Appendix: Error Characterization

(A1) Errors in TCCON column-averaged CO_2

In this section, we develop the error characterization for (1) the estimates of TCCON CO_2 column averages from the profile retrievals for a 4-hour time window around each aircraft CO_2 profile measurement and (2) comparisons of TCCON estimates against forty-one aircraft profiles.

As discussed in the text (Section 4), the retrieval vector is defined by:

$$\boldsymbol{\gamma} = \begin{bmatrix} \gamma_{1[\mathrm{CO_2}]} \\ \vdots \\ \gamma_{10[\mathrm{CO_2}]} \\ \gamma_{[\mathrm{H_2O}]} \\ \gamma_{[\mathrm{HDO}]} \\ \gamma_{[\mathrm{CH_4}]} \\ \gamma_{\mathrm{cl}} \\ \gamma_{\mathrm{ct}} \\ \gamma_{\mathrm{fs}} \\ \gamma_{\mathrm{zo}} \end{bmatrix} \qquad (A1.1)$$

Each element of $\boldsymbol{\gamma}$ is a ratio between the state vector ($\boldsymbol{x}$) and its *a priori* ($\boldsymbol{x_a}$). For the target gas CO_2, altitude dependent scaling factors are retrieved. For other interferential gases, a constant scaling factor for the whole profile is retrieved. The last four are for the instrument parameters (continuum level: 'cl', continuum title: 'ct', frequency shift: 'fs', and zero level offset: 'zo'). To obtain a concentration profile, the retrieved scaling factors are mapped from the retrieval grid (i.e. 10 levels for CO_2 and 1 level for other three gases) to the 71 forward model levels.

$$\boldsymbol{\beta} = \mathbf{M}\boldsymbol{\gamma} \qquad (A1.2)$$

where $\mathbf{M} = \frac{\partial \boldsymbol{\beta}}{\partial \boldsymbol{\gamma}}$ is a linear mapping matrix relating retrieval levels to the forward model altitude grid. Multiplying the scaling factor ($\boldsymbol{\beta}$) on the forward model level to the concentration *a priori* ($\boldsymbol{x_a}$) gives the estimates of the gas profile. We define $\mathbf{M}_{\boldsymbol{x}} = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{\beta}}$ where $\mathbf{M}_{\boldsymbol{x}}$ is a diagonal matrix filled by the concentration *a priori* ($\boldsymbol{x_a}$):

$$\widehat{\boldsymbol{x}} = \mathbf{M}_x \widehat{\boldsymbol{\beta}} \qquad (A1.3)$$

From Eq. (A1.3), it follows that $\boldsymbol{x_a} = \mathbf{M}_x \boldsymbol{\beta_a}$ and $\boldsymbol{x} = \mathbf{M}_x \boldsymbol{\beta}$. The Jacobian matrix of retrieved parameter with respect to the radiance is

$$\mathbf{K}_{\boldsymbol{\gamma}} = \frac{\partial \boldsymbol{L}(\mathbf{M}\boldsymbol{\gamma})}{\partial \boldsymbol{\gamma}} \qquad (A1.4)$$

Using the chain rule, we can obtain the equation relating the retrieval Jacobians to the full-state Jacobian

$$\frac{\partial \boldsymbol{L}}{\partial \boldsymbol{\gamma}} = \frac{\partial \boldsymbol{L}}{\partial \boldsymbol{x}} \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{\beta}} \frac{\partial \boldsymbol{\beta}}{\partial \boldsymbol{\gamma}} \qquad (A1.5)$$

or

$$\mathbf{K}_{\gamma} = \mathbf{K}_x \mathbf{M}_x \mathbf{M} = \mathbf{K}_{\beta} \mathbf{M} \qquad (A1.6)$$

If the estimated state is "close" to the true state, then the estimated state for a single measurement can be expressed as a linear retrieval equation (Rodgers, 2000):

$$\widehat{\boldsymbol{\beta}} = \boldsymbol{\beta_a} + \mathbf{A}_{\beta}(\boldsymbol{\beta} - \boldsymbol{\beta_a}) + \mathbf{M}\mathbf{G}_{\gamma}\boldsymbol{\varepsilon_n} + \sum_{\boldsymbol{l}} \mathbf{M}\mathbf{G}_{\gamma}\mathbf{K}_{\boldsymbol{b}}^{\boldsymbol{l}} \Delta \boldsymbol{b}^{\boldsymbol{l}} \qquad (A1.7)$$

where $\boldsymbol{\varepsilon_n}$ is a zero-mean noise vector with covariance $\mathbf{S_e}$ and the vector $\Delta \boldsymbol{b}^{\boldsymbol{l}}$ is the error in true state of parameters (l) that also affect the modeled radiance, e.g. temperature, interfering gases, spectroscopy. The $\mathbf{K}_{\boldsymbol{b}}^{\boldsymbol{l}}$ is the Jacobian of parameter (l). In this study, we found the systematic error is primarily due to the temperature uncertainty ($\boldsymbol{\varepsilon_T}$) and spectroscopic error ($\boldsymbol{\varepsilon_L}$). $\mathbf{G}_\gamma$ is the gain matrix, which is defined by

$$\mathbf{G}_\gamma = \frac{\partial \boldsymbol{\gamma}}{\partial \boldsymbol{L}} = (\mathbf{K}_\gamma^{\mathrm{T}} \mathbf{S}_{\mathbf{e}}^{-1} \mathbf{K}_\gamma + \mathbf{S}_{\mathbf{a}}^{-1})^{-1} \mathbf{K}_\gamma^{\mathrm{T}} \mathbf{S}_{\mathbf{e}}^{-1} \quad (A1.8)$$

The averaging kernel for $\boldsymbol{\beta}$ in forward model dimension is

$$\mathbf{A}_{\boldsymbol{\beta}} = \mathbf{M}\mathbf{G}_\gamma \mathbf{K}_{\boldsymbol{\beta}} \qquad (A1.9)$$

We can define $\mathbf{A}_x = \mathbf{M}_x \mathbf{A}_{\boldsymbol{\beta}} \mathbf{M}_x^{-1}$ as the averaging kernel for $\boldsymbol{x}$. In order to convert Eq. ($A1.7$) to the state vector of concentration ($\hat{\boldsymbol{x}}$), we apply Eq. ($A1.7$) into Eq. ($A1.3$) and obtain:

$$\hat{\boldsymbol{x}} = \boldsymbol{x_a} + \mathbf{A}_x(\boldsymbol{x} - \boldsymbol{x_a}) + \mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\boldsymbol{\varepsilon_n}$$
$$+\mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_T\boldsymbol{\varepsilon_T} + \mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_L\boldsymbol{\varepsilon_L} \qquad (A1.10)$$

The temperature uncertainty ($\boldsymbol{\varepsilon_T}$) and spectroscopic error ($\boldsymbol{\varepsilon_L}$) represent the systematic errors ($\Delta\boldsymbol{b^l}$).

A1.1 Total error budget

The error for a single retrieval is

$$\boldsymbol{\delta}\hat{\boldsymbol{x}} = \hat{\boldsymbol{x}} - \boldsymbol{x} = (\mathbf{I} - \mathbf{A}_x)(\boldsymbol{x_a} - \boldsymbol{x}) + \mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\boldsymbol{\varepsilon_n}$$
$$+\mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_T\boldsymbol{\varepsilon_T} + \mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_L\boldsymbol{\varepsilon_L} \qquad (A1.11)$$

The second order statistics for the error is

$$\mathbf{S}_{\delta\hat{x}} = \hat{\mathbf{S}}_{\mathrm{sm}} + \hat{\mathbf{S}}_{\mathrm{m}} + \hat{\mathbf{S}}_T + \hat{\mathbf{S}}_L\,, \qquad (A1.12)$$

where the smoothing error covariance is

$$\hat{\mathbf{S}}_{\mathbf{sm}} = (\mathbf{I} - \mathbf{A}_x)\mathbf{S}_a(\mathbf{I} - \mathbf{A}_x)^{\mathbf{T}} \qquad (A1.23);$$

a measurement error covariance is

$$\hat{\mathbf{S}}_{\mathbf{m}} = \mathbf{M}_x\mathbf{MGS}_{\mathbf{e}}(\mathbf{M}_x\mathbf{MG})^{\mathbf{T}} \qquad (A1.24);$$

and two systematic error covariance matrices are

$$\hat{\mathbf{S}}_T = \mathbf{M}_x\mathbf{MGK}_T\mathbf{S}_T(\mathbf{M}_x\mathbf{MGK}_T)^{\mathbf{T}} \qquad (A1.25);$$

$$\hat{\mathbf{S}}_L = \mathbf{M}_x\mathbf{MGK}_L\mathbf{S}_L(\mathbf{M}_x\mathbf{MGK}_L)^{\mathbf{T}} \qquad (A1.26)$$

$\mathbf{S_a}$ is the *a priori* covariance for CO_2, $\mathbf{S_e}$ is the covariance describing the TCCON measurement noise, $\mathbf{S}_T$ is the *a priori* covariance for temperature and is based on the *a priori* covariance used for the Aura TES temperature retrievals (Worden et al., 2004); this temperature covariance is based on the expected uncertainty in the re-analysis fields that are inputs to the TES retrievals. $\mathbf{S}_L$ is the covariance associated with spectroscopic error.

A1.2 Individual error budget terms

For comparisons of TCCON retrievals to each aircraft profile we choose the TCCON measurements taken within a 4-hour time window centered about the aircraft measurement. This time window is short enough so that we can assume the atmospheric state hasn't changed but it is also long enough that there are enough samples of retrievals for good statistics (e.g. ~100 samples).

There are forty-one aircraft measurements that measured CO_2 profiles over Lamont in 2009. On any given day (or *i*th day), we have n_i TCCON retrievals within a 4-hour time window around aircraft measurement where n_i varies by day (or aircraft profile comparison). The difference of the mean of these retrievals to the aircraft measurement is the error on that day. The average of the errors from these forty-one comparison estimates the mean bias error. Which term contributes to the uncertainties will be discuss in follow.

A1.2.1 Error due to extrapolation of CO_2 above aircraft profile

In reality, the true state ($\boldsymbol{x}$) is unknown and can only be estimated by our best measurements, such as by aircraft, which have a precision of 0.02 ppm. With the validation standard, the error in the retrieval ($\boldsymbol{\delta\hat{x}}$) can be estimated by the comparison of the retrieved state vector ($\boldsymbol{\hat{x}}$) to the validation standard ($\boldsymbol{\hat{x}_{std}}$). In order to do an inter-comparison of the measurements from two different instruments, we apply a smoothing operator described in Rodgers and Connor (2003) to the complete profile ($\boldsymbol{x_{FLT}}$) based on aircraft measurement so that it is smoothed by the averaging kernel and *a priori* constraint from the TCCON profile retrieval:

$$\boldsymbol{\hat{x}_{std}} = \boldsymbol{x_a} + \mathbf{A}_x(\boldsymbol{x_{FLT}} - \boldsymbol{x_a}) \qquad (A1.27)$$

$\boldsymbol{\hat{x}_{std}}$ is the profile that would be retrieved from TCCON measurements for the same air sampled by the aircraft without the presence of other errors. $\boldsymbol{x_{FLT}}$ is the complete CO_2 profile based on aircraft measurement.

Several aircraft only measure CO_2 up to approximately 6 km, but three of them go up to 10 km or higher. Therefore, the lower part of $\boldsymbol{x_{FLT}}$ is from the direct aircraft measurements. Above that, the TCCON *a priori* is scaled to the measured CO_2 values at the top of the aircraft measurement so that the profile is continuously extended up to 71 km. We use this approximation because the free tropospheric CO_2 is well mixed (vertical variations in free troposphere is less than 1 ppm) (Wofsy et al., 2011). Then the complete profile based on the aircraft measurement is

$$\boldsymbol{x_{FLT}} = \begin{bmatrix} \boldsymbol{x_{FLT}^{meas}} \\ \boldsymbol{\lambda x_a^F} \end{bmatrix} = \boldsymbol{x} - \boldsymbol{\delta x_{FLT}} = \boldsymbol{x} - \begin{bmatrix} \boldsymbol{\delta x_{FLT}^{meas}} \\ \boldsymbol{x^F} - \boldsymbol{\lambda x_a^F} \end{bmatrix} \qquad (A1.28)$$

where $\boldsymbol{x_{FLT}^{meas}}$ is the direct aircraft measurements in the lower atmosphere, which has been mapped to forward model grid. $\boldsymbol{\delta x_{FLT}^{meas}}$ is its unknown error relative to the 'truth' and is order of 0.02 ppm. $\boldsymbol{\lambda}$ is the ratio between the CO_2 at the top of aircraft measurement to the *a priori* CO_2 on that level. $\boldsymbol{x_a^F}$ and $\boldsymbol{x^F}$ represent the *a priori* and 'true' state above direct aircraft measurement in the free troposphere and above. $\boldsymbol{\lambda x_a^F}$ is the shifted *a priori* to smoothly extend the profile up to stratosphere. $\boldsymbol{x_{FLT}}$ represents the complete profile based combining *a priori.* $\boldsymbol{\delta x_{FLT}}$ is the unknown error in the $\boldsymbol{x_{FLT}}$ to the true state.

Subtracting Eq. (A1.27) from Eq. (A1.10) results in the following expression:

$$\boldsymbol{\delta\hat{x}} = \boldsymbol{\hat{x}} - \boldsymbol{\hat{x}_{std}} = \mathbf{A}_x\boldsymbol{\delta x_{FLT}} + \mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\boldsymbol{\varepsilon_n}$$
$$+\mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_T\boldsymbol{\varepsilon_T} + \mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_L\boldsymbol{\varepsilon_L} \qquad (A1.29)$$

The second order statistics for the error in the complete aircraft based profile, $\boldsymbol{\delta x_{FLT}}$, is:

$$\mathbf{S}_{\delta x_{FLT}} = \boldsymbol{E}[\boldsymbol{\delta x_{FLT}} - \boldsymbol{E}(\boldsymbol{\delta x_{FLT}})][\boldsymbol{x_{FLT}} - \boldsymbol{E}(\boldsymbol{\delta x_{FLT}})]^{\boldsymbol{T}}$$
$$= \begin{bmatrix} \mathbf{S}_{FLT}^{meas} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}_\mathbf{a}^\mathbf{F} \end{bmatrix} \qquad (A1.30)$$

$\mathbf{S}_{FLT}^{meas}$ is the error covariance for direct aircraft measurements, which is a diagonal matrix with a constant value of the square of 0.02 ppm (the accuracy of aircraft instruments). $\mathbf{S}_\mathbf{a}^\mathbf{F}$ is the sub matrix of TCCON *a priori* covariance matrix above the aircraft measurements. Since we scale the *a priori* to the aircraft data, the actual error covariance in the upper atmosphere should be much smaller than $\mathbf{S}_\mathbf{a}^\mathbf{F}$.

The uncertainty in retrieved column averages driven by the smoothing error can be estimated by

$$\boldsymbol{\sigma}_{sm}(\boldsymbol{\delta X}_{\mathrm{CO_2}}) = \sqrt{\boldsymbol{h}^{\mathrm{T}}\mathbf{A}_x\mathbf{S}_{\delta x_{FLT}}\mathbf{A}_x^{\mathrm{T}}\boldsymbol{h}} \qquad (A1.31)$$

The upper limit of this uncertainty is approximately 0.5 ppm when using the *a priori* covariance in the upper atmosphere where the aircraft measurement is missing (e.g. above 6 km). Since the free troposphere is well mixed and the upper atmosphere is constrained by the aircraft measurement, the actual uncertainty for the validation standard should be much smaller than above estimates. For example, if we assume conservatively that the term, $\mathbf{S}_{\delta x_{FLT}}$, is half the size of the $\mathbf{S_a}$ used to describe our CO_2 covariance, then this term becomes negligible relative to the temperature error.

A1.2.2 measurement error

The measurement noise vector $\boldsymbol{\varepsilon_n}$ is a zero-mean random variable. In a 4-hour time window, the measurement error covariance will drive the variability of the retrieved column averages. The uncertainty in retrieved column averages driven by the measurement error can be estimated by

$$\boldsymbol{\sigma_m}(\boldsymbol{\delta X}_{\mathrm{CO_2}}) = \sqrt{\boldsymbol{h}^{\mathrm{T}}\hat{\mathbf{S}}_{\mathbf{m}}\boldsymbol{h}} \qquad (A1.32)$$

$\hat{\mathbf{S}}_{\mathbf{m}}$ is defined in Eq. (A1.24). We calculate that this term is approximately 0.32 ppm. The error on the mean is related to the number of samples in 4-hour time window:

$$\boldsymbol{\sigma_m}(\boldsymbol{\delta X}_{\mathrm{CO_2}}) = \sqrt{\frac{\boldsymbol{h}^{\mathrm{T}}\hat{\mathbf{S}}_{\mathbf{m}}\boldsymbol{h}}{n_i}} \qquad (A1.33)$$

where n_i is number of retrieval samples within 4-hour on ith day (listed in table 1).

A1.2.3 Temperature error

Within a 4-hour time window, we assume that variations in temperature do not result in variations in the CO_2 estimate; however, the uncertainty in the temperature profiles will result in a bias:

$$\overline{(\boldsymbol{\delta X}_{\mathrm{CO_2}})_{\boldsymbol{T_i}}} = \boldsymbol{h}^{\mathrm{T}}\mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_{\boldsymbol{T}}\boldsymbol{\varepsilon}_{\boldsymbol{T}_i} \qquad (A1.34)$$

However, $\boldsymbol{\varepsilon}_{\boldsymbol{T}_i}$ varies from day to day. The mean bias error from temperature uncertainties over days becomes

$$\overline{(\boldsymbol{\delta X}_{\mathrm{CO_2}})_{\boldsymbol{T}}} = \boldsymbol{h}^{\boldsymbol{T}}\mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_{\boldsymbol{T}}\left(\frac{1}{m}\sum_{\boldsymbol{i=1}}^{\boldsymbol{m}}\boldsymbol{\varepsilon}_{\boldsymbol{T}_i}\right) \quad (A1.35)$$

with a covariance of

$$\boldsymbol{\sigma_T}(\boldsymbol{\delta X}_{\mathrm{CO_2}}) = \sqrt{\boldsymbol{h}^{\mathrm{T}}\hat{\mathbf{S}}_{\mathbf{T}}\boldsymbol{h}} \qquad (A1.36)$$

where $\hat{\mathbf{S}}_{\mathbf{T}}$ is from Eq. (A1.25). The estimate of this term is, on average, approximately 0.69 ppm.

A1.2.4 Spectroscopic error

The spectroscopic error is another significant source of systematic error. Different from temperature error, it does not vary significantly on any time scales and even over different sites (Wunch et al., 2010). Therefore, its covariance is always negligible. However, it is found to be the primary source of the bias error.

$$\overline{(\boldsymbol{\delta X}_{\mathrm{CO_2}})_{\boldsymbol{L}}} = \boldsymbol{h}^{\mathrm{T}}\mathbf{M}_x\mathbf{M}\mathbf{G}_\gamma\mathbf{K}_{\boldsymbol{L}}\boldsymbol{\varepsilon}_{\boldsymbol{L}} \quad (A1.37)$$

The estimate of this term is about -5 ppm. It is mainly due to the error in O_2 cross section.

(A2) Errors in PBL column-averaged CO_2

We estimate the PBL CO_2 by subtracting the TES assimilated free tropospheric CO_2 from the TCCON total column CO_2. The TCCON dry-air total column estimated by weighted to the retrieved O_2 column has a bias of approximately -5.66 ppm. Therefore, we remove the bias using Eq. (9) before subtracting the free tropospheric partial column amount. Because the TCCON estimates and TES/GEOS-Chem estimates are independent estimates of CO_2, the uncertainties in the boundary layer estimates are simply the uncertainties summed in quadrature:

$$\sigma\left(\boldsymbol{\delta X}_{\mathrm{CO_2}}^{\mathrm{PBL}}\right) = \sqrt{\sigma^2\left(\boldsymbol{\delta X}_{\mathrm{CO_2}}^{\mathrm{TES}}\right) + \sigma^2\left(\boldsymbol{\delta X}_{\mathrm{CO_2}}^{\mathrm{TCCON}}\right)} \quad (A2.1)$$

The estimate of this term is 0.90 ppm. The TES assimilated free tropospheric bias error and uncertainty is estimated by the comparison to the free tropospheric estimates from the aircraft-based profile ($\boldsymbol{x_{FLT}}$). The TCCON total column mean bias error and uncertainty has been discussed in previous section Eq. (A1.34) and Eq. (A1.37).

(A3) Estimating the free tropospheric CO_2 column using TES and GEOS-Chem

To estimate the free tropospheric CO_2, retrieved TES CO_2 fields are assimilated into the GEOS-Chem model. GEOS-Chem is a global 3-D chemical transport model (CTM) for atmospheric composition, with sources and additional modifications specific to the carbon cycle as described in (Nassar et al., 2010) and (Kulawik et al., 2011). TES at all pressure levels between 40S and 40N, along with the predicted sensitivity and errors, was assimilated for the year 2009 using 3d-var assimilation. We compare model output with and without assimilation to surface based in situ aircraft measurements from the U.S. DOE Atmospheric Radiation Measurement (ARM) Southern Great Plains site during the ARM-ACME (www.arm.gov/campaigns/aaf2008acme) and HIPPO-2 (hippo.ucar.edu/) mission (Kulawik et al., 2012). We find improvement in the seasonal cycle amplitude in the mid-troposphere at the SGP site, but also discrepancies with HIPPO at remote oceanic sites, particularly outside of the latitude range of assimilation (Kulawik et al., manuscript in preparation).

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