



Impacts of updated spectroscopy on thermal infrared retrievals of methane evaluated with HIPPO data

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Abstract. Errors in the spectroscopic parameters used in the forward radiative transfer model can introduce spatially, temporally, and altitude-dependent biases in trace gas retrievals. For well-mixed trace gases such as methane, where the variability of tropospheric mixing ratios is relatively small, reducing such biases is particularly important. We use aircraft observations from all five missions of the HIAPER Pole-to-Pole Observations (HIPPO) of the Carbon Cycle and Greenhouse Gases Study to evaluate the impact of updates to spectroscopic parameters for methane (CH₄), water vapor (H₂O), and nitrous oxide (N₂O) on thermal infrared retrievals of methane from the NASA Aura Tropospheric Emission Spectrometer (TES). We find that updates to the spectroscopic parameters for CH₄ result in a substantially smaller mean bias in the retrieved CH₄ when compared with HIPPO observations. After an N₂O-based correction, the bias in TES methane upper tropospheric representative values for measurements between 50° S and 50° N decreases from 56.9 to 25.7 ppbv, while the bias in the lower tropospheric representative value increases only slightly (from 27.3 to 28.4 ppbv). For retrievals with less than 1.6 degrees of freedom for signal (DOFS), the bias is reduced from 26.8 to 4.8 ppbv. We also find that updates to the spectroscopic parameters for N₂O reduce the errors in the retrieved N₂O profile.

1 Introduction

Methane (CH₄) is an important greenhouse gas (GHG), a critical component of the Earth's carbon cycle, and a source of background tropospheric O₃ (Ciais et al., 2013; Myhre et al., 2013). Globally averaged surface concentrations of CH₄ have risen from 722 ± 25 ppb in 1750 to 1803 ± 2 ppb by 2011 (Myhre et al., 2013), primarily due to increased anthropogenic emissions of CH₄. While CH₄ concentrations appeared to stabilize in 1999 (Rigby et al., 2008), they began increasing again in 2007 (Dlugokencky et al., 2011) and the sources of this renewed increase are not yet clear. Cutting anthropogenic CH₄ emissions has been identified as one of the most efficient methods to mitigate the radiative forcing of GHGs on decadal time scales due to the strong warming potential of CH₄ (86 times higher than CO₂ on a 20-year time horizon, Myhre et al., 2013) and the relatively short lifetime of CH₄ in the atmosphere (9.14 years ± 10 %, Ciais et al., 2013). Quantifying the anthropogenic and natural emissions of CH₄ is thus essential to determining CH₄ emission reduction targets and verifying that these targets have been met. Atmospheric observations can provide “top-down” constraints to improve the bottom-up CH₄ emission inventories (Weiss and Prinn, 2011). Satellite observations can provide global, spatially and temporally dense data covering many years, and are therefore extremely valuable to these top-down studies. Methane retrievals from measurements of solar backscatter in the shortwave infrared (SWIR) have been used to provide data on the spatial distribution of CH₄ (e.g.,

Bergamaschi et al., 2007, 2009; Frankenberg et al., 2011; Meirink et al., 2008). The SWIR retrievals are sensitive to the entire tropospheric column but their dependence on reflected sunlight precludes observations at night, over most ocean surfaces, and over most cloudy targets. Measurements of terrestrial radiation in the thermal infrared (TIR) have also been utilized to study the emissions and transport of CH₄ (e.g., Worden et al., 2013a, b; Crevoisier et al., 2009, 2013; Massart et al., 2014; Razavi et al., 2009; Xiong et al., 2008, 2009, 2010). TIR retrievals have limited sensitivity to the lower troposphere but can be performed day and night, over land and ocean, and for partly cloudy scenes. In recent years, there has been interest in utilization of TIR measurements together with SWIR measurements in order to separate boundary layer and free tropospheric contributions to the methane columns (Herbin et al., 2013). Minimizing retrieval biases in both the TIR and SWIR retrievals are a critical factor in the success of these efforts.

The Tropospheric Emission Spectrometer (TES), flying on the Aura satellite, measures TIR radiances, including the 8 μm CH₄ region. The high spectral resolution of the TES instrument (0.06 cm^{-1}) allows it to separate the signals from interfering species more easily than other satellite-based nadir TIR sounders, and TES can therefore provide additional insight into retrieval biases from these instruments. In this paper, we evaluate the impact of recent updates to the spectroscopic parameters in Version 6 (V006) of the TES retrieval products on the retrieved profile of CH₄. In addition, we evaluate the impact of proposed updates to the N₂O spectroscopic parameters in the forward model of the TES retrieval algorithm on the retrieved CH₄. We perform these validations using the extensive set of vertical profiles of CH₄ measured from aircraft by the five campaigns of the HIAPER Pole-to-Pole Observations (HIPPO) of Carbon Cycle and Greenhouse Gases Study over the Pacific (Wofsy et al., 2011). This evaluation follows the methods of Wecht et al. (2012), but differs from that previous study in the following ways: (a) we are evaluating the performance of the upcoming TES Version 6 products, whereas Wecht et al. (2012) evaluated the TES Version 4 and 5 products; (b) we use all five HIPPO campaigns, whereas Wecht et al. (2012) only had access to data from the first two HIPPO campaigns; (c) we examine the spectral residuals as part of the evaluation. We characterize the errors in individual profiles and the mean biases, and the variability of these mean biases with latitude and height. We also illustrate the impact of two post-retrieval bias-correction algorithms on the TES CH₄ products: the N₂O-based correction of Worden et al. (2012) and a global bias correction based on the results of this validation study.

Section 2 describes the TES and HIPPO measurements. Section 3 describes the TES CH₄ retrieval algorithm, including the changes to spectroscopic parameters. This section also describes updates to the a priori profiles for the version being evaluated in this study, although these are shown to

have a minor impact on the retrieval results. Section 4 describes the methodology of our validation study. Sections 5 and 6 present the results for TES Version 6 and the proposed updates to the N₂O spectroscopic parameters, respectively.

2 Data

2.1 TES

TES is a nadir-viewing Fourier-transform infrared (FTIR) spectrometer aboard the NASA Aura spacecraft (Beer et al., 2001). Aura is in a sun-synchronous orbit that repeats every 16 days with daytime and nighttime overpasses at 13:30 and 01:30 (mean local solar time). TES Global Survey observations are about 180 km apart along the orbit track, while special observation modes, such as Step & Stare and Transect, can be used for increased spatial sampling (generally 45 and 12 km, respectively) over specific regions. TES's high spectral resolution (0.06 cm^{-1}), spatial resolution ($5\times 8\text{ km}^2$), and radiometric stability (Connor et al., 2011) provide the capacity to measure atmospheric concentrations of many gas species, including O₃ (Worden et al., 2007; Nassar et al., 2008), CO (Rinsland et al., 2006; Luo et al., 2007), CH₄ (Worden et al., 2012, 2013a, b; Wecht et al., 2012), CO₂ (Kulawik et al., 2010, 2013), HDO (Worden et al., 2012), NH₃ (Shephard et al., 2011; Zhu et al., 2013; Pinder et al., 2011), CH₃OH (Cady-Pereira et al., 2012; Wells et al., 2012), HCOOH (Cady-Pereira et al., 2014), OCS (Kuai et al., 2014), and PAN (Alvarado et al., 2011; Payne et al., 2014).

2.2 HIPPO

Measurements from the HIPPO aircraft campaigns provide an excellent data set for satellite validation, due to the large number of measurements, the extensive latitudinal coverage, and the vertical extent of the profiles (up to 14 km for some cases). Figure 1 shows the flight paths of the NSF's Gulfstream V (GV) during the five HIPPO missions (HIPPO I in January 2009; HIPPO II in October–November 2009; HIPPO III in March–April 2010; HIPPO IV in June–July 2011; and HIPPO V in August–September 2011). The GV transected the Pacific Ocean from 87° N to 67° S, performing vertical profiles every $\sim 220\text{ km}$ or 20 min (Wofsy et al., 2011, 2012). CH₄ was measured with a quantum cascade laser spectrometer (QCLS) at 1 Hz frequency with accuracy of 1.0 ppb and precision of 0.5 ppb (Kort et al., 2011). HIPPO CH₄ data are reported on the NOAA calibration scale and have been used in several other studies to evaluate satellite retrievals of CH₄ (e.g., Wecht et al., 2012; Crevoisier et al., 2013; Massart et al., 2014). Comparisons with flask data from the NOAA Whole Air Sampler (NWS) showed a mean positive bias of 0.85 ppb for the QCLS measurements against the NOAA flask data during the HIPPO campaigns, which is consistent with the estimated QCLS accuracy of 1.0 ppb (Santoni et al., 2014).

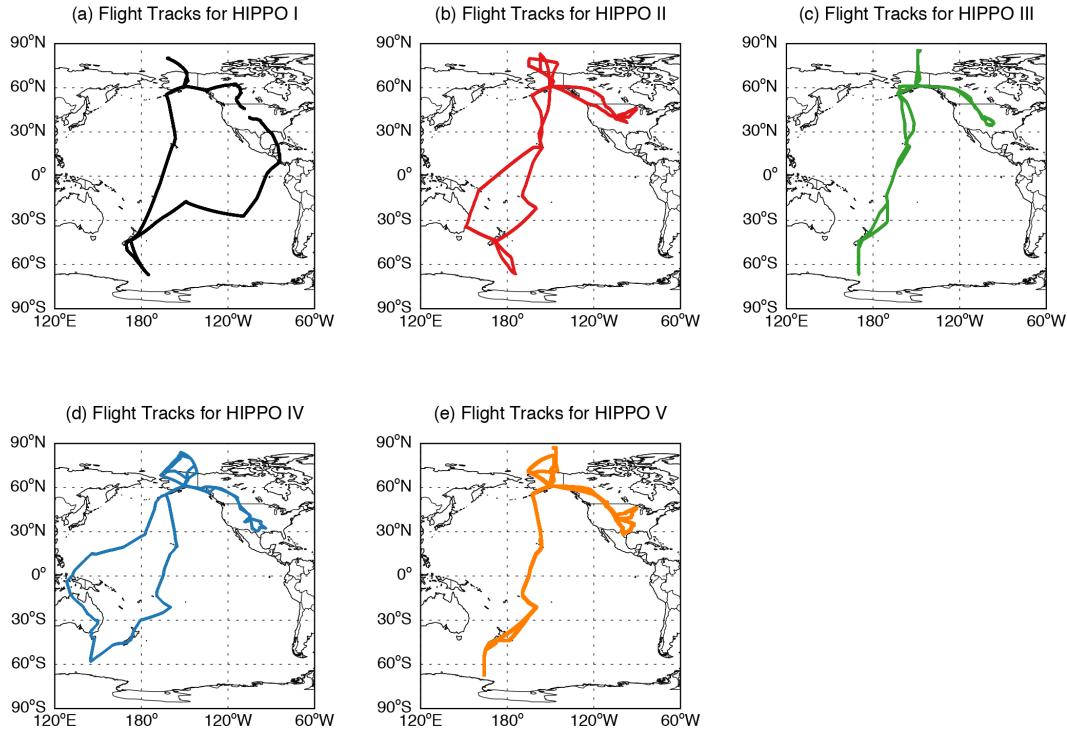


Figure 1. Flight tracks for HIPPO campaigns I through V.

3 TES CH₄ retrieval algorithm

TES retrievals of trace gas profiles are based on an optimal estimation approach (with a priori constraints, e.g., Rodgers, 2000; Bowman et al., 2006) that minimizes the differences between the TES Level 1B spectral radiances \mathbf{L} and a radiative transfer calculation that uses absorption coefficients calculated with the line-by-line radiative transfer model LBLRTM (Clough et al., 2005, 2006). That is, the algorithm solves for the state vector \mathbf{x} that minimizes the cost function:

$$J = [\mathbf{L} - \mathbf{F}(\mathbf{x})]^{-T} \mathbf{S}_m^{-1} [\mathbf{L} - \mathbf{F}(\mathbf{x})] + [\mathbf{x} - \mathbf{x}^a]^{-T} \mathbf{S}_a^{-1} [\mathbf{x} - \mathbf{x}^a], \quad (1)$$

where $\mathbf{F}(\mathbf{x})$ is the non-linear radiative transfer calculation (also called the “forward model”) that relates the state vector to the calculated radiances, \mathbf{S}_m is the covariance of the measurement noise, \mathbf{x}^a is the a priori value of the state vector, and \mathbf{S}_a^{-1} is the “constraint matrix”, generally the inverse of the covariance of a prior climatology of \mathbf{x} .

The CH₄ retrieval algorithm for TES Version 5 is described in detail in Worden et al. (2012), and the same basic approach is used in TES Version 6. In this approach, joint estimates of H₂O, HDO, CH₄, and N₂O are retrieved simultaneously from TES radiances covering the spectral region between 1100 and 1330 cm⁻¹ with the exception of a 10 cm⁻¹ wide region centered at 1280 and a 2 cm⁻¹ wide region centered at 1308 cm⁻¹, which contain a strong CFC absorption

feature and the CH₄ Q branch, respectively. The state vector for the joint estimate is

$$\mathbf{x} = \begin{bmatrix} \mathbf{x}_{\text{H}_2\text{O}} \\ \mathbf{x}_{\text{HDO}} \\ \mathbf{x}_{\text{CH}_4} \\ \mathbf{x}_{\text{N}_2\text{O}} \\ T_{\text{surf}} \\ P_{\text{cloud}} \\ \tau_{\text{cloud}} \end{bmatrix} = \mathbf{M} \begin{bmatrix} \mathbf{z}_{\text{H}_2\text{O}} \\ \mathbf{z}_{\text{HDO}} \\ \mathbf{z}_{\text{CH}_4} \\ \mathbf{z}_{\text{N}_2\text{O}} \\ T_{\text{surf}} \\ P_{\text{cloud}} \\ \tau_{\text{cloud}} \end{bmatrix}, \quad (2)$$

where the column vectors \mathbf{x}_i are the natural logarithms of the volume mixing ratios (VMRs) of the various retrieved species on the 67 level pressure grid from 1000 to 0.1 hPa used in the TES forward model. Updated estimates of surface temperature (T_{surf}), cloud pressure (P_{cloud}), and cloud effective optical depth (τ_{cloud}) are also retrieved. The atmospheric species are actually retrieved on subsets of this grid (the levels of the vectors \mathbf{z} in Eq. 2), related to the forward model grid by the mapping matrix \mathbf{M} , but for the sake of brevity we exclude this mapping in subsequent equations.

The retrieved CH₄ profile $\hat{\mathbf{x}}_{\text{CH}_4}$ is related to the true profile \mathbf{x}_{CH_4} by the equation (Worden et al., 2012):

$$\hat{\mathbf{x}}_{\text{CH}_4} = \mathbf{x}_{\text{CH}_4}^a + \mathbf{A}_{\text{cc}} (\mathbf{x}_{\text{CH}_4} - \mathbf{x}_{\text{CH}_4}^a) + \mathbf{A}_{\text{cn}} (\mathbf{x}_{\text{N}_2\text{O}} - \mathbf{x}_{\text{N}_2\text{O}}^a) + \mathbf{A}_{\text{cj}} (\mathbf{x}_j - \mathbf{x}_j^a) + \mathbf{G}_c \mathbf{K}_b (\mathbf{b} - \mathbf{b}^a) + \mathbf{G}_c \mathbf{n}, \quad (3)$$

where \mathbf{A}_{cc} is the averaging kernel matrix describing the sensitivity of the retrieved CH_4 profile to the true state: $\mathbf{A}_{cc} = \frac{\partial \hat{\mathbf{x}}_{\text{CH}_4}}{\partial \mathbf{x}_{\text{CH}_4}}$. \mathbf{A}_{cn} and \mathbf{A}_{cj} are the sensitivity of $\hat{\mathbf{x}}_{\text{CH}_4}$ to the jointly retrieved N_2O profile and all other jointly retrieved parameters, respectively. $\mathbf{K}_b = \frac{\partial \mathbf{L}}{\partial \mathbf{b}}$ is the partial-derivative (i.e., Jacobian) matrix of the sensitivity of the radiances to unretrieved model parameters \mathbf{b} . The vector \mathbf{n} is the noise in the radiance measurement as a function of wavelength, while \mathbf{G}_c is the gain matrix, or the sensitivity of $\hat{\mathbf{x}}_{\text{CH}_4}$ to the radiance:

$$\mathbf{G}_c = \frac{\partial \hat{\mathbf{x}}_{\text{CH}_4}}{\partial \mathbf{L}} = \left(\mathbf{K}_c^T \mathbf{S}_m^{-1} \mathbf{K}_c + \mathbf{S}_a^{-1} \right)^{-1} \mathbf{K}_c^T \mathbf{S}_m^{-1}, \quad (4)$$

where $\mathbf{K}_c = \frac{\partial \mathbf{L}}{\partial \mathbf{x}_{\text{CH}_4}}$ is the sensitivity of the radiances to changes in the true state of CH_4 , and \mathbf{S}_a^{-1} is the CH_4 constraint matrix, which is derived as the inverse of the covariance of a set of CH_4 profiles from version 4 of the Whole Atmosphere Community Climate Model (WACCM, Marsh et al., 2013), modified based on knowledge gained from in situ and satellite observations (Kulawik et al., 2006; Worden et al., 2011, 2012).

The raw retrieved CH_4 profile from TES ($\hat{\mathbf{x}}_{\text{CH}_4}$) can have a significant positive bias due to errors in unretrieved model parameters (\mathbf{b}) such as the temperature profile, surface emissivity, and spectroscopic parameters. Worden et al. (2012) assumed that (1) errors that affect the retrieved profile of N_2O will have a similar effect on CH_4 and that (2) all deviations of the retrieved N_2O from the a priori profile are due to systematic errors (e.g., errors in the temperature profile, surface temperature, clouds, and surface emissivity). Thus the retrieved N_2O profile is used to adjust the CH_4 profile via the equation:

$$\hat{\mathbf{x}}_{\text{CH}_4}^{\text{adj}} = \hat{\mathbf{x}}_{\text{CH}_4} - \hat{\mathbf{x}}_{\text{N}_2\text{O}} + \mathbf{x}_{\text{N}_2\text{O}}^a. \quad (5)$$

The idea of this N_2O correction is similar to the use of CO_2 in “proxy” retrievals of CH_4 from SWIR measurements (Frankenberg et al., 2005). The N_2O -corrected CH_4 profile $\hat{\mathbf{x}}_{\text{CH}_4}^{\text{adj}}$ is then related to the true profile by the following equation (Worden et al., 2012):

$$\begin{aligned} \hat{\mathbf{x}}_{\text{CH}_4}^{\text{adj}} &= \mathbf{x}_{\text{CH}_4}^a + (\mathbf{A}_{cc} - \mathbf{A}_{nc}) \left(\mathbf{x}_{\text{CH}_4} - \mathbf{x}_{\text{CH}_4}^a \right) \\ &\quad - (\mathbf{A}_{nn} - \mathbf{A}_{cn}) \left(\hat{\mathbf{x}}_{\text{N}_2\text{O}} - \mathbf{x}_{\text{N}_2\text{O}}^a \right) \\ &\quad + (\mathbf{A}_{cj} - \mathbf{A}_{nj}) \left(\hat{\mathbf{x}}_j - \mathbf{x}_j^a \right) + \mathbf{G}_R \mathbf{K}_b (\mathbf{b} - \mathbf{b}^a) + \mathbf{G}_R \mathbf{n}, \end{aligned} \quad (6)$$

where \mathbf{G}_R is the gain matrix for $\hat{\mathbf{x}}_{\text{CH}_4}$ minus the gain matrix for $\hat{\mathbf{x}}_{\text{N}_2\text{O}}$ ($\mathbf{G}_R = \mathbf{G}_c - \mathbf{G}_n$), \mathbf{A}_{nn} is the averaging kernel for N_2O , \mathbf{A}_{nj} is the sensitivity of the retrieved N_2O to all other jointly retrieved parameters, and \mathbf{A}_{nc} is the sensitivity of the retrieved N_2O to the retrieved CH_4 . Note that the cross-averaging kernels are small relative to the averaging kernels for N_2O and CH_4 ($\mathbf{A}_{nc} \ll \mathbf{A}_{cc}$ and $\mathbf{A}_{cn} \ll \mathbf{A}_{nn}$), and so these cross-averaging kernels can be neglected.

Comparisons of Version 5 of the TES CH_4 product with HIPPO showed a remaining positive bias that was generally constant with latitude (Wecht et al., 2012), and we find that the same is true in TES Version 6 (see Sect. 5.3). Thus a second, global correction is applied to the TES retrieved CH_4 :

$$\hat{\mathbf{x}}_{\text{CH}_4}^{\text{cor}} = \hat{\mathbf{x}}_{\text{CH}_4}^{\text{adj}} - \mathbf{A}_{cc} \mathbf{q}, \quad (7)$$

where each element of \mathbf{q} is set to 0.015, which generally minimizes the bias in the lower-tropospheric representative value for CH_4 (see Sect. 5.4).

3.1 Spectroscopic updates

The accuracy of the radiative transfer model $\mathbf{F}(\mathbf{x})$ in Eq. (1) depends on the accuracy of the spectroscopic line parameters and continua for the various gas-phase species used to calculate the molecular absorption coefficients. Thus improvements in these spectroscopic parameters should lead to improvements in the retrieved profiles of various species, all other things being equal. Table 1 summarizes the spectroscopic parameters evaluated in this study. In going from TES Version 5 to TES Version 6, the spectroscopic parameters for H_2O , CO_2 , and CH_4 were substantially updated based on recent evaluations of the spectroscopic parameters used in LBLRTM with ground-based and satellite radiance data (e.g., Shephard et al., 2009; Mlawer et al., 2012; Alvarado et al., 2013).

In TES Version 5, the CH_4 spectroscopic parameters were taken from HITRAN 2004 (Rothman et al., 2005). For Version 6, the CH_4 parameters were taken from HITRAN 2008 (Rothman et al., 2009) with first-order line coupling parameters calculated for the ν_4 ($\sim 1311 \text{ cm}^{-1}$) and ν_3 ($\sim 3019 \text{ cm}^{-1}$) bands of CH_4 with the method and relaxation matrices of Tran et al. (2006), as in LBLRTM v12.1. Alvarado et al. (2013) found that these updated CH_4 line coupling parameters reduced the positive bias in CH_4 retrievals from IASI (Infrared Atmospheric Sounding Interferometer), but that significant spectral residuals remained, most likely due to remaining errors in the CH_4 spectroscopy. Furthermore, they found that including the line coupling parameters for CH_4 had little impact on the retrieved CH_4 profile or the mean spectroscopic residuals in the spectral range used by the retrieval ($1292\text{--}1305 \text{ cm}^{-1}$), although there was some improvement in the residuals in the ν_4 Q-branch between 1305 and 1310 cm^{-1} .

In TES Version 5, the spectroscopic parameters for H_2O came from HITRAN 2004 (Rothman et al., 2005), including the 2006 updates. For Version 6, the H_2O parameters were updated to HITRAN 2008, with the exception that the line positions and intensities in the range $10\text{--}2500 \text{ cm}^{-1}$ were taken from Coudert et al. (2008), as in LBLRTM v12.1. Shephard et al. (2009) and Alvarado et al. (2013) showed that this combination of parameters is more consistent across the H_2O ν_2 band than the HITRAN 2008 parameters alone, and that the Coudert et al. (2008) parameters lead to a $\sim 10\%$

Table 1. Sources of spectroscopic line parameters used in this study.

Species	TES Version 5	TES Version 6	Experimental version
CH ₄	HITRAN 2004 ^a	HITRAN 2008 ^b with line mixing ^c	HITRAN 2008 ^b with line mixing ^c
H ₂ O	HITRAN 2004 ^a with 2006 updates	HITRAN 2008 ^b + Coudert et al. (2008)	HITRAN 2008 ^b + Coudert et al. (2008)
CO ₂	Niro et al. (2005) ^d	Lamouroux et al. (2010) ^d	Lamouroux et al. (2010) ^d
N ₂ O	HITRAN 2000 ^e	HITRAN 2000 ^e	HITRAN 2008 ^b

^a Rothman et al. (2005); ^b Rothman et al. (2009); ^c Tran et al. (2006); ^d Includes P-, Q-, and R-branch line mixing parameters; ^e Rothman et al. (2003)

reduction in the upper tropospheric H₂O mixing ratio retrieved from IASI. Both versions used v2.4 of the MT_CKD self and foreign water vapor continua (Mlawer et al., 2012), as this version performs better than MT_CKD v2.5 in the CO fundamental band (Alvarado et al., 2013).

For CO₂, the differences between the two sets of line parameters used in TES Version 5 and Version 6 are negligible in the regions used for CH₄ retrieval. However, since the CO₂ line parameters can affect the temperature retrieval, and the CH₄ retrieval step uses the retrieved temperature, we include this information for completeness. For CO₂, TES Version 5 used the line parameters of Niro et al. (2005), including first-order line coupling parameters for the P, Q, and R branches of the CO₂ bands. In TES Version 6, these are updated to the parameters of Lamouroux et al. (2010), which are based on the HITRAN 2008 line parameters and also include P-, Q-, and R-branch line coupling parameters. Both versions used the CO₂ foreign continuum from MT_CKD v2.5 (Mlawer et al., 2012). Validations tests against radiosonde data showed little difference in the mean temperature profiles retrieved using the two sets of CO₂ and H₂O spectroscopy (B. Herman, personal communication, 16 October 2013).

In addition to the updates to CH₄, H₂O, and CO₂ made in TES Version 6, we also evaluate the impact of updates to the spectroscopic parameters of N₂O that may be included in future TES versions. In both TES Version 5 and 6, the N₂O line parameters are based on HITRAN 2000 (Rothman et al., 2003). Here we test the impact of updating these to the HITRAN 2008 parameters (Rothman et al., 2009), which include the almost complete revision of the N₂O line list performed for HITRAN 2004 (Rothman et al., 2005).

3.2 A priori profile updates

In the optimal estimation approach, the retrieved profile of CH₄ depends on the a priori estimate of the profiles of CH₄, of the co-retrieved trace gases (through $\mathbf{x}_{N_2O}^a$ and \mathbf{x}_j^a in Eq. 6) and of the a priori estimates of the profiles of temperature and other trace gases (through \mathbf{b}^a in Eq. 6). The a priori estimates of temperature, H₂O, N₂O, CH₄, and O₃ were changed be-

tween Version 5 and Version 6 of the TES products. These updates are described below.

The TES a priori profiles of temperature and H₂O, as well as the estimates of surface temperature and pressure, come from the NASA Global Modeling and Assimilation Office (GMAO) Goddard Earth Observing System Model, Version 5 (GEOS-5, Rienecker et al., 2008). TES Version 5 products used data from version v5.2 of the GEOS-5 model as a priori values, while TES Version 6 uses v5.9.1.

The TES Version 5 N₂O a priori profiles used a monthly mean climatology every 30° latitude and 60° longitude based on the Model for OZone and Related chemical Tracers (MOZART)-2 chemistry-transport model (CTM) (Brasseur et al., 1998; Park et al., 2004). A yearly increase of 0.22 % was applied based on the trends in surface flask measurements from the NOAA Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD). TES Version 6 uses an updated monthly mean N₂O climatology from the Specified Dynamics version of WACCM-4 (Marsh et al., 2013), in which the horizontal winds and temperatures are relaxed to the GEOS-5 meteorological fields in the troposphere and stratosphere. The horizontal resolution with latitude was increased from 30 to 1°. The simulation was done for 2004 through 2010 by Doug Kinneson (UCAR); the a priori profiles for years after 2010 were based on the 2010 data.

The CH₄ climatology used for the TES Version 5 a priori consisted of monthly average fields in 10° latitude bins from the same MOZART run as was used for N₂O above. This previous climatology accounted for seasonal cycles, but the CH₄ values for a given month were static from one year to the next. Measurements from the NOAA Global Cooperative Air Sampling Network have shown that from 1999 to 2006, globally averaged CH₄ was relatively constant. However, 2007 marked a return to a positive CH₄ growth rate (Dlugokencky et al., 2011). The TES Version 6 CH₄ climatology was updated in order to account for the post-2007 CH₄ growth rate using surface flask measurements from the NOAA ESRL GMD. At the time when the work on the TES CH₄ climatology update was underway, monthly mean data were available up to the end of 2010. The flask data was

binned into 10° latitude bands and an average, globally uniform increase for each year since 2004, relative to 2004, was calculated. For the years 2011 to 2014, the growth rate was extrapolated from the approximately linear growth rate observed from 2008 to 2010 inclusive.

There were also updates to the O_3 climatology for TES Version 6. The impact of the O_3 climatology update on the CH_4 retrievals is not expected to be significant, but could have some impact via the temperature retrievals, since there are O_3 lines in the CO_2 region used for the temperature retrievals. For TES Version 5, the O_3 a priori climatology was based on MOZART-3, which extended the earlier MOZART-2 tropospheric chemistry model into the stratosphere and mesosphere (surface – 0.001 hPa). The climatology had unrealistically strong vertical gradients in ozone, and thus higher-than-observed ozone abundances, in the extratropical upper troposphere lower stratosphere (UTLS) region. The ozone climatology for the TES Version 6 O_3 a priori was generated by merging the climatological monthly mean tropospheric/lower stratospheric ozone field from a 1997–2004 simulation from the MOZART-4 CTM (Emmons et al., 2010), which extends from the surface to 0.2 hPa, with the climatological monthly mean stratospheric and mesospheric ozone field from a 2005–2010 simulation from the Specified Dynamics version of WACCM. This revised O_3 climatology agrees better with Microwave Limb Sounder (MLS) observations of the O_3 climatology in the UTLS.

4 TES CH_4 validation methodology

Our validation approach is based on that used by Wecht et al. (2012) to evaluate CH_4 retrievals from TES V004 and V005 with data from the HIPPO I and II campaigns, and is described in detail below.

4.1 Coincidence criteria

One of the key issues in comparing satellite retrievals of trace gases with aircraft profiles is sampling: the aircraft generally does not sample the atmosphere in the exact time and place as the satellite observations. Thus to compare the TES and HIPPO CH_4 profiles we must choose appropriate coincidence criteria in space and time. Wecht et al. (2012) found that collocation error between TES Version 4 and 5 and HIPPO CH_4 profiles was not significant on scales up to 750 km and 24 h, most likely due to the fact that the HIPPO profiles are remote from major sources of CH_4 , and thus show little fine-scale variability. We thus adopt the same coincidence criteria (TES overpass within 750 km and 24 h of the HIPPO profile) here. We also require that the HIPPO profile have a sufficient number of valid CH_4 data points to define the tropospheric profile using the following quality criteria: (a) there are at least 10 data points in the profile; (b) the minimum pressure in the profile was less than or equal to

Table 2. Number of TES (bold) and HIPPO (italic) scans matched for each combination of spectroscopy, a priori, and corrections. Values are given for scans with DOFS ≥ 1.6 and DOFS < 1.6 .

Spectroscopy	TES Version 5 a priori	TES Version 6 a priori
TES Version 5	DOFS ≥ 1.6 : 404 (197) DOFS < 1.6 : 114 (56)	DOFS ≥ 1.6 : 402 (195) DOFS < 1.6 : 107 (50)
TES Version 6	DOFS ≥ 1.6 : 406 (197) DOFS < 1.6 : 111 (55)	DOFS ≥ 1.6 : 389 (191) DOFS < 1.6 : 108 (51)
Experimental version	DOFS ≥ 1.6 : 408 (198) DOFS < 1.6 : 109 (54)	DOFS ≥ 1.6 : 402 (195) DOFS < 1.6 : 107 (50)

250 hPa; and (c) the difference between the minimum and maximum pressure in the profile was at least 400 hPa. With these criteria, a worst-case HIPPO CH_4 profile would have at least 10 valid data points between 250 and 650 hPa, which is generally adequate to define the tropospheric profile. The number of TES and HIPPO profiles matched using these criteria for each combination of spectroscopic parameters and a priori profiles is given in Table 2.

4.2 TES observation operator for HIPPO profiles

A second issue with comparing satellite and aircraft profiles is that (a) the vertical resolution of the satellite profile is substantially coarser than that of the aircraft data and (b) the retrieved satellite profile reflects the influence of the choice of a priori profile (Rodgers and Connor, 2003). To address this, we first interpolate each HIPPO profile (expressed as the natural logarithm of the mixing ratio) to the 67 levels of the TES pressure grid, extrapolating above the GV ceiling using the shape of the TES a priori profile (i.e., scaling the TES a priori to match the top of the HIPPO profile) and extrapolating below the lowest altitude measured by assuming that the profile is constant below this height. We then apply the TES observation operator to the resulting HIPPO profile, h_{CH_4}

$$\hat{h}_{CH_4} = x_{CH_4}^a + A_{cc} (h_{CH_4} - x_{CH_4}^a). \quad (8)$$

Here \hat{h}_{CH_4} is the HIPPO profile corrected for the smoothing error of the TES retrieval and including the influence of the a priori CH_4 profile. It represents the profile that would have been retrieved if (a) TES had sampled the same air as HIPPO and (b) the retrieval errors due to jointly retrieved parameters, other model parameters, and instrument noise were negligible.

The trace of the averaging kernel A_{cc} gives the degrees of freedom for signal (DOFS) for the retrieval (Rodgers, 2000). The TES Version 5 and 6 CH_4 retrievals generally have between 0.6 and 2.3 degrees of freedom for signal (Worden et al., 2012), and thus provide at most one or two independent pieces of information on the vertical profile of

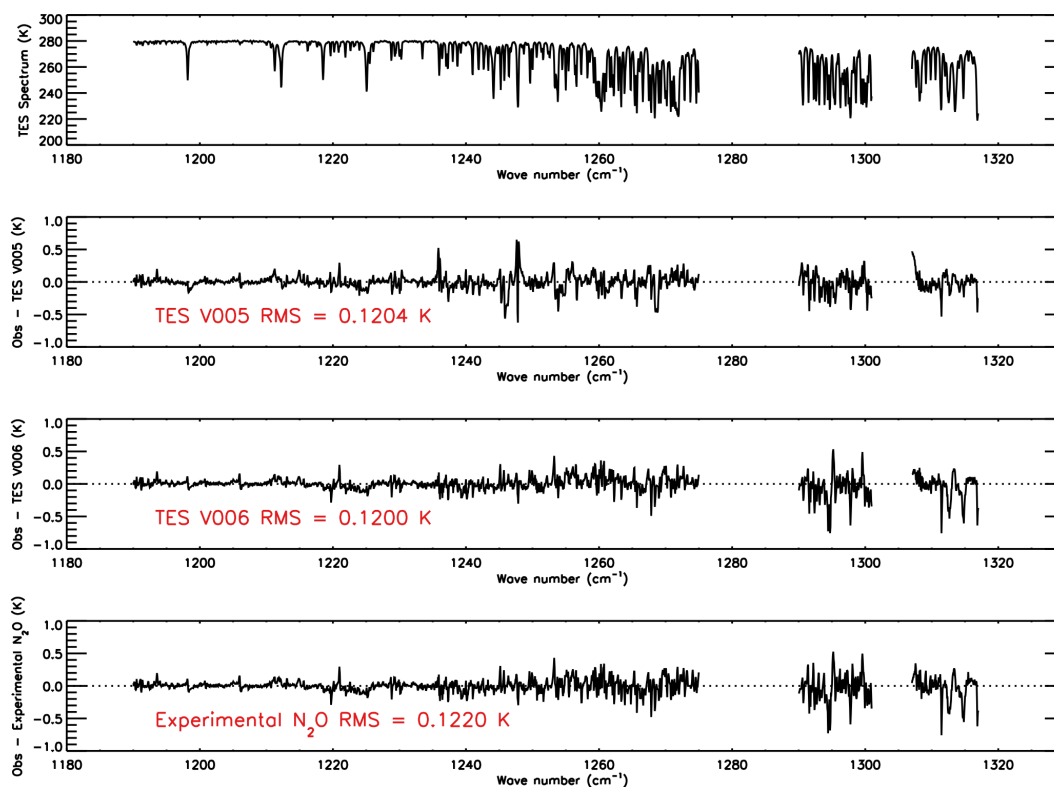


Figure 2. Mean spectral residuals after retrieval in the areas used to simultaneously retrieve CH_4 , N_2O , HDO , and H_2O from TES radiances. (a) Example TES spectrum. (b) Mean TES residuals after TES Version 5 retrievals for the 518 TES scans analyzed in this study (see Table 2). (c) Mean TES residuals after TES Version 6 retrievals. (d) Mean TES residuals after retrievals as in TES Version 6, but with the proposed updated N_2O spectroscopy from HITRAN 2008.

CH_4 . We thus reduce the retrieved TES CH_4 profiles $\hat{x}_{\text{CH}_4}^{\text{COR}}$ and the smoothed HIPPO profiles \hat{h}_{CH_4} to one or two representative tropospheric volume mixing ratios (RTVMRs), following the approach of Payne et al. (2009) and Wecht et al. (2012). For TES profiles with DOFS of 1.6 or less, a single RTVMR value (y_{R}) was calculated by remapping the 67-level retrieved CH_4 profile to a four-level grid with points at (1) the Earth's surface, (2) the altitude of maximum TES sensitivity to CH_4 (i.e., the level where the sum of the rows of \mathbf{A}_{CC} is largest), (3) the tropopause, and (4) the top of the atmosphere, as in Payne et al. (2009). The value of the CH_4 mixing ratio at the second level of this four-level grid is the RTVMR. For retrievals with DOFS of 1.6 or more, two representative values are produced by remapping the retrieved CH_4 profile to a five-level grid with points at (1) the Earth's surface, (2) the altitude of the lower maximum of TES sensitivity to CH_4 (defined as the level where the sum of the diagonal of \mathbf{A}_{CC} from the surface to this level is 20 % of the DOFS), (3) the altitude of the upper maximum of TES sensitivity to CH_4 (i.e., the level where the sum of the diagonal of \mathbf{A}_{CC} from the surface is 60 % of the DOFS), (4) the tropopause, and (5) the top of the atmosphere. The remapped CH_4 values at points (2) and (3) are then defined as the lower

tropospheric (y_{L}) and upper tropospheric (y_{U}) representative values. The same remapping is applied to the corresponding HIPPO profiles.

5 Changes between TES Version 5 and Version 6

5.1 Changes in spectral residuals

One method for evaluating changes in the spectroscopic parameters of a radiative transfer model is to examine the remaining spectral residuals (i.e., observed minus modeled radiances or brightness temperatures) after retrieval. When averaged over a large number of spectra, remaining systematic residuals indicate likely spectroscopic errors in the radiative transfer model (e.g., Shephard et al., 2009; Alvarado et al., 2013).

Figure 2 shows the average of 518 TES brightness temperature spectra in the spectral ranges TES uses to retrieve CH_4 along with the mean spectral brightness temperature residuals for TES Version 5 and Version 6. The root-mean-square (RMS) errors for each set of mean residuals are printed in red on the figure. The change to V006 has mixed results: while the spectroscopic parameters used in TES Version 6 do

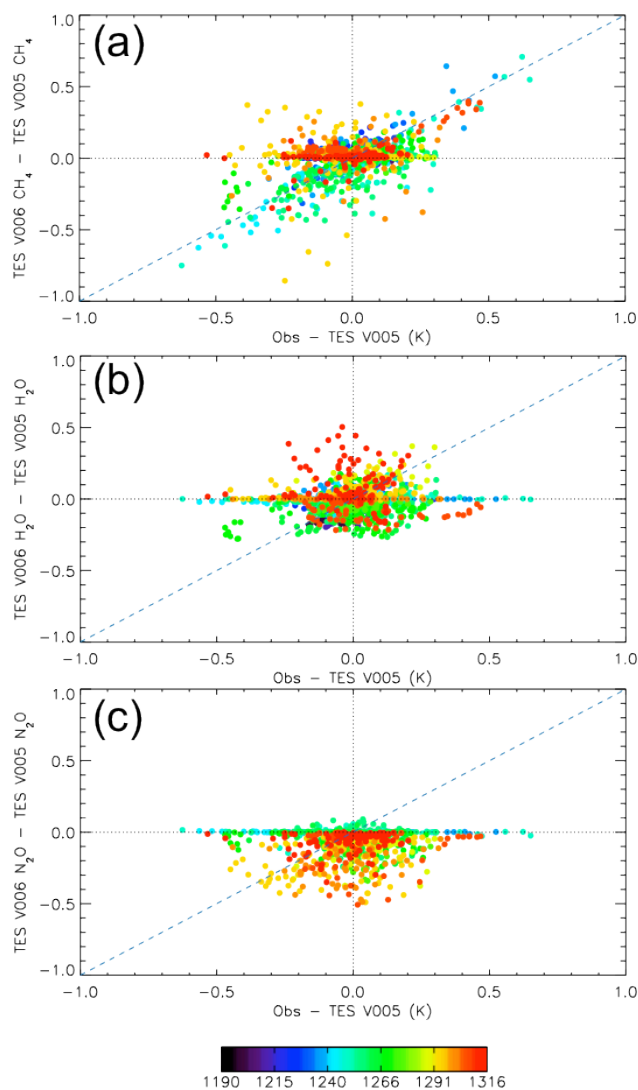


Figure 3. Plots of the TES Version 5 mean residuals for each retrieval channel versus the change in brightness temperature due to replacing the TES Version 5 spectroscopic parameters with (a) the TES Version 6 CH₄ parameters, (b) the TES Version 6 H₂O parameters, and (c) the experimental N₂O parameters for the AFGL (Air Force Geophysics Laboratory) standard tropical atmosphere and a surface temperature of 300.8 K. The points are colored according to wave number in cm⁻¹. Points lying near the dashed blue $x = y$ line indicate an improvement in the spectroscopic parameters.

remove several of the strong residual features between 1190 and 1280 cm⁻¹ (especially the strong residuals near 1245–1247 cm⁻¹), the spectral regions above 1290 cm⁻¹ show stronger residual spikes that are generally associated with strong CH₄ and H₂O lines. The overall RMS decreases very slightly (by 0.0004 K) in Version 6, suggesting that it is not clear if this spectroscopy is an overall improvement over that in Version 5, at least for the spectral regions used in the TES retrievals. This is also consistent with the results for the updated CH₄ spectroscopic parameters in Alvarado

et al. (2013), where although the introduction of line mixing improved the residuals in the Q-branch (not used in TES retrievals), the updated CH₄ spectroscopy was not a clear improvement between 1292 and 1305 cm⁻¹.

In order to separate the impact of the different spectroscopic parameter changes on the spectral residuals, Fig. 3 shows the TES Version 5 mean residuals for each retrieval channel versus the change in brightness temperature due to replacing the TES Version 5 spectroscopic parameters with (a) the TES Version 6 CH₄ parameters, (b) the TES Version 6 H₂O parameters, and (c) the experimental N₂O parameters (discussed in Sect. 6). The brightness temperature changes due to the spectroscopic parameter changes were calculated for the Air Force Geophysics Laboratory (AFGL) standard tropical profile (Anderson et al., 1986) and a surface temperature of 300.8 K using LBLRTM v12.1 (Clough et al., 2005; Alvarado et al., 2013). The points are also colored according to wave number.

In these plots, an improvement in the spectroscopy would be noted by points lying near the line $x = y$ (plotted as a dashed blue line in Fig. 3), as that would suggest that the new spectroscopy would generally move the residuals closer to 0. This is the case for the CH₄ spectroscopic updates in Fig. 3a, which show that many of the improvements in the residuals in the spectral range 1230–1270 cm⁻¹ in Fig. 2 are primarily due to the improvements in the CH₄ spectroscopic parameters in this region. In contrast, Fig. 3b implies that the H₂O spectroscopic updates increase the absolute value of the residuals about as often as they reduce it. These results suggest that most of the improvement in the spectroscopic residuals between TES Version 5 and TES Version 6 is due to the updated CH₄ spectroscopic parameters.

5.2 Changes in uncorrected TES CH₄ retrievals

We wish to know how the updated spectroscopic parameters, along with the updated a priori profiles, impact the retrieval of CH₄. We start by evaluating the errors in the “uncorrected” CH₄ retrieved from TES spectra with the HIPPO data described in Sect. 2.2. In TES Version 5 these uncorrected CH₄ profiles were biased high in the upper troposphere and lower stratosphere. The TES Version 5 biases for all five HIPPO campaign periods can be seen in Fig. 4, which shows the latitudinal profiles of the bias in y_L , y_U , and y_R for TES Versions 5 and 6. The blue triangles are the TES-HIPPO differences for the individual TES scans, with blue lines showing the estimated retrieval error reported with the TES retrievals. The black circles are the mean bias for the scans binned by 10° latitude, while the black error bars represent the standard deviation in each bin. The dashed black line is the mean bias for each parameter. The uncorrected CH₄ retrievals from TES Version 5 show a strong positive mean bias of 123 ± 58 ppbv in the upper tropospheric representative value y_U , over twice as large as the bias in the lower tropospheric representative value y_L (46.8 ± 42.6 ppbv) and the RTVMR

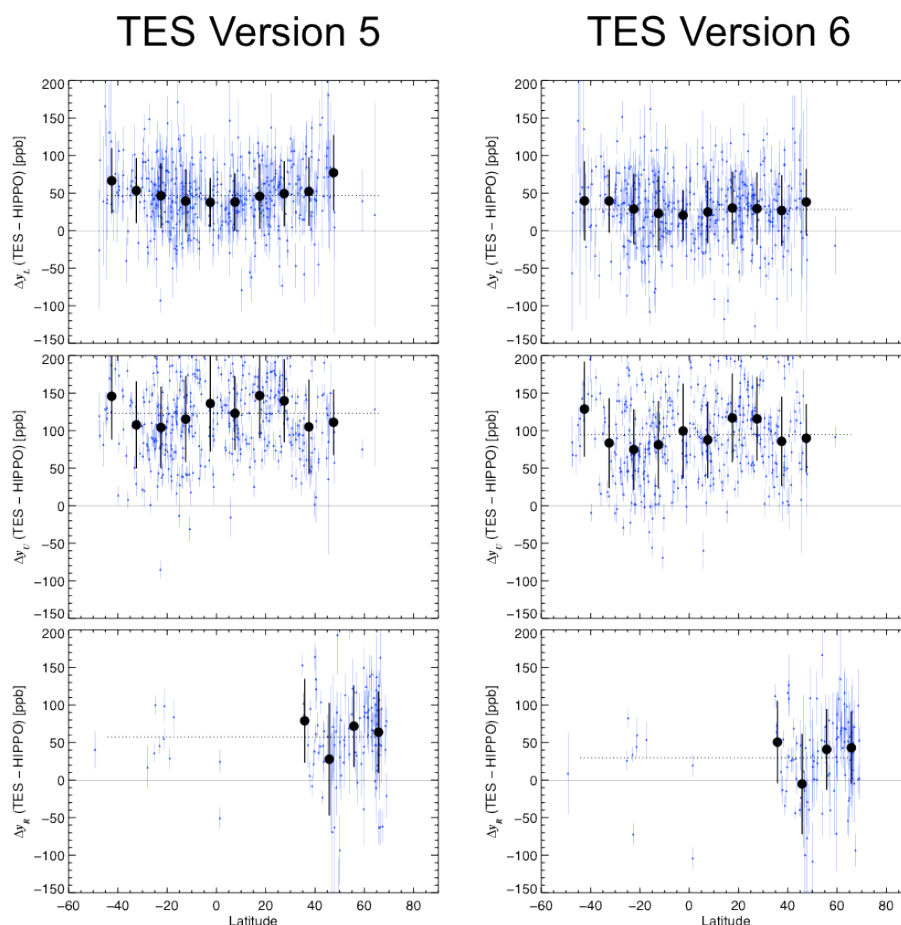


Figure 4. Latitudinal profiles of the differences between the uncorrected TES CH₄ retrievals and HIPPO CH₄ measurements for all five HIPPO campaigns. The left column has the results for TES Version 5, and the right column has the results for TES Version 6. The top two panels of each column show the results for the upper and lower tropospheric representative volume mixing ratios (Δy_L and Δy_U , respectively) for TES retrievals where the degrees of freedom for signal (DOFS) is ≥ 1.6 . The bottom panel shows the results for the RTVMR (Δy_R) in scenes where the DOFS is < 1.6 . The blue triangles are the differences for the individual TES retrievals, with blue lines showing the estimated retrieval error. The black circles show the mean bias for the scans binned by 10° latitude, while the black error bars are the standard deviation in each bin. Circles are only plotted when at least 10 scans are in a bin.

y_R (57.4 ± 60.6 ppbv). However, these biases in the uncorrected TES CH₄ are all substantially reduced in TES Version 6: the mean bias in y_U is decreased to 94.8 ± 59.1 ppbv, the mean bias in y_L is reduced to 28.3 ± 45.9 ppbv, and the mean bias in y_R is reduced to 29.8 ± 58.8 ppbv. This is consistent with the findings of Alvarado et al. (2013), who found that these updated H₂O and CH₄ spectroscopic parameters reduced the positive mean bias in the average CH₄ retrieved from 120 IASI spectra below the 100 hPa surface by 44 ppbv. Therefore we conclude that the updated CH₄ spectroscopic parameters in TES Version 6 substantially reduce the positive bias in the retrieved CH₄ profiles prior to the application of any corrections. However, the remaining bias in the uncorrected CH₄ profiles from TES Version 6 suggest that further improvement of the CH₄ spectroscopic parameters is needed to remove the necessity of the N₂O-based correction.

5.3 Changes in the N₂O-corrected TES CH₄ retrievals

As discussed by Worden et al. (2012) and noted in Sect. 3, much of the bias in the retrieved TES CH₄ can be removed through the use of a correction that assumes (a) that any deviations of the retrieved N₂O profile from its a priori value are the result of systematic error and (b) that systematic errors that affect the retrieved TES N₂O profiles also impact the co-retrieved CH₄. This “N₂O-corrected” CH₄ retrieval is what is used in atmospheric studies that use TES CH₄ (e.g., Worden et al., 2013a, b) and is provided in the TES “lite” product files. In this section we examine the remaining bias in the TES CH₄ retrievals from Version 5 and 6 after this correction has been applied, but before the application of global bias correction given by Eq. (7). The impact of the global bias correction is discussed in Sect. 5.4 below.

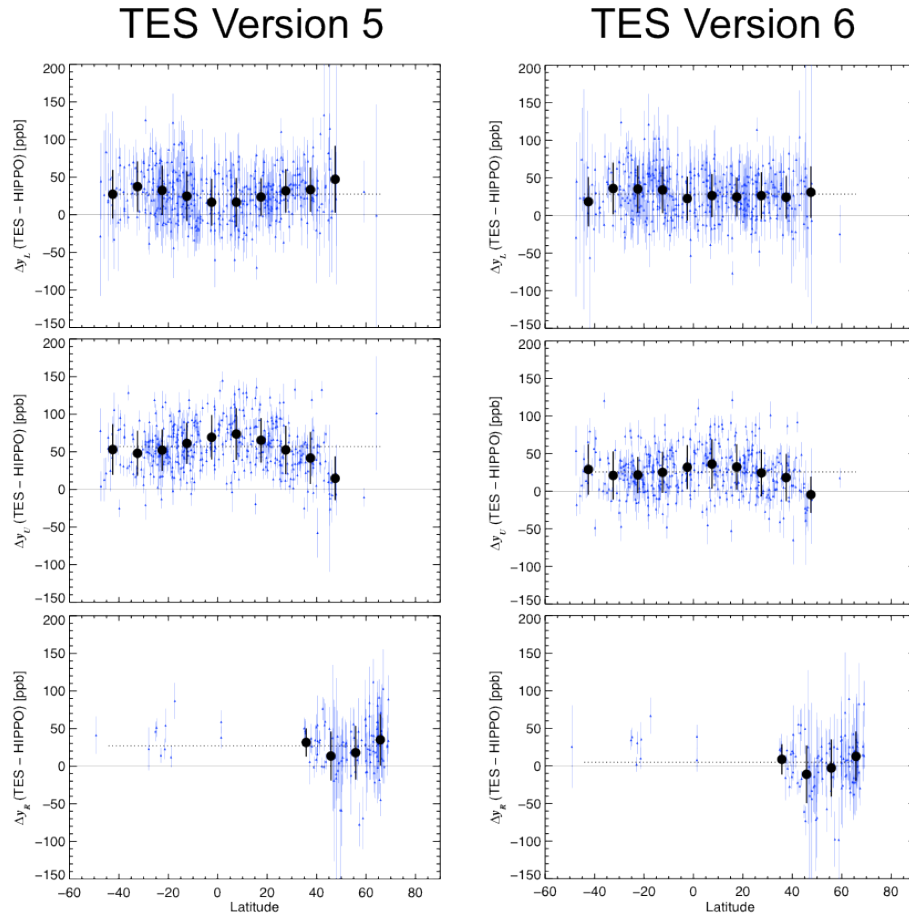


Figure 5. As in Fig. 4, but for the N_2O -corrected TES CH_4 retrievals (see Eq. (5) and Worden et al., 2012).

Table 3. Mean bias ($\pm 1\sigma$, in ppb) of the lower (y_L) and upper (y_U) troposphere RTVMR for TES CH_4 retrievals with $\text{DOFS} \geq 1.6$ and overall RTVMR (y_R) for retrievals with $\text{DOFS} < 1.6$.

Spectroscopy	TES Version 5 a priori		TES Version 6 a priori	
	With N_2O correction applied	With N_2O and bias correction applied	With N_2O correction applied	With N_2O and bias correction applied
TES Version 5	y_U : 56.9 ± 32.8	y_U : 28.7 ± 32.5	y_U : 56.2 ± 32.4	y_U : 28.1 ± 32.2
	y_L : 27.3 ± 33.0	y_L : 2.0 ± 31.7	y_L : 26.9 ± 32.0	y_L : 1.6 ± 31.7
	y_R : 26.8 ± 33.0	y_R : 2.7 ± 32.7	y_R : 24.6 ± 34.7	y_R : 0.2 ± 34.4
TES Version 6	y_U : 25.6 ± 31.0	y_U : -2.1 ± 30.6	y_U : 25.7 ± 30.4	y_U : -2.0 ± 30.0
	y_L : 29.1 ± 30.0	y_L : 3.8 ± 29.6	y_L : 28.4 ± 30.5	y_L : 3.0 ± 30.0
	y_R : 6.1 ± 36.8	y_R : -17.8 ± 36.5	y_R : 4.8 ± 35.0	y_R : -19.4 ± 34.7
Experimental version	y_U : 60.8 ± 31.7	y_U : 32.6 ± 31.3	y_U : 59.8 ± 31.3	y_U : 31.6 ± 30.8
	y_L : 38.1 ± 30.2	y_L : 12.6 ± 29.8	y_L : 38.3 ± 30.9	y_L : 12.7 ± 30.5
	y_R : 30.4 ± 34.6	y_R : 6.3 ± 34.1	y_R : 28.5 ± 36.3	y_R : 3.9 ± 35.7

Table 3 gives the mean bias and standard deviation of the errors between the TES and HIPPO profiles, as determined by the representative values y_L , y_U , and y_R , for each combination of spectroscopic parameters, a priori profiles, and corrections. For N_2O -corrected TES CH_4 retrievals

with $\text{DOFS} \geq 1.6$, the positive mean bias of the lower tropospheric RTVMR (y_L) only increases slightly between Versions 5 and 6 (27.3 ± 33.0 ppbv and 28.4 ± 30.5 ppbv, respectively). However, the positive mean bias of the upper tropospheric RTVMR (y_U) decreases by more than half (from

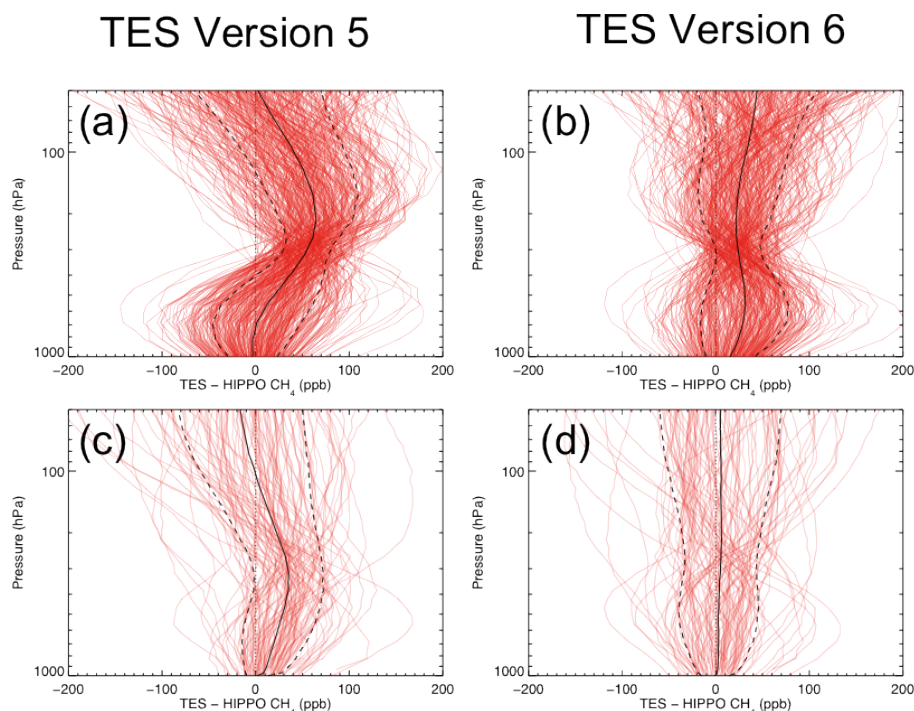


Figure 6. The differences between the N_2O -corrected TES CH_4 retrievals (see Eq. (5) and Worden et al., 2012) and the HIPPO CH_4 profiles versus pressure (altitude). Red lines are the differences for individual TES retrievals. The solid black line is the mean difference and the dashed black lines show the standard deviation. Panels (a) and (c) are the TES Version 5 CH_4 retrievals with $\text{DOFS} \geq 1.6$ and $\text{DOFS} < 1.6$, respectively. Panels (b) and (d) are the TES Version 6 CH_4 retrievals with $\text{DOFS} \geq 1.6$ and $\text{DOFS} < 1.6$, respectively.

56.9 ± 32.8 ppbv for Version 5 to 25.7 ± 30.4 ppbv for Version 6). For N_2O -corrected TES retrievals with $\text{DOFS} < 1.6$, the positive mean bias of the single RTVMR value (y_R) also decreases dramatically between Versions 5 and 6 (from 26.8 ± 33.0 to 4.8 ± 35.0 ppbv). The results in Table 3 show that this decrease in the bias of y_U and y_R is primarily due to the spectroscopic changes between TES Versions 5 and 6, with the a priori changes having a minor impact (see also Sect. 5.5). The spectroscopic changes made in TES Version 6 thus significantly reduce, but do not eliminate, the positive bias in the TES CH_4 profiles that remains after the N_2O correction is applied.

In order to evaluate the TES CH_4 retrievals, we must also look at the dependence of the retrieval bias against (a) latitude and (b) altitude. Figure 5 shows the latitudinal profiles of the bias in y_L , y_U , and y_R for TES Versions 5 and 6 (again with only the N_2O correction applied). For TES retrievals with $\text{DOFS} \geq 1.6$, the average bias within a latitude bin for both y_L and y_U is fairly constant with latitude between 50° S and 40° N in TES Version 6, with the changes in the bias with latitude in this range less pronounced than in Version 5: The difference between the minimum and maximum bias of the bins is 20.7 ppbv (y_L) and 31.9 ppbv (y_U) in Version 5, but only 17.6 ppbv (y_L) and 17.9 ppbv (y_U) in Version 6. North of 40° N, nearly all the TES retrievals have less than 1.6 DOFS, and so have a single RTVMR (y_R). The changes

in the bias of y_R with latitude north of 40° N are similar between TES Version 5 and 6 (21.6 and 23.9 ppbv between the minimum and maximum bins, respectively), and are slightly larger than those seen for the high DOFS retrievals south of 40° N in Version 6.

The greater similarity between the remaining positive bias in y_L and y_U in TES Version 6 already suggests that the bias is more constant with altitude in Version 6 than in Version 5. This is confirmed by Fig. 6, which shows the differences between the TES and HIPPO profiles versus pressure for each retrieval in red, with the mean and standard deviation of these differences plotted in black. The left column has results for TES Version 5, with Version 6 results on the right, while the top row is for retrievals with $\text{DOFS} \geq 1.6$ and the bottom row is for $\text{DOFS} < 1.6$. We can see that while there were large swings in the mean bias versus altitude in Version 5, the mean biases in Version 6 are fairly constant with height. However, the error for any individual scan seems to create an “S” shape or an “inverted S” shape, with a cross point at ~ 300 hPa. While these vertically varying errors cancel out in the average for TES Version 6, further work is still needed to explain the origin of these “S” and “inverted S” error patterns with height, and to find a method to remove them from the retrieval results or mitigate their impacts.

Figure 7 shows the vertical structure of the theoretical observation errors for each TES CH_4 retrieval for both

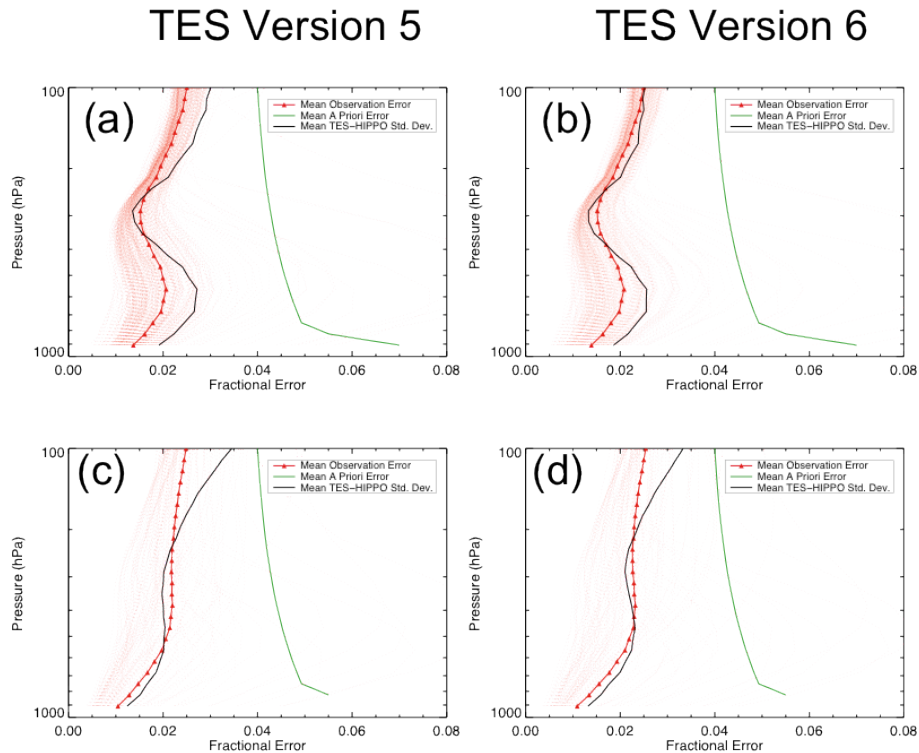


Figure 7. Theoretical observations errors for each TES CH_4 retrieval (dotted red lines) and the mean theoretical error (solid red line and triangles) versus pressure, along with the mean a priori error estimate (green line) and the standard deviation of the TES-HIPPO differences. (a) and (c) are the TES Version 5 CH_4 retrievals with $\text{DOFS} \geq 1.6$ and $\text{DOFS} < 1.6$, respectively. (b) and (d) are the TES Version 6 CH_4 retrievals with $\text{DOFS} \geq 1.6$ and $\text{DOFS} < 1.6$, respectively.

Versions 5 and 6 and for the mean of the retrievals, along with the actual errors, where the latter is defined as the standard deviation of the TES-HIPPO CH_4 differences after the N_2O -based correction ($\hat{x}_{\text{CH}_4}^{\text{adj}} - \hat{h}_{\text{CH}_4}$). For CH_4 retrievals with $\text{DOFS} \geq 1.6$, the mean actual errors in TES Version 6 are smaller and closer to the mean theoretical errors than in TES Version 5 above 300 hPa and are also slightly improved in the lower error peak near 560 hPa (0.0255 in Version 6 versus 0.0272 in Version 5). The errors for retrievals with less than 1.6 DOFS are fairly similar between the two versions.

5.4 Impact of the global bias correction

As discussed above, a global bias correction following Eq. (7), with every element of the vector \mathbf{q} set to 0.015 was found to generally remove the remaining bias in the lower tropospheric representative value (y_L) from TES Version 5. This can be seen in Table 3, which shows that for Version 5 TES CH_4 retrievals with $\text{DOFS} \geq 1.6$ the positive mean bias y_L is reduced from 27.3 ± 33.0 to 2.0 ± 31.7 ppbv by the global bias correction. In addition, the bias in y_U in Version 5 is reduced from 56.9 ± 32.8 to 28.7 ± 32.5 ppbv by the global bias correction, and the positive mean bias y_R is reduced from 26.8 ± 33.0 to 2.7 ± 32.7 ppbv.

Table 3 also shows that this same global bias correction nearly eliminates the bias in y_L and y_U in Version 6, decreasing from 28.4 ± 30.5 to 3.0 ± 30.0 and from 25.7 ± 30.4 to -2.0 ± 30.0 , respectively. Figures 8 and 9 show that the relative latitudinal and vertical dependence of the errors in y_L and y_U are mostly unchanged by this bias correction as well. However, the global bias correction results in a negative bias of -19.4 ± 34.7 ppbv for the TES Version 6 retrievals with $\text{DOFS} < 1.6$ (primarily north of 40°N).

In addition to the RTVMR approach of Payne et al. (2009), another common way of using TES CH_4 data is to calculate a tropospheric average VMR by averaging the TES retrieved VMR between 900 hPa and the tropopause, as was done in Worden et al. (2013a, b). Figure 10 shows the difference of the TES and HIPPO average tropospheric VMR versus latitude after the N_2O and global bias corrections have been applied. These results are very similar to the corresponding RTVMR results in Fig. 8, with the TES Version 6 spectroscopy reducing the positive bias in the average tropospheric VMR from 15.7 ± 17.1 to 2.1 ± 17.1 ppbv for retrievals with $\text{DOFS} \geq 1.6$, while changing a positive bias of 6.6 ± 32.0 ppbv to a negative bias of -18.2 ± 33.9 ppbv in retrievals with $\text{DOFS} < 1.6$.

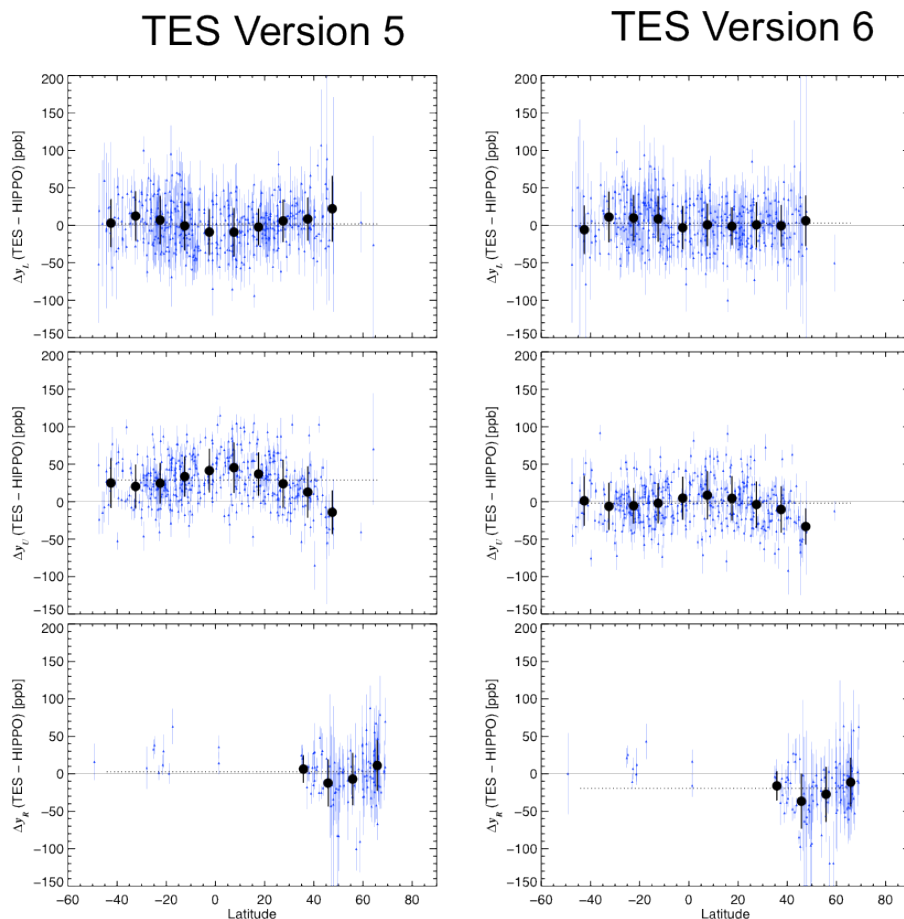


Figure 8. As in Fig. 5, but with the global bias correction (Eq. (7) and Sect. 5.4) applied.

5.5 Impact of the a priori changes

The changes to the a priori estimates of temperature, H_2O , N_2O , CH_4 , O_3 , and CO_2 between TES Version 5 and Version 6 have a minor impact on the CH_4 retrievals, as can be seen in Table 3. Using the TES Version 6 spectroscopic parameters, the mean bias in the lower tropospheric RTVMR (y_L , after both the N_2O correction and the global bias correction) improves slightly from 3.8 ± 29.6 to 3.0 ± 30.0 ppbv, as does the upper tropospheric value y_U (from -2.1 ± 30.6 to -2.0 ± 30.0 ppbv), while the mean bias in y_R for scans with less than 1.6 DOFS becomes slightly worse (from -17.8 ± 36.5 to -19.4 ± 35.7 ppbv). The a priori profiles also have a negligible impact on the dependence of the CH_4 bias with latitude and the vertical profile of the bias (not shown). Thus the reduction in positive bias seen between Version 5 and Version 6 is primarily due to the improvements in the spectroscopic parameters for CH_4 and other species discussed in Sect. 3.1.

6 Impact of proposed updates to N_2O spectroscopic parameters

6.1 Impact on the spectral residuals

Figure 2d shows the mean spectral residuals after the CH_4 retrieval when the TES Version 6 spectroscopy is modified to include the updated N_2O spectroscopic parameters from HITRAN 2008 (the “experimental version” in Table 1). The main difference from the mean residuals from TES Version 6 is an increase in the number of residual spikes between 1260 – 1275 cm^{-1} , resulting in a “fuzzier” appearance of the residuals in this region. The overall RMS error is also slightly increased from Version 6 (by 0.002 K). In addition, Fig. 3c suggests that the updated N_2O spectroscopic parameters worsen the spectral residuals about as often as they improve them, consistent with the increase in the overall RMS. Thus the analysis of the residuals after retrieval does not suggest that the updated N_2O spectroscopic parameters are a significant improvement over the parameters used in TES Version 6, but neither do they introduce significantly larger errors.

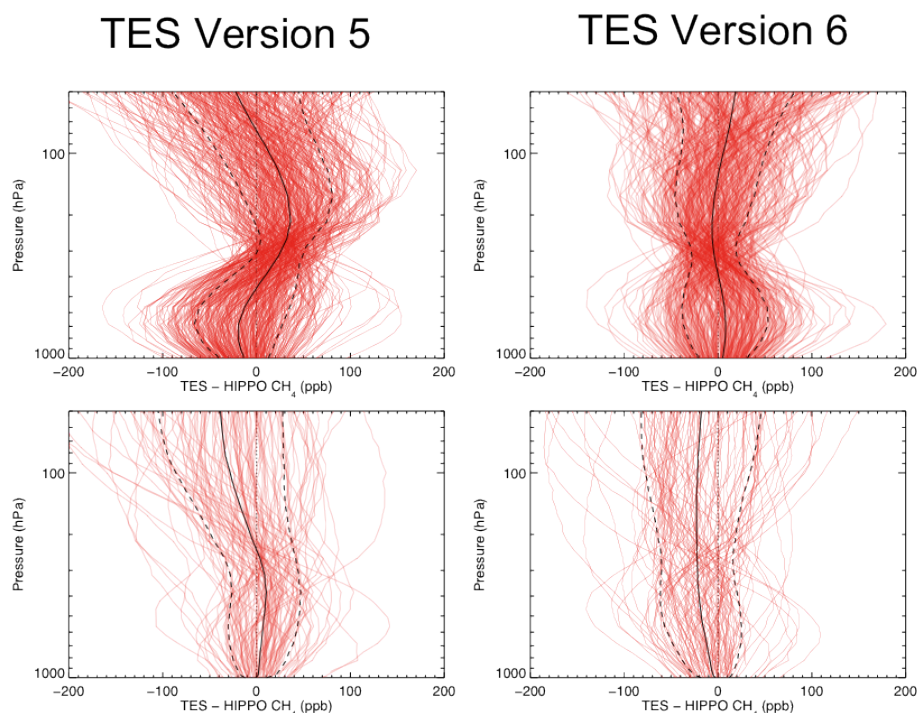


Figure 9. As in Fig. 6, but with the global bias correction (Eq. (7) and Sect. 5.4) applied.

6.2 Impact on TES CH₄ retrievals

The results in Table 3 show that the use of the updated N₂O spectroscopy generally increases the bias in the CH₄ retrievals over Version 6. When the Version 6 a priori profiles are used and only the N₂O correction is applied, the bias in y_U and y_L increases from 25.7 ± 30.4 and 28.4 ± 30.5 ppbv, respectively, in Version 6 to 59.8 ± 31.3 and 38.3 ± 30.9 ppbv, respectively. In addition, the bias in y_R also increases from 4.8 ± 35.0 to 28.5 ± 36.3 ppbv.

The impact of the N₂O spectroscopic parameters on the N₂O-corrected TES CH₄ retrievals does not arise through changes in the uncorrected CH₄ profile retrieved, but rather is due to a reduction in strength in the N₂O correction. Figure 11 compares the uncorrected CH₄ profiles retrieved in TES Version 6 with those retrieved by the experimental version. We can see that the mean bias in the uncorrected CH₄ profiles is nearly identical in these cases. However, Fig. 12 shows the N₂O profiles retrieved by both versions of the TES algorithm with the N₂O observations from HIPPO. We can see that the updated N₂O spectroscopic parameters in the experimental version have reduced the bias in the TES retrieved N₂O, which would suggest that the updated N₂O spectroscopy is an improvement. Reducing the bias of the retrieved N₂O reduces the strength of the N₂O correction via Eq. (5), and thus less of the bias in the CH₄ profiles is removed than is the case in TES Version 6. Thus the N₂O correction method of Worden et al. (2012), which works reasonably well to remove the bias in the retrieved CH₄ for TES

Versions 5 and 6 (using HITRAN 2000 N₂O parameters), is less effective with the updated N₂O spectroscopic parameters from HITRAN 2008. However, we note that even with the updated N₂O spectroscopic parameters it is better to use the N₂O-corrected TES CH₄ data for scientific studies than the raw CH₄ retrievals.

In order to determine why the N₂O-based correction method is less effective with the experimental version of the TES CH₄, we examined the assumptions behind the correction method. As stated in Sect. 5.3 above, the N₂O-based correction method assumes that any deviations from the TES N₂O a priori are due to systematic errors. We can examine the validity of this assumption by comparing the TES N₂O a priori profiles from TES Version 5 and 6 with the measured N₂O profiles from HIPPO, as shown in Fig. 13. We can see that for cases where the TES CH₄ retrievals have at least 1.6 DOFS, which are generally in latitudes between 50° S and 50° N, the assumption that on average the TES N₂O a priori is generally the same as the true N₂O profile appears to be valid – while individual N₂O a priori profiles can show differences of up to 5 ppbv from the HIPPO measurements, the mean of the differences is very small (< 0.5 ppbv). The difference between the TES N₂O a priori and HIPPO is larger for cases where the TES CH₄ retrievals have less than 1.6 DOFS, which are generally in latitudes north of 40° N. Here the mean difference between the N₂O a priori and the HIPPO observations is ~ 1.5 ppbv, with the TES a priori generally underestimating the HIPPO N₂O profile. However, in both cases the differences are fairly minor, especially compared

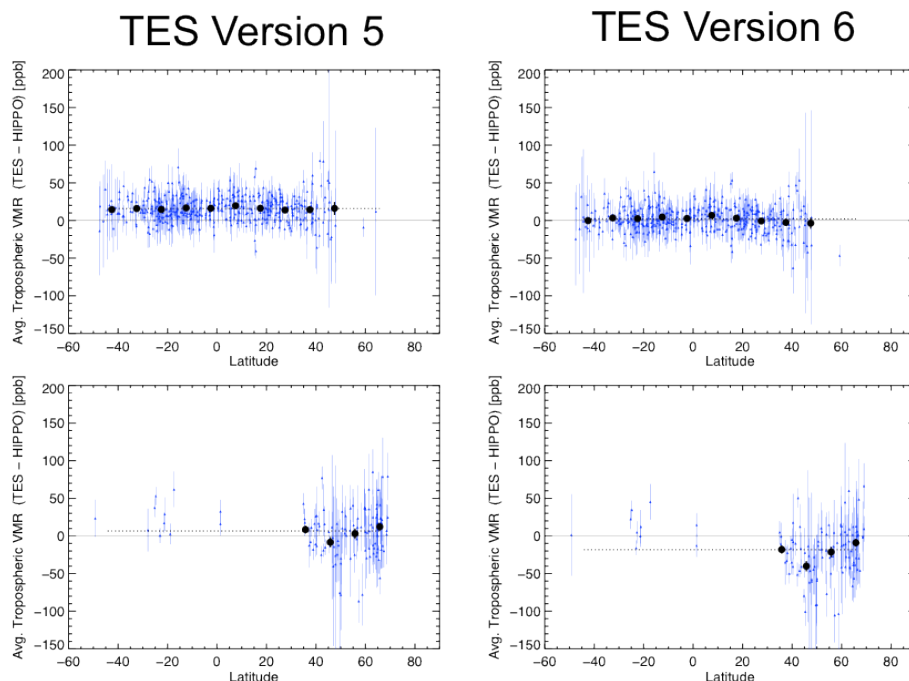


Figure 10. Latitudinal profiles of the differences between average tropospheric volume mixing ratios (VMRs) of the N₂O- and global bias-corrected TES CH₄ retrievals and HIPPO CH₄ measurements for all five HIPPO campaigns. The average tropospheric VMR is calculated as the mean of the VMRs on the TES retrieval grid between 900 hPa and the tropopause. The left column has the results for TES Version 5, and the right column has the results for TES Version 6. The top panel of each column shows the results for TES retrievals where the degrees of freedom for signal (DOFS) is ≥ 1.6 . The bottom panel shows the results in scenes where the DOFS is < 1.6 . The blue triangles are the differences for the individual TES retrievals, with blue lines showing the estimated retrieval error. The black circles show the mean bias for the scans binned by 10° latitude, while the black error bars are the standard deviation in each bin. Circles are only plotted when at least 10 scans are in a bin.

with the 10–20 ppbv positive mean bias seen in the N₂O profiles retrieved by TES.

Thus it is more likely that remaining bias is symptomatic of inadequacies in the assumption that the errors that impact the N₂O retrieval impact the CH₄ retrieval in a similar manner. The improvement in the retrieved N₂O when the updated N₂O parameters are used suggests that rather than the same systematic errors causing the positive bias in the TES retrievals of CH₄ and N₂O, these remaining biases are primarily due to spectroscopic errors, a significant fraction of which are independent.

We note that we have demonstrated in Sect. 5 above that the N₂O-corrected, bias-corrected TES CH₄ retrievals from Version 6 match the measured HIPPO profiles well for cases in which the TES retrievals have more than 1.6 DOFS, and we still recommend the use of both corrections with TES Version 6 data.

Our results suggest that further work is needed on either the CH₄/H₂O spectroscopy, or on empirical, post hoc correction approaches, before the updated N₂O spectroscopy can bring improvements to the TES CH₄ product.

7 Conclusions

We have evaluated the impact of spectroscopic updates on TES CH₄ retrievals, using measured CH₄ profiles from all five HIPPO campaigns, following the methods previously used in Wecht et al. (2012) to evaluate TES Version 5 (V005) products with HIPPO I and II data. We find that the updated spectroscopic parameters for CH₄ and H₂O in TES Version 6 result in a significant decrease of the positive bias in both the uncorrected TES CH₄ retrievals and in the TES CH₄ retrievals after the N₂O-based correction of Worden et al. (2012) is applied (while the updated a priori profiles in Version 6 have little impact). Examinations of the spectral residuals after retrievals suggest that most of the improvement in the retrieved CH₄ is due to the updates in the CH₄ spectroscopic parameters, rather than those of H₂O. For the N₂O-corrected TES CH₄ profiles with at least 1.6 DOFS (generally between 50° S and 50° N), the bias in the upper tropospheric representative value decreases from 56.9 to 25.7 ppbv, while the bias in the lower tropospheric representative value only increases slightly (from 27.3 to 28.4 ppbv). For retrievals with less than 1.6 DOFS, and thus a single-parameter RTVMR, the bias is reduced from 26.8 to

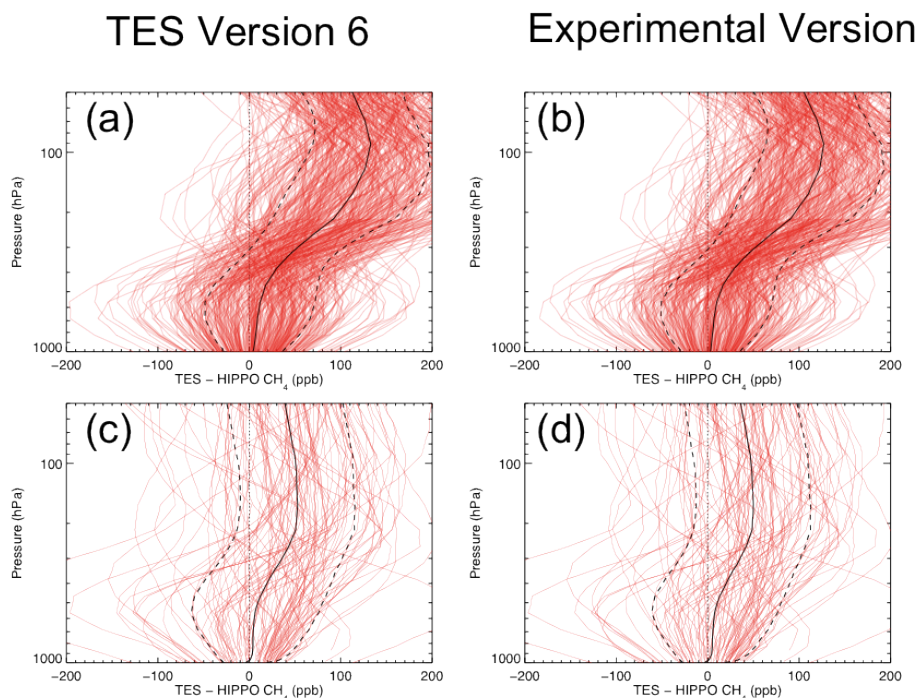


Figure 11. As in Fig. 6, but for the uncorrected CH_4 retrievals from TES Version 6 and the experimental version (see Table 1).

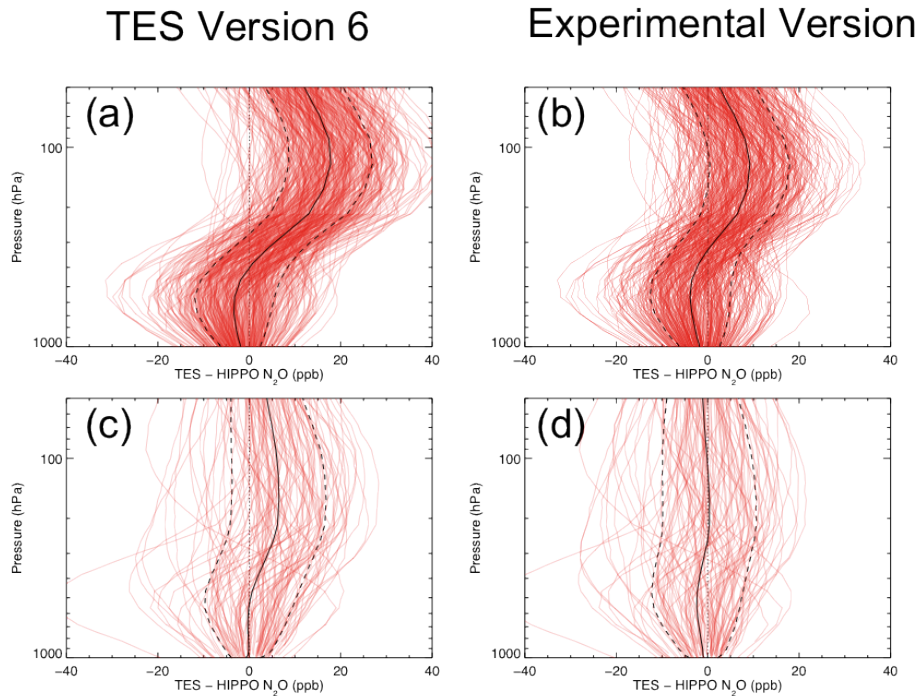


Figure 12. Differences between the retrieved TES N_2O profiles and the measured HIPPO N_2O profiles. The red lines are for each TES spectra analyzed, while the black solid line shows the mean differences and the black dashed lines show the standard deviation. (a) TES Version 5 N_2O for TES CH_4 retrievals with $\text{DOFS} \geq 1.6$. (b) TES Version 6 N_2O retrievals with $\text{DOFS} \geq 1.6$. (c) TES Version 5 N_2O for TES CH_4 retrievals with $\text{DOFS} < 1.6$. (d) TES Version 6 N_2O for TES CH_4 retrievals with $\text{DOFS} < 1.6$.

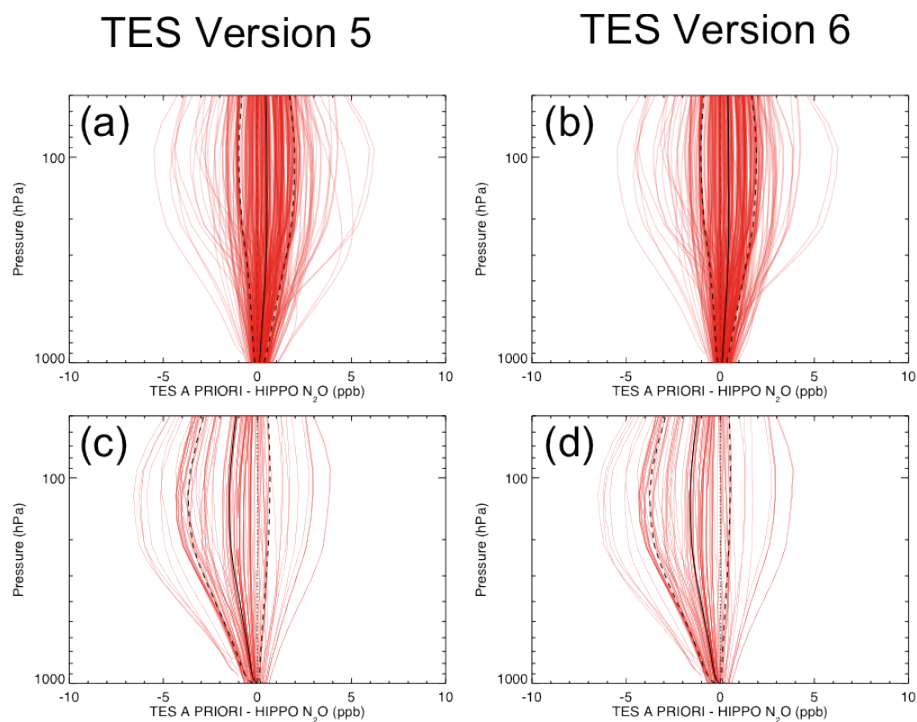


Figure 13. Differences between the TES N_2O a priori profiles and the measured HIPPO N_2O profiles. The red lines are for each TES spectra analyzed, while the black solid line shows the mean differences and the black dashed lines show the standard deviation. (a) TES Version 5 N_2O a priori for TES CH_4 retrievals with $\text{DOFS} \geq 1.6$ (generally between 50°S and 50°N). (b) TES Version 6 N_2O a priori for TES CH_4 retrievals with $\text{DOFS} \geq 1.6$. (c) TES Version 5 N_2O a priori for TES CH_4 retrievals with $\text{DOFS} < 1.6$ (generally between 30°N and 70°N). (d) TES Version 6 N_2O a priori for TES CH_4 retrievals with $\text{DOFS} < 1.6$.

4.8 ppbv. There is little evidence of a latitudinal dependence of the biases for either TES Version 5 or Version 6. In addition, the mean bias in the N_2O -corrected CH_4 is reasonably constant with height for Version 6, although errors in individual scans show a characteristic “S” or “inverted S” shape with height. An additional global bias correction can be applied to remove the remaining bias in TES CH_4 retrievals with at least 1.6 DOFS. We thus conclude that the TES Version 6 CH_4 is a significant improvement on TES Version 5.

We also examined the impact of adding the updated N_2O spectroscopic parameters from HITRAN 2008 to the TES Version 6 retrievals. These updated N_2O parameters have little impact on the uncorrected CH_4 retrieved by TES and do reduce the positive bias in the TES retrievals of N_2O . For TES this reduces the strength of the N_2O -based correction for the CH_4 retrieval bias, and would result in a more biased CH_4 product if corrected in a similar fashion as in TES Versions 5 and 6. Further work is needed, either on the $\text{CH}_4/\text{H}_2\text{O}$ spectroscopy or on a new post hoc correction methodology, in order to allow the inclusion of the updated N_2O spectroscopic parameters to bring improvements to the TES retrieval CH_4 product. Nonetheless, we conclude that in terms of N_2O retrievals, the HITRAN 2008 N_2O parameters are an improvement over the HITRAN 2000 list.

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