
O ₂	7885.00	240.00	Rothman et al. (2009)
			Yang et al. (2005)
			Gordon et al. (2010)
HF	4038.95	0.32	Rothman et al. (2009)
H ₂ O	6076.90	3.85	Rothman et al. (2009) Toth (2005) Jenouvrier et al. (2007)
	6099.35	0.95	
	6125.85	1.45	
	6177.30	0.83	
	6255.95	3.60	
	6301.35	7.90	
	6392.45	3.10	
	6401.15	1.15	
	6469.60	3.50	

Table 2. Aircraft instrumentation used in this study.

Flight	Instrument	Measurement
HIPPO	HAIS/Harvard Quantum Cascade Laser Spectrometer (QCLS)	CO ₂ , CH ₄ , CO, N ₂ O
	NCAR Airborne Oxygen (AO2) Li-840	CO ₂
	NCAR Research Aviation Facility (RAF)	CO
	HAIS/SWS Vertical Cavity Surface Emitting Laser	H ₂ O
	Hygrometer (VCSEL, Zondlo et al., 2010)	
START-08/pre-HIPPO	HAIS/Harvard Quantum Cascade Laser Spectrometer (QCLS)	CO ₂ , CO, N ₂ O
	NCAR Airborne Oxygen (AO2) Li-840	CO ₂
	NCAR Research Aviation Facility (RAF)	CO
	HAIS/SWS Vertical Cavity Surface Emitting Laser	H ₂ O
	Hygrometer (VCSEL, Zondlo et al., 2010)	
	NOAA Unmanned Aircraft Systems Chromatograph for Atmospheric Trace Species (UCATS)	CH ₄ , H ₂ O
Learjet	NOAA Flask Samplers	CO ₂ , CH ₄ , CO, N ₂ O
Beechcraft King Air 200T	CO ₂ Continuous Measurement Equipment (CME)	CO ₂
	Li-COR 840 non-dispersive infrared analyser	
	Hand-operated Flask Sampling Equipment (HSE)	CH ₄

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.

Site	Aircraft Campaign	Dates	Species
Park Falls	INTEX-NA and COBRA-ME	July 12–August 15, 2004	CO ₂ , CO
	START-08/pre-HIPPO	May 12, 2008	CO ₂ , CO, CH ₄ , N ₂ O, H ₂ O
Darwin	TWP-ICE	January–February 2006	CO ₂ H ₂ O (RS92-15 Vaisala radiosonde)
Lamont	HIPPO	January 30, 2009	CO ₂ , CO, CH ₄ , N ₂ O, H ₂ O
	Lear	July 31–August 5, 2009	CO ₂ , CO, CH ₄ , N ₂ O H ₂ O (RS92-KL Vaisala radiosonde)
Lauder	HIPPO	January 21, 2009	CO ₂ , CO, CH ₄ , N ₂ O, H ₂ O H ₂ O (RS92 Vaisala radiosonde)
Tsukuba	Beechcraft King Air 200T	January 7 and 15, 2009	CO ₂ , CH ₄ H ₂ O (RS2-91 Meisei Electric Co., Ltd. radiosonde)

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.

Molecule	Scale Factor (TCCON/Aircraft)	Best Fit Standard Error	TCCON:Aircraft Ratio Uncertainty (2σ)	Species Uncertainty (2σ)	WMO Recommendation
CO ₂	0.989	0.001	0.002	0.8 ppm	0.1 ppm
CO	0.99	0.02	0.04	4 ppb	2 ppb
CH ₄	0.978	0.002	0.004	7 ppb	2 ppb
N ₂ O	0.958	0.005	0.01	3 ppb	0.1 ppb
H ₂ O	1.024	0.004	0.1	0.4 ppth	—