Methane and nitrous oxide from ground-based FTIR at Addis Ababa: observations, error analysis and comparison with satellite data.

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Abstract. A ground-based high spectral resolution Fourier transform infrared (FTIR) spectrometer has been operational at Addis Ababa, Ethiopia (9.01° N, 38.76° E, 2443 m a.s.l) since May 2009 to obtain information on the total column abundances and vertical distribution of various constituents in the atmosphere. The retrieval strategy and the results of information content and corresponding full error budget evaluation for methane and nitrous oxide retrievals are presented. They reveal the high quality of FTIR measurements at Addis Ababa. The FTIR products of CH_4 and N_2O have been compared to coincident volume mixing ratio (VMR) measurements obtained from the reduced spectral resolution (Institute of Meteorology and Climate Research) IMK/IAA MIPAS satellite instrument (Version V5R_CH4_224 and V5R_N2O_224), the Microwave Limb Sounder on board of the Aura satellite (Aura/MLS) (MLS v3.3 of N_2O and CH_4 derived from MLS v3.3 products of CO, N_2O and H_2O) and the Atmospheric Infrared Sounder (AIRS). From comparison of FTIR CH_4 and IMK/IAA MIPAS_CH4_224, a statistically significant bias between -4.8 and +4.6 % in the altitude ranges of the upper troposphere and lower stratosphere (15- 27 km) are determined. The largest negative bias in FTIR CH_4 is found in the altitude range of 11-19 km with a maximum difference of -0.08 ppmv (-4.8 %) at around 15 km, a positive bias of less than 0.14 ppmv (9 %) is found in the altitude range of 21 to 27 km with a maximum value at around 27 km with respect to AIRS. On the other hand, a comparison of CH_4 from ground-based FTIR and MLS-derived CH_4 (version 3.3) indicates the existence of a significant positive bias of 2.3 % to 11 % in the altitude range of 20 to 27 km and a negative bias -1.7 % at 17 km. In the case of N_2O derived from FTIR and MIPAS_N2O_224 comparison, a significantly positive bias of less than 15 % in the altitude range 22-27 km with a maximum value at around 25 km and a negative bias of -7 % have been found at 17 km. A positive bias of less than 18.6 % in FTIR N_2O for the altitude below 27 km is noted when compared to MLS v3.3 N_2O. Precision of ground-based FTIR CH_4 and N_2O in the upper troposphere and lower stratosphere over Addis Ababa are better than 7.2 % and 9 %, respectively which are comparable to the bias obtained from the comparisons.

1 Introduction

Methane (CH_4), nitrous oxide (N_2O) and chlorofluorcarbons (CFCs) are tropospheric species which are the main source gases to the chemical families NO_x, ClO_x, and HO_x (Jacobson, 2005). The reaction of CH_4 with hydroxyl radicals reduces ozone in the troposphere and it influences the lifetime or production of other atmospheric constituents such as stratospheric water vapour and CO_2 (Michelsen et al., 2000; Boucher et al., 2009), whereas the lifetime of N_2O is determined by its rate of UV photolysis or reaction with $O(^1D)$ (Collins et al., 2010).

Methane retrievals from near-infrared spectra recorded by the SCIAMACHY instrument onboard ENVISAT suggested unexpectedly large tropical CH_4 emissions and the impact of water spectroscopy on methane retrievals with the largest impacts in the tropics (Frankenberg et al., 2008b). The recent increasing impact of CH_4 and N_2O to global warming has also been assessed by the last AR4 IPCC report (IPCC, 2007; Sussmann et al., 2012). Nitrous oxide (N_2O) becomes the dominant ozone-depleting substance emitted in the 21^{st} century (Ravishankara et al., 2009). In 2007 and 2008, The Infrared Atmospheric Sounding Interferometer (IASI) on-board METOP-1 observed an increase of mid-tropospheric methane in the tropical region of 9.5 ± 2.8 and 6.3 ± 1.7 ppbv yr^{-1} respectively (Crevoisier et al., 2012). Long lived compounds ascend in the tropics, across the tropical tropopause and are subsequently redistributed by the Brewer-Dobson circulation (Holton, 2004). According to the World Meteorological Organization (WMO), the 2010 report (WMO, 2010), 96 % of the increase in radiative forcing is due to the five long-lived greenhouse gases: carbon dioxide, methane, nitrous oxide, CFC-12, and CFC-11. The sources and sinks of atmospheric methane (CH_4) and its budget in the tropics are not yet well quantified and have large uncertainty. Which is due to the scarcity of measurements (e.g. Meirink et al. (2008b)).

Tropics is the location where two important exchange processes in the atmosphere are taking place, the interhemispheric exchange and the entry of tropospheric air mass into the stratosphere (Petersen et al., 2010; Fueglistaler et al., 2009). The composition of a tropical atmosphere also plays a critical role in stratospheric chemistry (Solomon, 1999; IPCC, 2007). Measurements and interpretation of atmospheric trace gas composition of tropics is vital for a better understanding of the budgets, sources and sinks of trace gases in the atmosphere and their effects on atmospheric chemistry, greenhouse effect and climate changes globally. Emissions within the tropics contribute substantially to the global budgets of many important trace gases (IPCC, 2007; Frankenberg et al., 2008).

The ground-based FTIR measurement at the Addis Ababa site has been launched since 2009 in collaboration with Karlsruhe Institute of Technology, Germany to measure concentrations of various trace gases in the lower and middle atmosphere over Addis Ababa. The quality of ground-based FTIR measurements of atmospheric trace gases and their use to understand various lower and middle atmospheric processes have been reported in a number of previous studies (Takele Kenea et al., 2013; Mengistu Tsidu et al., 2015; Schneider et al., 2015, 2016; Barthlott et al., 2017). H_2O VMR profiles and integrated column amounts from ground-based FTIR measurements of the Addis Ababa site were also compared with the coincident satellite observations of Tropospheric Emission Spectrometer (TES), Atmospheric Infrared Sounding (AIRS) and Modular Earth Submodel System (MESSy) model and the result confirmed reasonably good agreement (Samuel Kenea, 2014). Laeng et al. (2015) found the MIPAS CH_4 profiles V5R_CH4_222 below 20 to 25 km biased high and provided +14 % as the most likely bias. For a later and improved data version, namely V5R_CH4_224/225, Plieninger et al. (2016) found a positive bias between 0.1 and 0.2 ppmv. For the MIPAS N_2O data version V5R_N2O_224/225, Plieninger et al. (2016) determined the bias to be between 0 and +30 ppb.

In this study, the previous work on intercomparison is extended to source gases CH_4 and N_2O from ground-based FTIR. Intercomparisons of vertical profiles and column amounts retrieved from solar spectra observed by the Fourier Transform Spectrometer at the Addis Ababa site with satellite observations (MIPAS, MLS, and AIRS) were made. The observed differences between ground-based FTIR and satellite observation of CH_4 and N_2O are analysed using the statistical tools detailed in von Clarmann (2006). The measurement site and the FTIR spectrometer along with the retrieval approach will be introduced in Section 2 and the retrieved information content and spectral analysis will be discussed in Section 3. A short description of satellite measurement techniques followed by the detailed intercomparison with satellite products will be presented in Section 4 and 5 respectively. Finally, a summary and conclusions are given in Section 6.

2 Measurement site and Instrumentation

2.1 Measurement site

The ground-based FTIR at the Addis Ababa was established to acquire high-quality long-term measurements of trace gases to understand chemical and dynamical processes in the atmosphere and to validate models and satellite measurements of atmospheric constituents. The geographic position of the observatory is 9.01° N, 38.76° E, 2443 m a.s.l. and its suitability has been confirmed from the measurements of tropical stratospheric ozone, precipitable water vapour and isotopic composition of water vapour (Takele Kenea et al., 2013; Mengistu Tsidu et al., 2015; Schneider et al., 2015, 2016; Barthlott et al., 2017). Addis Ababa is a tropical high altitude observing site and as such important to understand processes near the tropical tropopause. Physical process in tropics, mainly around tropopause layer has a vital role in climate change and the general circulation of the tropical troposphere, which would control the transport of energy, water vapour and trace gases in the climate system derived by the deep convection (Holton and Gettelman, 2001). Thus, the observed variation in the measurement of atmospheric trace gases would help us to understand the effects of tropical dynamics on the site. Besides, it fills gap to the scarcity of ground based measurements in tropical.

2.2 The FTIR Spectrometer and Retrieval

Fourier transform spectroscopy has been applied successfully to study trace gases in the atmosphere by examining atmospheric absorption lines in the infrared spectrum from solar. Measurement of Sun's spectra at the earth surface provides information about atmospheric composition. This technique uses the Sun as a light source to quantify molecular absorptions in the atmosphere and then retrieve trace gases abundance. The high-resolution FTIR Spectrometer, Bruker IFS120M upgraded with 125 M electronics, from the Bruker Optics Company in Germany was installed in May 2009 at the Addis Ababa site. This interferometer is equipped with indium-antimonide (InSb) detector, which allows the coverage of the 1500-4400 cm^{-1} spectral interval. In this spectral range, a large number of species that reside in the atmosphere can be detected. For the work presented in this paper, we used the retrieval code PROFFIT (Ver95) (Hase et al., 2004). It has been developed based on semi-empirical implementation of the Optimal Estimation Method (Rodgers, 2000) to derive the VMR profiles and column amounts of multiple species. Hence, CH_4 and N_2O profiles from measured spectra in the micro windows that span a spectral range of 2400-2800 cm^{-1} have been discussed in this paper. A Tikhonov-Phillips regularization method on a logarithmic scale were used to derive the profiles. The retrieved state vector $\hat{\boldsymbol{x}}$ is related to the a priori ($\boldsymbol{x}_a$) and the true state vectors ($\boldsymbol{x}$) by the following mathematical expression

$$\hat{\boldsymbol{x}} = \boldsymbol{x}_a + \hat{\mathbf{A}}(\boldsymbol{x} - \boldsymbol{x}_a) + \varepsilon \tag{1}$$

where $\hat{\mathbf{A}}$ is averaging kernel matrix and ε is the measurement error. Moreover, actual averaging kernels matrix depends on several parameters including the solar zenith angle, the spectral resolution and signal to noise ratio, the choice of retrieval spectral micro windows, and the a priori covariance matrix $\mathbf{S}_a$. The elements of averaging kernel for a given altitude gives the sensitivity of retrieved profiles at which the real profile is present and its full width at half maximum is a measure of the vertical resolution of the retrieval at that altitude (Rodgers and Connor, 1990). Error estimation analysis is based on the analytical method suggested by Rodgers (2000):

$$\hat{\boldsymbol{x}} - \boldsymbol{x} = (\mathbf{A} - \mathbf{I})(\boldsymbol{x} - \boldsymbol{x}_x) + \mathbf{G}\mathbf{K}_b(\mathbf{b} - \mathbf{b}_a) + \mathbf{G}\varepsilon \tag{2}$$

The averaging kernel matrix can be defined as A = GK, **I** is the identity matrix and **G** is gain matrix that represents the sensitivity of retrieved parameters to the measurement, $\mathbf{K}_b$ the sensitivity matrix of the spectrum to the forward model parameters **b**. Since we do not know the true state of the atmosphere, we can't specify the actual retrieval error but we can only make a statistical estimate of it, which is expressed in terms of a covariance matrix. The total error in the retrieved profile can be described as a combination of measurement error and forward model parameter error. It has been suggested by Rodgers (2000) to include smoothing error to the total error budget but this concept has been revised by von Clarmann (2014). The quality of the measurements during the time period of May 2009-February 2011 has revealed by Takele Kenea et al. (2013).

3 Information content and error analysis

3.1 Spectroscopic data and a priori profiles

In our retrieval strategy, the profiles of CH_4 and N_2O were retrieved, while the profiles of interfering species (see Table 1) were scaled. The a priori profiles are based on available data sets from the Whole Atmosphere Community Climate Model (WACCM, http://www2.cesm.ucar.edu/working_groups/?ref=nav) as recommended by the NDACC/IRWG ((Network for the Detection of Atmospheric Composition Change Infrared Working Group). Daily Profiles of pressure and temperature were taken from the NCEP reanalysis are made available through the NASA Goddard Space Flight Centre auto mailer from https://hyperion.gsfc.nasa.gov/. The spectroscopic parameters were taken from the High Resolution Transmission (HITRAN) database version 2004 with the 2009 and 2012 updates (Rothmann et al., 2004, 2013). The updated HITRAN data of 2009 for H_2O and HITRAN 2012 for CO_2, CH_4, NO_2 and hit08 of N_2O were used during retrieval of CH_4 and N_2O.

Both methane (CH_4) and nitrous oxide (N_2O) are well-mixed in the troposphere and their VMR decrease with height and becomes negligible with no variation above 55 km. The vertical variability of N_2O and CH_4 in the lower stratosphere is characterized by somewhat higher vertical gradient as compared to the other layers. The vertical profiles over Addis Ababa have been obtained by fitting five and four selected spectral regions for CH_4 and N_2O respectively. The spectral micro-windows used for the retrieval are selected such that the absorption features of the target species along with a minimal number of interfering absorption lines are presented. The microwindows have been adopted from different sources (Senten et al., 2008; Sussmann et al., 2011; Arndt et al., 2004). The microwindows as well as interfering gases for the two target species in this paper are shown in Table 1. However, the microwindows are somehow modified for tropics from the windows recommended by NDACC as mentioned in a result of work done Within the EU projects UTFIR (www.nilu.no/uftir) and HYMN (www.knmi.nl/samenw/hymn). Methane and nitrous oxide vertical profiles over Addis Ababa have been obtained by fitting five and four micro windows respectively. The retrieved state vector contains the retrieved volume mixing ratios of the target gas defined in 41 layers of the tropical atmospheric conditions. The retrieved profiles were derived using a Tikhonov-Phillips method on a logarithmic scale.

The spectral fit and residual between measured and simulated spectra at five micro windows for CH_4 is shown in Fig. 1 for spectra recorded on Feb. 26, 2013. Whereas, four micro windows are used for N_2O and depicted in Fig. 2 for spectra recorded on Dec 31, 2009. The last column of Table 1 provides typical values for the degrees of freedom for signal (DOFS) and it indicates the possible independent pieces of information of the target gases distribution. The magnitude of residuals of spectral fits span a range of a maximum of +0.25 % to -0.64 % for CH_4 and + 0.34 % to -0.34 % for N_2O. The magnitude of residuals indicates that measured spectra which we have used to derive the concentration or amount of both CH_4 and N_2O was quality as they are less than 1. An optimized retrieval strategy for tropics has been established within the framework of this paper for the retrieval of CH_4 and N_2O by applying it first to single spectra as test cases, and later routinely to the full set of measurements.

3.2 Vertical resolution and sensitivity assessment

The spectral resolution of a measurement affects the amount of vertical information derived from the spectral line shape of a measured species (Livesey et al., 2008). Figure 3 shows averaging kernel matrices for the retrieval of the vertical profiles of CH_4 and N_2O mixing ratios, respectively, from the FTIR measurements. The rows of the averaging kernel matrices at selected altitudes which indicate the sensitivity of retrieved CH_4 and N_2O values at the level to true mixing ratios are also presented. The dotted line represents the sum of all the rows of the averaging kernel, which represents the overall sensitivity of the FTIR measurement to observe CH_4 and N_2O.

Figure 3 shows a strong sensitivity in the altitude range of the troposphere and lower stratosphere , i.e. 2.45 up to 27 km for the retrieval of CH_4 and N_2O. Thus, sum of rows of **A** for all the retrieval values of CH_4 and N_2O are greater than 0.5 up to 27 km. The trace of the averaging kernel CH_4, which is 2.25 for the spectra recorded on Feb. 26, 2013 and 2.11 ± 0.06 for the whole data which implies that partial columns representing two different altitude ranges in the atmosphere can be obtained

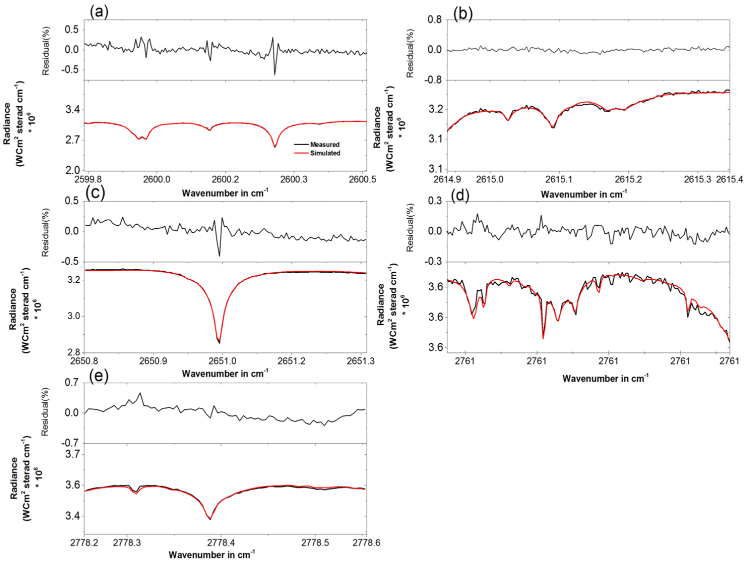

Figure 1. The five spectral micro-windows used for retrieval of CH_4, with the measured spectrum in red, the simulated spectrum in black, and residuals on top of the respective microwindow. The spectrum was recorded on Feb 26, 2013, time: 10h17m15s, root mean square (RMS) =0.1189, solar zenith angle (SZA)= 20.6° , Optimal Path Difference (OPD)=116.1, DOF = 2.23, Field Of View (FOV)=2.27 mrad.

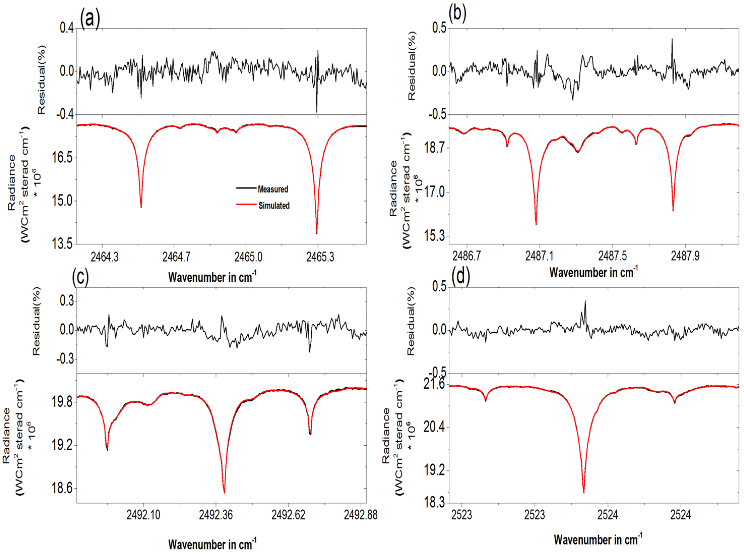

Figure 2. The four spectral micro-windows used for retrieval of N_2O, with the measured spectrum in red, the simulated spectrum in black, and residuals on top of the respective microwindow. The spectrum was recorded on Dec 31, 2009, time: 09h3m727s,solar zenith angle (SZA) = 13.4°, Optimal Path Difference (OPD) =100, DOF = 3.35.

Table 1. Microwindows, interfering gases and their DOFS listed in the table are used for the retrieval of VMR profiles and column amounts of CH_4 and N_2O from FTIR spectra recorded at Addis Ababa.

Gas	micro-window(cm^{-1})	interfering species	DOFS
CH_4	(2599.8,2600.5)		
	(2614.87,2615.4)		
	(2650.8,2651.29)	H_2O, CO_2, NO_2	2.045
	(2760.6,2761.23)		±0.18
	(2778.22,2778.55)		
N_2O	(2464.2,2465.57)		
	(2486.55,2488.18)	H_2O, CO_2,CH_4	3.38
	(2491.86,2492.9)		±0.15
	(2522.95,2524.1)		

from the observations of CH_4 in tropical atmospheric conditions. Similarly, the trace of the averaging kernel N_2O is 3.38 ± 0.15 for the whole data.

The amplitude of the averaging kernels indicates the sensitivity of the retrieval and the full widths at half maximum (FWHM) indicate the vertical resolution of the corresponding layer. We also ignore the altitude range were the resolution of the instrument becomes beyond 20 km, which has been computed using the reciprocal of the diagonal values of averaging kernels and multiplying by the intervals of the layers as reported in Rinsland et al. (2005). The vertical resolution is less than 20 km for the altitude below around 27 km (not shown).

3.3 Error estimation

The error calculations conducted here are based on the error estimation package incorporated in the PROFFIT retrieval algorithm that was developed based on the analytical method suggested by Rodgers (2000). The quantified sources of errors are temperature, measurement noise, instrumental line shape, solar lines, line of sight, zero level baselines offset, and spectroscopy. It has been observed that baseline and atmospheric temperature uncertainties are the leading contribution to the total uncertainty. Details about the evaluation of the individual contributions to the error budget are provided in Senten et al. (2008). Figure 4 shows the statistical (random) error, systematic error and total fractional error (left to right) for CH_4 (top) and N_2O (bottom) retrieval from a spectrum recorded on Feb. 26, 2013 and Dec. 31, 2009 respectively. It can be noted from Fig. 4 that the main systematic error source is the uncertainty of spectroscopic parameters, whereas the major statistical error source is the baseline. Random errors are dominated by the baseline offset uncertainty and the measurement noise in the troposphere. Total estimated random error due to parameter uncertainties is depicted as dark yellow line (see Fig. 4, top panel). The total statistical error of CH_4 retrieval is about 0.07 ppmv (4.4 %) in the lower troposphere and about 0.04 ppmv (2.25 %) in the UT/LS region.

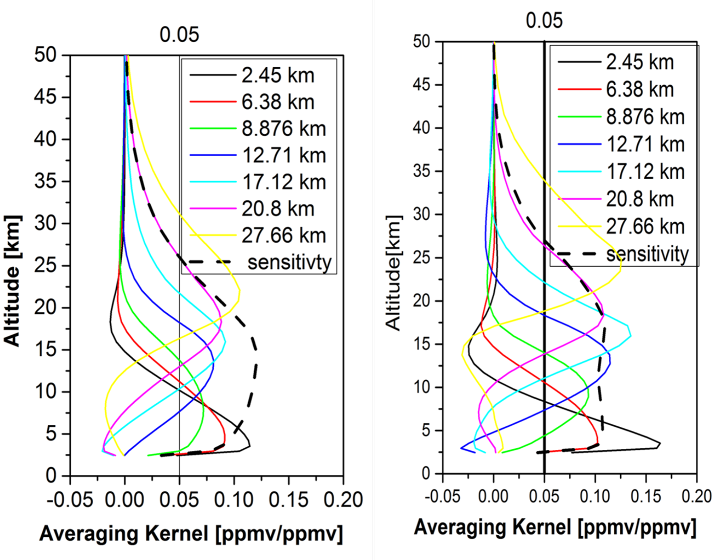

Figure 3. Sensitivity analysis of the retrieved profiles of CH_4 (left) and N_2O (right) at Addis Ababa using the selected rows of the averaging kernels as a function of altitude. The dotted lines are the sum of the rows of the averaging kernels for a spectrum measured on Feb. 26, 2013 for CH_4 and Dec 31, 2009 for N_2O.

Concerning systematic errors, spectroscopic parameters are the dominant uncertainty sources and estimated total systematic error is about 0.05 ppmv (3.5 %) and 0.1 ppmv (7.2 %) for the lower troposphere and the UT/LS region, respectively.

Figure 4 (bottom panel) shows the estimated random and systematic errors for the N_2O profile retrieved from FTIR. Random errors are dominated by the baseline offset uncertainty and temperature in the troposphere. The total statistical errors in middle and upper troposphere are between 0.009 ppmv (3.5 %) and 0.03 ppmv (9 %) with its major contribution from the baseline. Spectroscopic parameters and baselines are the dominant uncertainty sources for systematic errors. The estimated total systematic error is less than 0.025 ppmv (8 %) in the altitude below 22 km. The total fractional error of CH_4 and N_2O retrieved from ground-based FTIR has been shown in the last column of Fig. 4. Fractional error of CH_4 is less than 10 % in the altitude below 27 km with minimum fractional error of 4 % at middle troposphere. On the other hand, the total fraction error of N_2O retrieval is less than 13 % in the altitude below 27 km with a minimum value of 4 % at 6 km and 7.5 % at 17 km.

Time series partial Column amount

Concentrations of CH_4 and N_2O were derived from 166 spectra of NDACC filter 3 recorded from Dec. 2009 to March, 2013. Figure 5 shows the time series of the retrieved total column amounts (in molecules cm^{-2}) of CH_4 and N_2O obtained from the Addis Ababa FTIR measurement site from 2009-2013. The mean total column amounts of CH_4 and N_2O measured at Addis Ababa are 2.9×10^{19} molecules $cm^{-2}\pm3.4$ % and 5.23×10^{18} molecules $cm^{-2}\pm6.93$ % respectively. The sensitivity of

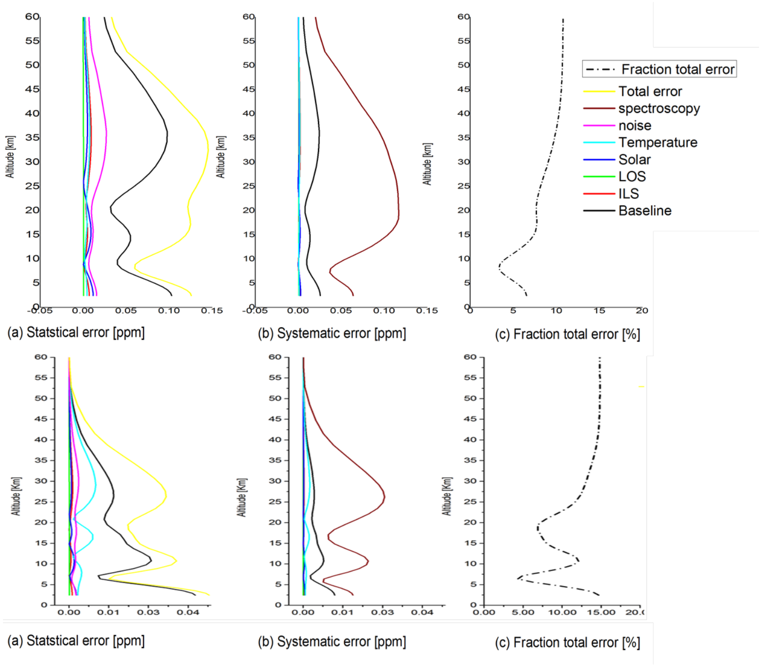

Figure 4. Estimated errors for the profiling retrieval of CH_4 (Top) and N_2O (bottom) over Addis Ababa: (a) statistical (random) errors (b) systematic errors of parameter listed in the legends, (c) Fractional total error [%].

the observation in measuring CH_4 and N_2O trace gases is limited to an altitude of around 27 km as explained using averaging kernel row of the measurement. The mean partial column of CH_4 and N_2O within the sensitivity range of the instrument, which is from the surface to around 27 km, is determined as 2.85×10^{19} molecules $cm^{-2}\pm5.3$ % and 5.16×10^{18} molecules $cm^{-2}\pm6.95$ % respectively. The sensitivity from the averaging kernel analysis is used to determine the upper altitude limit up to which CH_4 and N_2O data from ground-based FTIR can reasonably be used. The DOFS within these partial columns limits are about 1.03 for CH_4 and 1.27 for N_2O. Error analysis indicates that the statistical error accounts for 2.3 % in the total column amounts of CH_4 and 2.0 % in total columns of N_2O. Similarly, the systematic error accounts for 2.1 % in total column of CH_4 and 2.26 % in the total columns of N_2O. Generally, the overall contribution of both statistical and systematic errors to the total error during the retrieval of CH_4 and N_2O from ground-based FTIR are 3.1 % and 3 % respectively.

4 Satellite measurements

4.1 Michelson Interferometer for Passive Atmospheric Sounding (MIPAS)

Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a Fourier transform spectrometer for the detection of limb emission spectra from the upper atmosphere to the lower thermosphere and designed for global vertical profile mea-

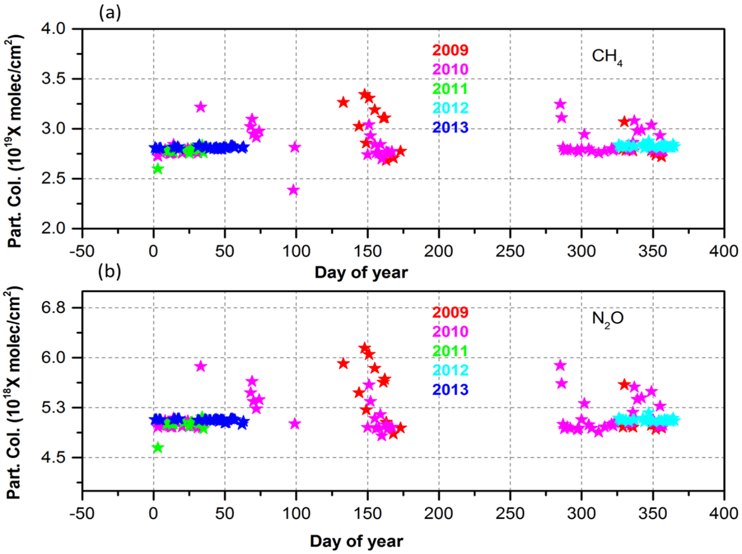

Figure 5. Partial columns of CH_4 (top) and N_2O (bottom) gases over Addis Ababa in the altitude range of 2.45 to 27 km.

surement of many atmospheric trace constituents relevant to the atmospheric chemistry, dynamics, and radiation budget of the middle atmosphere. The vertical resolution of MIPAS ranges from 2.5 to 7 km for CH_4, and from 2.5 to 6 km for N_2O in the reduced-resolution period (Plieninger et al., 2015). In this study, we have used the reduced spectral resolution (Institute of Meteorology and Climate Research) IMK/IAA MIPAS methane and nitrous oxide data product V5R_CH4_224 and V5R_N2O_224 (Plieninger et al., 2016, 2015). The analysis of the comparison between volume mixing ratio values derived from FTIR and MIPAS were performed for the data sets between March 2009 to December 2010. MIPAS profile points, where the diagonal element of the averaging kernels above 0.03 and the visibility flag is 1 have been used (Plieninger et al., 2016).

4.2 Microwave Limb Sounder (MLS)

The Earth Observing System (EOS) Microwave Limb Sounder (MLS) is one of four instruments on the NASA's EOS Aura satellite, launched on July 15, 2004 into a near polar sun-synchronous orbit at 705 km altitude (Schoeberl et al., 2006). The MLS measures N_2O in spectral region, 640 GHz from the stratosphere into upper troposphere (Waters, 2006). The spatial coverage of this instrument is nearly global (-82° S to 82° N) and individual profile spaced horizontally by 1.5° or 165 km along the orbit track. Roughly the satellite covers this latitudinal bands with 15 orbits per day or around 3500 vertical profiles per day. The vertical resolution is between 4 to 6 km for N_2O. This instrument ascends equatorial region at local time of around 13:45 hour.

MLS N_2O data set has been used to validate the ground-based FTIR measurements. However, methane (CH_4) data are derived using coincident measurements of atmospheric water vapor (H_2O), carbon monoxide (CO) and nitrous oxide (N_2O)

from the EOS MLS instrument on the NASA Aura satellite and detail are given in Minschwaner et al. (2015). Selection criteria were implemented as stated in Livesey et al. (2013). More details regarding the MLS experiment and data screening are provided in the above references in detail and at $http://mls.jpl.nasa.gov/data/datadocs.php$. MLS N_2O v2.2 has been validated and its precision and accuracy is respectively in Lambert et al. (2007). The authors reported that MLS N_2O precision is 24-14 ppbv (9-41 %) and the accuracy is 70-3 ppbv (9-25 %) in the pressure range 100-4.6 hPa.

4.3 Atmospheric Infrared Sounder (AIRS)

Operating in nadir sounding geometry, the Atmospheric Infrared Sounder (AIRS) on board the Aqua satellite launched into Earth orbit in May 2002 Chahine et al. (2006). AIRS is a medium-resolution infrared grating spectroradiometer and a diffraction grating disperses the incoming infrared radiation into 17 linear detector arrays comprising 2378 spectral samples. The satellite crosses the equator at approximately 1:30 A.M. and 1:30 P.M. local time, resulting in near global coverage twice a day. AIRS 2378 channels covers from 649 to 1136, 1217–1613 and 2169–2674 cm^{-1}. It also measures trace gases such as O_3, CO and to some extent CO_2. AIRS CH_4 and N_2O retrievals have been characterized and validated by Xiong et al. (2008) and Xiong et al. (2014) respectively.

5 Comparison of FTIR with MIPAS, MLS and AIRS observations

5.1 Comparison methodology

Comparisons of daily average ground-based FTIR measurement of CH_4 and N_2O with that of MIPAS were performed for time period of May, 2009 to December 2010. The comparison of FTIR with MLS for time period of May, 2009 to February, 2013 has also made. MIPAS, MLS and AIRS retrievals were used after averaging data obtained within coincident criteria of $\pm 2°$ of latitude and $\pm$ 10° of longitude from the ground-based FTIR site in Addis Ababa and within time difference of ±24hr.

The ground based FTIR measurements of CH_4 and N_2O have been validated at different locations (e.g. Senten et al. (2008)). MIPAS, MLS and AIRS have a better vertical resolution than ground-based FTIR profiles and high temporal and spatial coverage in the tropics. The analysis of the comparison between volume mixing ratio values derived from FTIR and MIPAS were performed for the data sets collected on March 2009 to December 2010. Furthermore, the comparison of FTIR (CH_4 and N_2O) with a MLS (CH_4 and N_2O) and AIRS (CH_4) for the time period of May 2009 to February 2013 has also made. Hence, the profiles from MIPAS, MLS and AIRS have been degraded to make a comparison between the FTIR and satellite observations. Therefore, the satellite measurement profiles are smoothed using the FTIR is averaging kernels of individual species obtained from the ground based FTIR retrieval by applying the procedures reported in Rodgers and Rodgers and Connor (2003) and given as

$$\mathbf{x}_{si} = \mathbf{x}_a + \mathbf{A}(\mathbf{x}_i - \mathbf{x}_a) \tag{3}$$

where $\mathbf{x}_{si}$ is the smoothed profile, $\mathbf{x}_a$ and $\mathbf{A}$ represents the a priori and averaging kernel for CH_4 and N_2O obtained from the ground-based FTIR instrument respectively and $\mathbf{x}_i$ is the initial retrieved profile obtained from satellite measurements after we interpolated it to the FTIR grid spacing. We also calculate the following error statistics that can characterize the features of the instruments and the parameters to be observed, such as the bias between the instruments using the difference (absolute or relative) of the daily mean profile. The absolute or relative difference at each altitude layers of a pair profile is calculated using

$$\delta_i(z) = [\mathrm{FTIR}_i(z) - \mathbf{x}_{si}(z)] \tag{4}$$

The mean squares error can be expressed as

$$MSE_i(z) = \sqrt{\frac{1}{N(z)-1}\sum_{i=1}^{N(Z)}[\delta_i(z)]^2} \tag{5}$$

The mean difference (absolute or relative) for a complete set of coincident pairs of profiles obtained from the ground-based FTIR and the correlative satellites is expressed as

$$\triangle_{\mathrm{rel}}(z) = 100(\%) \times \frac{1}{N(z)}\sum_{i=1}^{N(z)}\frac{[\mathrm{FTIR}_i(z) - \mathbf{x}_{si}(z)]}{[\mathrm{FTIR}_i(z) + \mathbf{x}_{si}(z)]/2} \tag{6}$$

where $\delta_i(z)$ is the difference (absolute or relative), $N(z)$ is the number of coincidences at z, $\mathrm{FTIR}_i(z)$ is the FTIR VMR at z and the corresponding $\mathbf{x}_{si}(z)$ volume mixing ratio derived from satellite instruments. The standard deviation from the mean differences (absolute or relative) $\sigma_{diff}(z)$ is important to partially characterize the measurement error. As reported in von Clarmann (2006), some use de-biased standard deviation, which measures the combined precision of the instruments instead of the standard deviation of the mean differences.

$$\sigma_{diff}(z) = \sqrt{\frac{1}{N(z)-1}\sum_{i=1}^{N(Z)}[\delta_i(z) - \triangle_{\mathrm{abs}}(z)]^2} \tag{7}$$

where $\delta_i(z)$ is the difference (absolute or relative) for the i^{th} coincident pair calculated using Eq.(4). The statistical uncertainty of the mean differences (absolute or relative), which is standard error of the mean (SEM) is the quantity used to judge the statistical significance of the estimated biases and it can be expressed in terms of the standard deviation of the mean:

$$SEM(Z) = \frac{\sigma(z)}{\sqrt{N(Z)}} \tag{8}$$

One can also conduct the comparison of FTIR and MIPAS using partial columns obtained from both FTIR and smoothed MIPAS CH_4 and N_2O. Hence, the relative difference between ground-based FTIR and smoothed MIPAS partial columns of CH_4 and N_2O by taking into account the lower altitude limit of MIPAS observations and upper limit of ground-based FTIR sensitivity has been calculated using

$$\mathrm{RDiff}(\%) = 100 * [\frac{(\mathrm{PC}_{\mathrm{FTIR}}(z) - \mathrm{PC}_{\mathrm{Sat}}(z))}{(\mathrm{PC}_{\mathrm{FTIR}}(z) + \mathrm{PC}_{\mathrm{Sat}}(z))/2}] \tag{9}$$

where PC is partial column of FTIR and the corresponding satellite measurements. Here in this paper coincidence and smoothing errors are not taken into account in the full error analysis of the comparisons between remotely sensed data sets (von Clarmann, 2006). Hence, we focus on the random uncertainties of each instrument (Combined random error) that has been used to evaluate the uncertainty of the comparison (standard deviation of the difference).

5.2 Comparison of FTIR CH_4

In Fig. 6 mean profiles, mean differences and estimated errors versus deviations of the difference between FTIR and MIPAS_CH4_224 mixing ratios are shown. The comparison has been made using 29 coincident data for a time period between Nov., 2009 and Dec., 2010. Middle panel of Fig. 6 indicate a negative bias of -4.8 % at around 16 km and 2 % at 22 km. Between 23 and 27 km the FTIR value is higher than MIPAS values. The difference increases with altitude increases from 23 to 27 km (4.6 %) with a maximum at 27 km. A large negative bias in FTIR CH_4 is obtained, i.e., FTIR CH_4 values are lower by 0.07 (4.8 %) to 0.04 ppmv (2.2 %).

Figure 6 (right panel) indicates that the standard deviation of the mean differences is larger than the combined random error of the two instruments throughout the altitude. For instance, it is twice the combined standard deviation in the altitude above 20 km and less below 20 km, which indicates the underestimation of random errors of one or both of the instruments. In addition, the overestimation of standard deviation of the difference may result from not taking all the error budget of MIPAS into account and the spatial and temporal criteria sets used to collect the coincidence data of MIPAS can create a discrepancy as well. The natural variation of the methane have also contributed to the overestimation of a standard deviation of the difference as biases vary with seasons as reported in Payan et al. (2009). Figure 7 (middle panel) shows the comparison between FTIR CH_4 profiles and CH_4 derived from MLS measurements of atmospheric water vapor (H_2O), carbon monoxide (CO) and nitrous oxide (N_2O) and indicates that no significant bias in FTIR CH_4 data is present between 18 and 20 km. In the tropopause layer, the comparison indicates a negative bias of -1.7 % at 17 km, i.e., the FTIR value is slightly high. FTIR CH_4 values are lower in altitude between 20-27 km with a bias of below 11 % which is maximum at 27 km or on average by 0.12 ppmv (6.7 %) between 20-27 km. The bias below 19 km and above 27 km can not be explained by the systematic errors of FTIR as the bias is larger than the systematic errors of FTIR and the later is also out of the sensitivity ranges of FTIR. Furthermore, the standard deviation of the difference is larger than the combined random errors of the instruments. A bias in altitude range of 20 to 27 km can be explained by the systematic error of FTIR. In Fig. 8 mean profiles, mean differences and estimated error versus deviation of the difference between FTIR and AIRS mixing ratios are shown. The largest negative bias is found in altitude between 11-19 km with a maximum difference of -0.08 ppmv at around 15 km. A negative bias that AIRS mixing ratio of CH_4 is higher than the FTIR as shown in Fig. 8. A positive bias existed at altitude between 7-9 km and similarly, it also shown in altitude between 21-27 km with a maximum value at around 27 km and its bias is 0.14 ppmv (9 %). The standard deviation of the difference agrees to the combined random error in altitude below 20 km and it overestimate above 20 km.

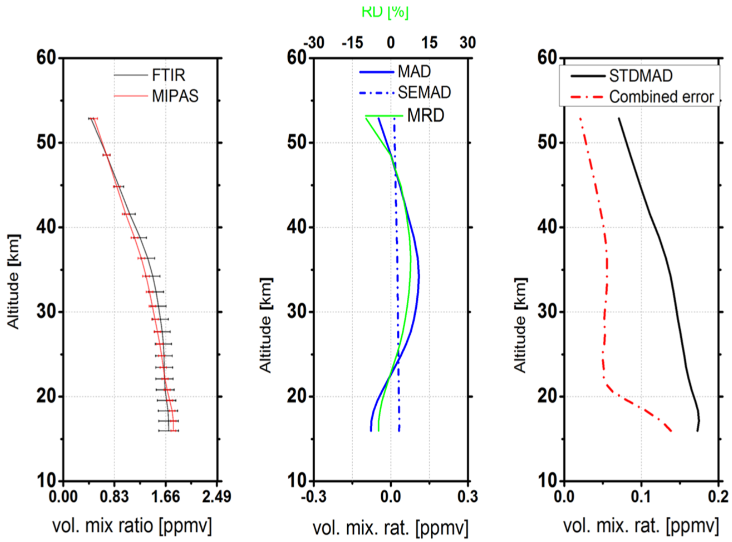

Figure 6. Comparison of CH$_4$ from MIPAS reduced resolution (V5R_CH4_224) and FTIR. Left panel: mean profiles of MIPAS (red) and FTIR (black) and their standard deviation (horizontal bars). Middle panel: mean difference FTIR minus MIPAS (MAD, blue solid), standard error of the difference (SEMAD, blue dotted),and mean relative differences FTIR minus MIPAS relative to their averaged (MRD, green, upper axis). Right panel: combined mean estimated statistical error of the difference (combined error,red dotted, contains MIPAS instrument noise error and FTIR random error budget), standard deviation of the difference (STDMAD, black solid).

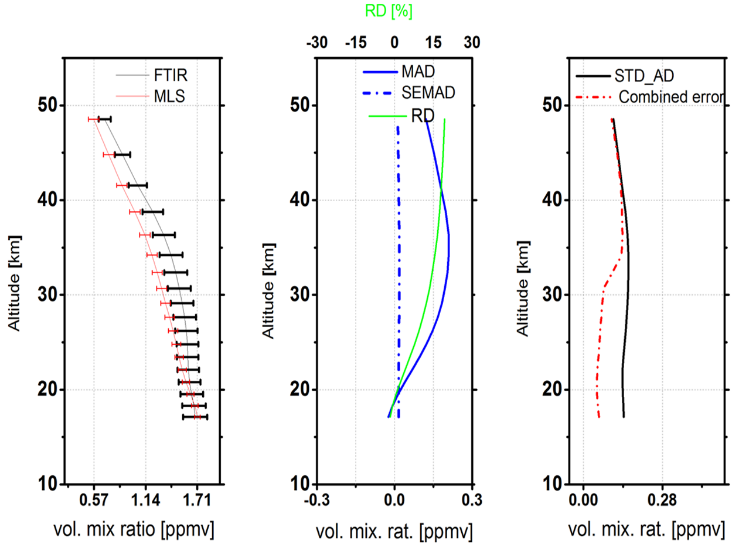

Figure 7. Comparison of CH$_4$ from MLS (V3.3) and FTIR. Details as in Fig. 6

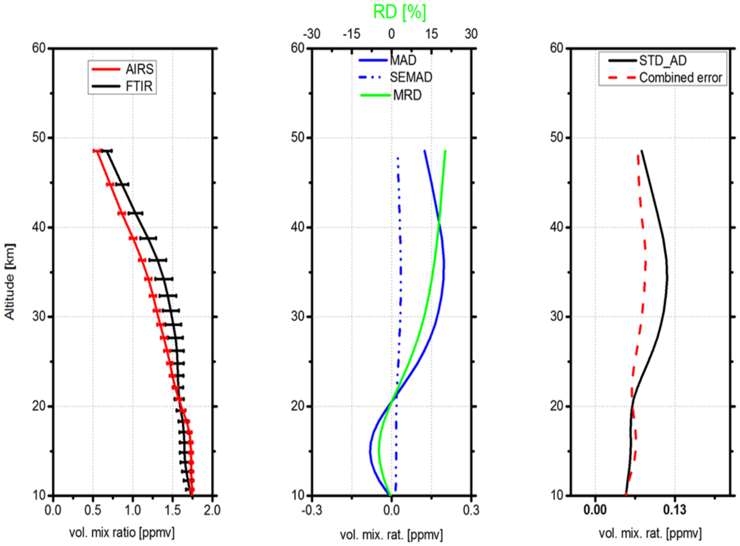

Figure 8. Comparison of CH_4 from AIRS and FTIR. Details as in Fig. 6

5.3 Comparison of FTIR N_2O

FTIR N_2O mixing ratio MIPAS comparison results are shown in Fig. 9, where it represents the mean profiles, mean absolute difference and standard deviation of the mean along with the combined errors of the two instruments. Mean profiles of FTIR show a maximum at around 23 km and decreases smoothly as altitude increases and that of MIPAS_N2O_224 value starts to decline starting from the lowermost stratosphere.

Comparison of FTIR N_2O profiles to MIPAS (V5R_N2O_224) measurements (see Fig. 9 (middle panel)) indicates that FTIR value is higher than the MIPAS above 20 km and the maximum mean absolute difference of N_2O is 15 % (0.04 ppmv) at around 24 km while, the FTIR value is less in altitude below 20 km with a maximum difference of -7 % (-0.02 ppmv) at around 17 km. The bias at 19 km is not statistically significant as the standard error of the mean is larger than the bias. In the remaining altitudes standard error of the mean is smaller than the mean bias and the biases are statistically significant. Since, the bias in altitude between 20 to 27 km is smaller than the FTIR systematic errors, the bias could be explained in terms of systematic uncertainties in FTIR (see Fig. 5 (bottom middle panel)). The standard deviation of the difference is larger than the combined error of the two instruments in the altitude above 20 km (see Fig. 9, right panel) and the standard deviation of the difference agrees with the estimated combined random error in the altitude ranges between 20 to 27 km. For the altitudes below 20 km, the estimated combined random error is overestimated.

The left panel of Fig. 10 represents the mean profiles of N_2O derived from the coincident pairs of FTIR and MLS N_2O. Throughout the whole altitude range, the value derived from FTIR is overestimated (relative to MLS). The FTIR values of N_2O are larger than the MLS value of N_2O by a factor of 1.2 and 1.1 at around 21 and 27 km. The mean relative difference of FTIR and MLS N_2O value increases as altitude increase, its value is less than 18.6 % in altitudes below 27 km and its bias below 22 km is less than 8 % that can be explained in terms of the systematic error of FTIR N_2O. The positive bias is statistically significant as the mean difference of the comparison is larger than the standard error of the mean.

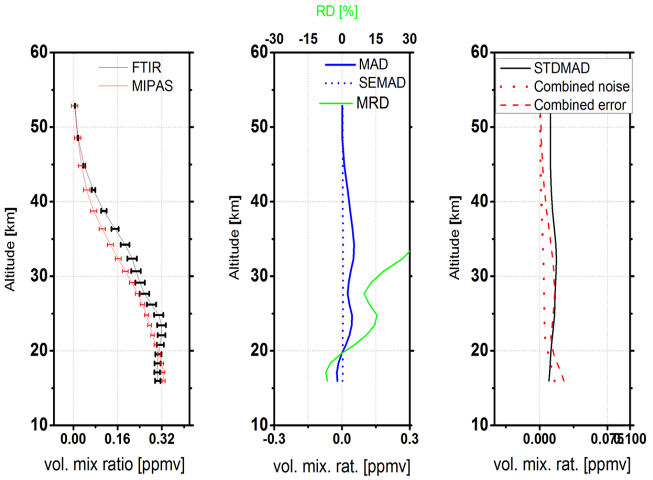

Figure 9. Comparison of N_2O from MIPAS (V5R_N2O_224) and FTIR. Details as in Fig. 6

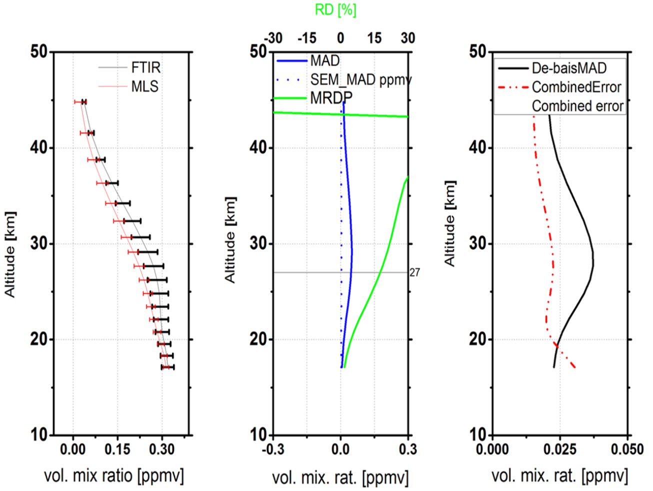

Figure 10. Comparison of N_2O from MLS (V3.3) and FTIR. Details as in Fig. 6

5.4 Comparisons of partial columns

For the partial column (PC) comparisons of FTIR with MIPAS, it is vital to take into account the lower altitude limit of MIPAS, which is 15 km for both target gases and the ground-based FTIR sensitivity is used to determine the upper altitude limit, which is reasonable up to $\sim$ 27 km for CH_4 and N_2O in the tropical atmospheric condition. Therefore the PC that we use in the comparison is limited to the altitude ranges covered by both instruments. The DOFS within the partial columns limit are about 1.00 for CH_4 and about 1.2 for N_2O.

Figure 11 shows the time series of the partial columns and relative differences of CH_4 (upper panel) and N_2O (lower panel). The partial column comparison of CH_4 between values of FTIR and MIPAS revealed a mean error of -5.5 %, mean squares error of 7.4 % and a standard deviation from the mean error of 5 %. Similarly, N_2O values between FTIR and MIPAS revealed a mean error of 0.5 %, mean square error of 3.7 % and standard deviation from mean error of 3.8 %. in the latter case a significant positive bias is observed and in CH_4 negative bias was obtained.

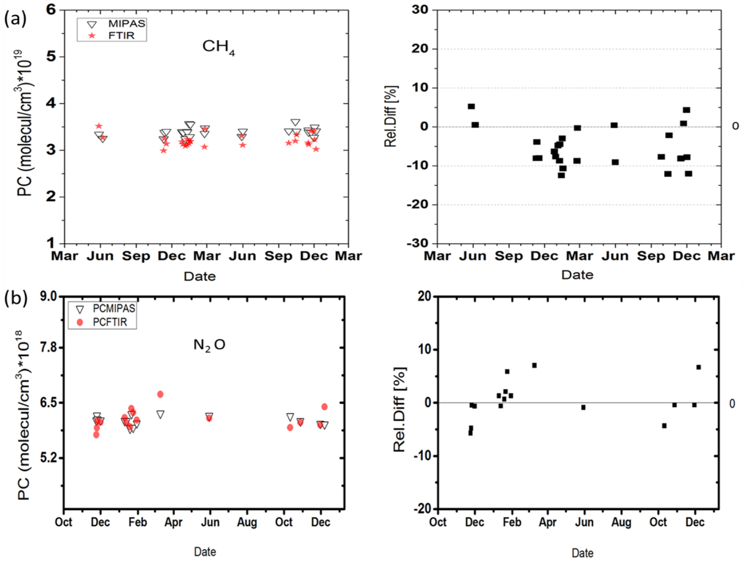

Figure 11. Time series of CH_4 and N_2O partial column comparisons: right panel: ground-based FTIR (stars) and MIPAS (V5R_CH4_224 and V5R_N2O_224) (triangular) partial columns. left panel: relative differences between ground-based FTIR and MIPAS (V5R_CH4_224 and V5R_N2O_224) partial columns.

6 Summary and conclusions

The vertical profiles and partial columns of CH_4 and N_2O over Addis Ababa, Ethiopia were derived from ground-based FTIR. The mean partial column of CH_4 and N_2O within the sensitivity ranges of the instrument, which is from the surface to around 27 km is determined as 2.85×10^{19} molecules $cm^{-2}\pm5.3$ % and 5.16×10^{18} molecules $cm^{-2}\pm6.95$ % respectively. The overall contribution of both statistical and systematic errors, i.e. a total error of CH_4 and N_2O from ground-based FTIR is 3.1 % and 3 %, respectively.

The comparison of FTIR CH_4 and N_2O with MIPAS IMK/IAA products of V5R_CH4_224 and V5R_N2O_224, version 3.3 MLS of N_2O and CH_4 data and AIRS CH_4 are discussed in this paper. However, Version 3.3 MLS of CH_4 data were not directly derived from MLS, but the vertical profiles used in the study are derived from coincident measurements of atmospheric water vapour (H_2O), carbon monoxide (CO) and nitrous oxide (N_2O) by EOS MLS (Earth Observing System Microwave Limb Sounder) instrument on the NASA Aura satellite. From comparison of FTIR CH_4 and IMK/IAA MIPAS_CH4_224 and V5R_N2O_224 products, a statistically significant maximum negative bias of -4.8 % in altitude 15 km that extends to 21 km and maximum positive bias of 4.6 % in an altitude 27 km were obtained. The largest negative bias is found in an altitude between 11-19 km with a maximum difference of -0.08 ppmv (-4.8 %) at around 15 km and a positive bias of less than 0.14 ppmv (9 %) is found in altitude between 21-27 km with a maximum value at around 27 km in FTIR CH_4 comparison with AIRS. On the other hand, a comparison of CH_4 from ground-based FTIR and MLS version 3.3 indicates a significant positive average bias of 0.12 ppmv (6.7 %) in the altitude range of 20-27 km and a negative bias -1.7 % is also found at 17 km. Whereas in the case of FTIR and MIPAS_N2O_224, a significant positive bias of less than 15 % in the altitude range 22-27 km with a maximum value at around 25 km and a negative bias of -7 % at 17 km has been obtained. A positive bias of less than 18.6 % for the altitude below 27 km is noted for N_2O between FTIR and MLS v3.3 and its bias below 22 km is less than 8 % that can be explained in terms of the systematic error of FTIR N_2O. Moreover, the FTIR values of N_2O is larger than MLS value by a factor of 1.2 and 1.1 at around 27 and 21 km, respectively. Therefore, the performance of the FTIR instrument in capturing CH_4 and N_2O values at the Addis Ababa station is vital to monitor and understand the atmosphere over Addis Ababa. In addition, the ground based observation has been used to supplement the satellite observations.

acknowledgements

. We are grateful to Goddard Space Flight Center and WACCM for providing temperature, pressure and a priori profiles of all molecules. AIRS and MLS data were obtained through the Goddard Earth Sciences Data and Information Services Center (http://daac.gsfc.nasa.gov/). We greatly acknowledge the MIPAS science teams for providing data used in this study. Finally, authors would like to thank Mekelle and Addis Ababa universities for the sponsorship and financial support.

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