



Long-term trend of CH₄ at northern mid-latitudes: Comparison between ground-based infrared solar and surface sampling measurements

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Abstract

We report average tropospheric CH₄ volume mixing ratios retrieved from a 27 year time series of high spectral resolution infrared solar absorption measurements recorded between May 1977 and July 2004 at the US National Solar Observatory station on Kitt Peak (31.9°N, 111.6°W, 2.09 km altitude) and their comparison with surface in situ sampling measurements recorded between 1983 and 2004 at the Climate Monitoring and Diagnostics Laboratory (CMDL) station at Niwot Ridge, Colorado (40.0°N, 105.5°W, 3013 m altitude). The two measurement sets therefore overlap for the 1983–2004 time period. An average tropospheric volume mixing ratios of 1814 ± 48 ppbv (1 ppbv = 10^{-9} per unit volume) has been derived from the solar absorption time series with a best-fit increase rate trend equal to 8.26 ± 2.20 ppbv yr⁻¹ in 1983 decreasing to 1.94 ± 3.69 ppbv yr⁻¹ in 2003. The CMDL measurements also show a continuous long-term CH₄ volume mixing ratio rise, with subsequent slowing down. A mean ratio of the retrieved average

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tropospheric volume mixing ratio to the CMDL volume mixing ratio for the overlapping time period of 1.038 ± 0.034 indicates agreement between both data sets within the quantified experimental errors.

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1. Introduction

Long-term monitoring of atmospheric composition and change are key goals of the Network for the detection of stratospheric change (NDSC) [1,2] (*URL:* <http://www.ndsc.ncep.noaa.gov>). Tropospheric and stratospheric species measurements are recorded from NDSC sites in both the northern and southern hemisphere with a variety of observational methods, including high spectral resolution infrared (IR) solar absorption spectroscopy. Methane (CH₄) is a key species for trend monitoring in both the troposphere and stratosphere. It is an important greenhouse gas with a lifetime of ~10 years. The atmospheric abundance of CH₄ has increased by a factor of 2.5 since pre-industrial times [3–5], and it plays a critical role in atmospheric chemistry with a radiative forcing half that of CO₂ [6]. It is therefore important to monitor the long-term evolution of this greenhouse gas within the frame of the Kyoto Protocol. CH₄ is also an important sink for tropospheric OH and a major source of tropospheric ozone [7]. Additionally, it impacts stratospheric ozone both by scavenging Cl radicals [8] and providing a source of water vapor [9]. Major anthropogenic sources of CH₄ include rice cultivation, livestock, landfills, fossil fuel production and consumption (natural gas venting, leakage, and coal mining), and biomass burning. Major natural sources include wetlands and termites with total emissions from all sources in the range 460–600 Tgyr⁻¹ [10].

The goal of this study is to report and discuss a time series of mean tropospheric CH₄ volume mixing ratios (VMRs) derived from the analysis of high spectral resolution IR solar absorption spectra recorded in southern Arizona from May 1977 to July 2004. We compare this measurement time series with surface in situ sampling measurements obtained from a station in Colorado with over 20 years of overlapping sampling coverage.

2. Kitt peak measurements and analysis

The solar absorption spectra were recorded with the custom-made Fourier transform IR spectrometer (FTIR) at the US National Solar Observatory station on Kitt Peak (31.9°N, 111.6°W, 2.09 km altitude) [11]. This mountain-top NDSC site is located in the Sonora desert, a semi-arid region of southwest Arizona, USA. Most CH₄ observations were obtained at spectral resolutions of 0.01–0.02 cm⁻¹, corresponding to maximum optical path differences of 94–50 cm with a weak apodizing function, either with a KCl or CaF₂ beam splitter.

Retrievals were performed with version 3.90 of the SFIT2 algorithm, which can retrieve vertical profiles of molecular species from simultaneous fits to one or more microwindows. The algorithm [12] is based on a semi-empirical implementation [13,14] of the optimal estimation method. The formalism of Rodgers [15] is assumed with Newtonian iteration to account for non-linearities in

the spectral calculation. First-order terms are used in the SFIT2 approach (terms with the second derivative of the forward model are ignored) with tests applied for convergence of the solution. The constraints on the retrieval consist of a priori estimates of the parameters to be retrieved, their uncertainties, and an assumed signal-to-noise for the selected microwindows. SFIT2 has been validated through comparison with independently-developed algorithms (see, for example, Goldman et al. [16] and Hase et al. [17], and the references cited therein). All simulated lines are assumed to have a Voigt line shape [18]. A new solar lines model is now included in the simulation and retrieval codes, based on the work of Hase et al. [19].

Adopted daily temperature profiles were obtained from National Centers for Environmental Prediction (NCEP) measurements for the location of Kitt Peak. Refractive ray-tracing and airmass-weighted pressures and temperatures in 37 atmospheric layers extending from the site altitude (2.09 km) to 100 km were performed based on the NCEP data (smoothly corrected to the 1976 US Standard Atmosphere temperature profile above 0.4 hPa (~ 55 km)) with the algorithm described by Meier et al. [20]. The vertical thickness of the layers increases smoothly with altitude from less than 1 km in the lowest layer to 2 km at 30 km with even wider layers above.

We adopted a reference set of a priori VMR versus altitude profiles for CH_4 and other infrared absorbing molecules. The a priori profile adopted for CH_4 assumes a constant VMR of 1800 ppbv (1 ppbv = 10^{-9} per unit volume) below 10 km decreasing to 847 ppbv at 30 km and 165 ppbv at 50 km, with further decreases above. It is based on balloon profile measurements obtained with a high spectral resolution FTIR [20,21]. Weak HDO absorption occurs in the window regions selected for the analysis. We adopted the H_2O a priori profile from the 1976 US Standard Atmosphere [22] as the a priori profile for HDO in the analysis.

Spectral parameters were taken primarily from the 2004 HITRAN compilation [23] (available from <http://cfa-www.harvard.edu/hitran/>). Three microwindows extending from 2650.85 to 2651.25, 2666.95 to 2667.35, and 2673.90 to 2674.21 cm^{-1} were fitted simultaneously to retrieve the CH_4 vertical profile from spectra recorded at solar astronomical zenith angles of 85° or less. Molecule-by-molecule simulations of the main absorbers for two of the three microwindows are presented in Fig. 1, together with a typical measured spectrum (labeled KP). A more complete simulation shows also some weak solar lines and weak O_3 and CO_2 lines, which do not affect the retrieval process. A signal-to-noise ratio of 250 was selected semi-empirically and the a priori covariance matrix was assumed to be diagonal with a relative uncertainty of 0.2 in each of the 37 forward model layers. The weak absorption by HDO was fitted by retrieving a multiplicative scaling factor for the a priori profile.

Fig. 2 illustrates VMR averaging kernels (for a discussion of the concept of averaging kernel, see, for example, Refs. [15,25]) calculated for merged layers at altitudes of 2.09–10, 10–14, and 14–50 km. In order to avoid the influence of stratospheric air masses on our results, a 10 km altitude limit was selected as the upper boundary for the tropospheric region; daily-average tropopause altitudes calculated from a $2.5^\circ \times 2.5^\circ$ NCEP analysis (for 2000 and 2001 interpolated to the location of Kitt Peak) indeed indicate that the tropopause height varies between 7.6 and 17.5 km, but less than 2% of the occurrences were below 10 km [24]. The VMR averaging kernel for the tropospheric region of interest here is broad, increasing from a minimum of 0.53 in the lowest layer to a maximum of 0.85 near 5.92 km, decreasing above. Calculations were performed with SFIT2 for a typical retrieval to estimate the number of degrees of freedom of signal, i.e. the

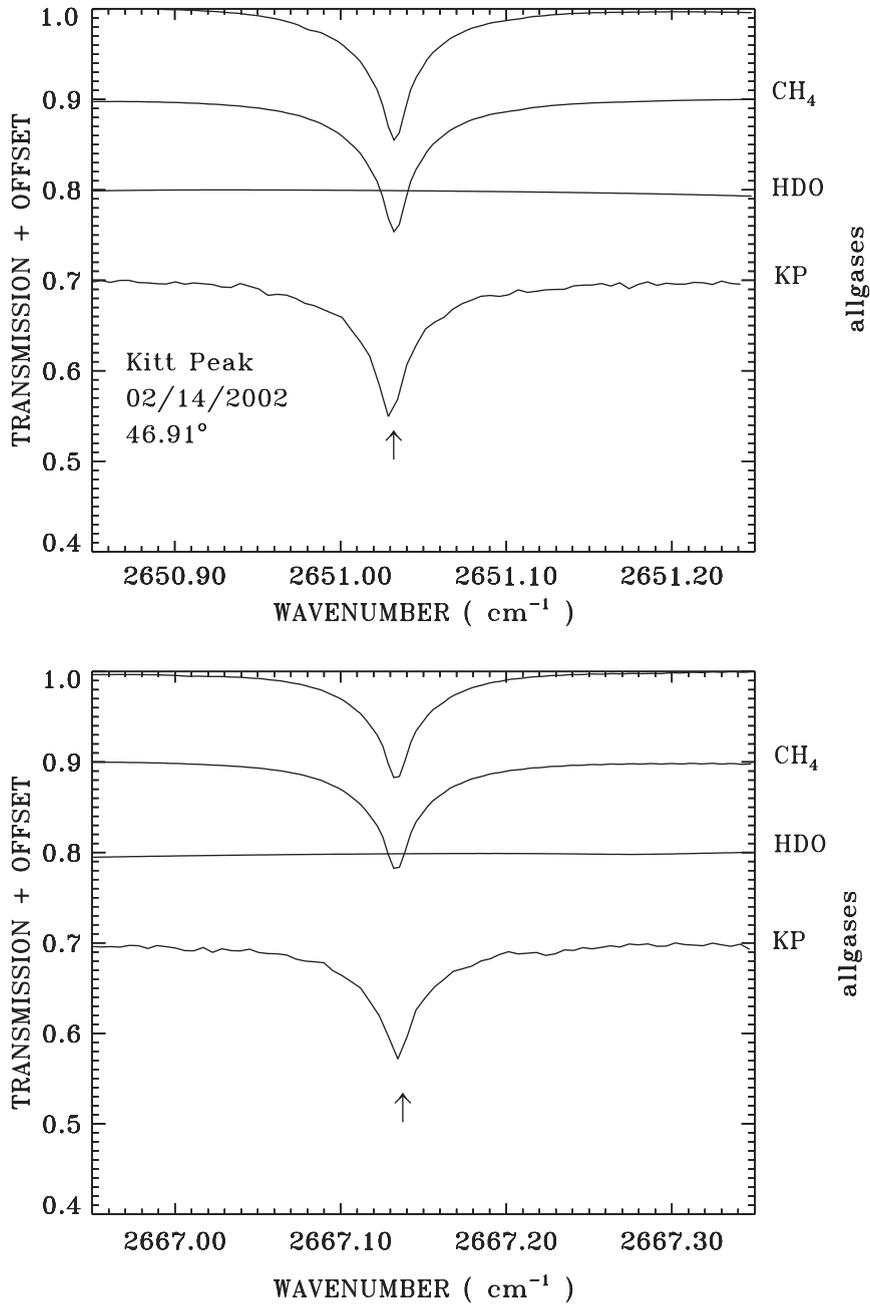


Fig. 1. Simulation of the absorption by the most important molecules in two of the three intervals analyzed in this study and the corresponding measured Kitt Peak solar spectrum, offset vertically for clarity (weak solar and atmospheric lines not shown in the simulations). The astronomical zenith angle and date of the measured spectrum are identified.

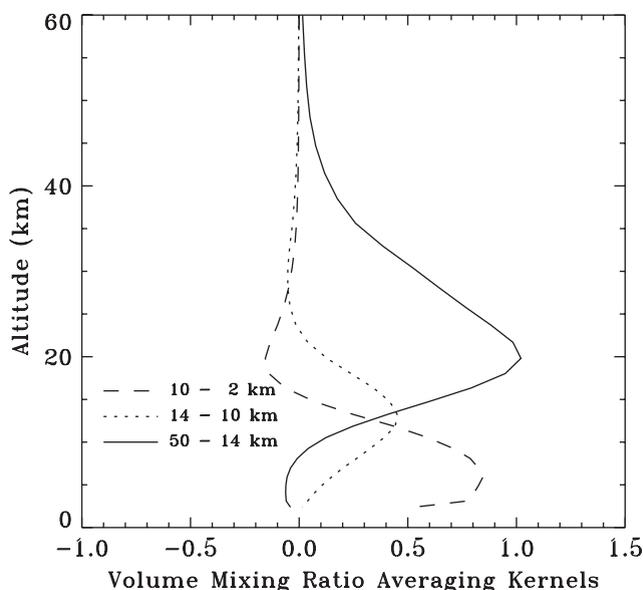


Fig. 2. Volume mixing ratio averaging kernels versus altitude for CH_4 for merged layers covering altitudes of 2.09–10, 10–14, and 14–50 km.

number of independent pieces of information, and a value of 2 was obtained. This is consistent with the broad averaging kernels shown in Fig. 2.

Fig. 3 illustrates a sample measurement and fit from the Kitt Peak time series. Residuals are shown on an expanded vertical scale. As in previous studies [12], objective criteria were used to eliminate measurements of weak absorption or high noise from the time series. After selection, the Kitt Peak time series contains a total of 566 measurements on 195 days and is one of the longest near continuous CH_4 NDSC measurements set reported to date.

Table 1 lists the most important random and systematic sources of error and gives estimates of their contribution to the error budget, for a typical spectrum. These values have been estimated as described previously [12]. Random error is reduced by considering merged tropospheric layers below 10 km, and by further calculating daily averages. Systematic error is the dominant source of uncertainty with a total relative error of 13% calculated from the root mean sum squares of the individual components. The largest error source is the a priori relative contribution to the retrieval.

Niwot Ridge (NWR) in situ VMR measurements were obtained weekly with gas chromatography, and analyzed with a flame ionization detector [26,27]. Precision of the NWR measurements is ~ 1 ppbv. The time series extended from June 1983 to December 2003.

Daily average tropospheric VMRs (2.09–10 km) derived from the Kitt Peak time series are displayed in Fig. 4 (plus symbols) and compared with the NWR surface in situ monthly average VMRs obtained between April 1993 and December 2003 (diamond symbols). The Kitt Peak time series was fitted with the expression

$$C_A = a_0 + a_1(t - t_0) + a_2(t - t_0)^2 + a_2 \cos(2\pi(t - t_0 - \phi)), \quad (1)$$

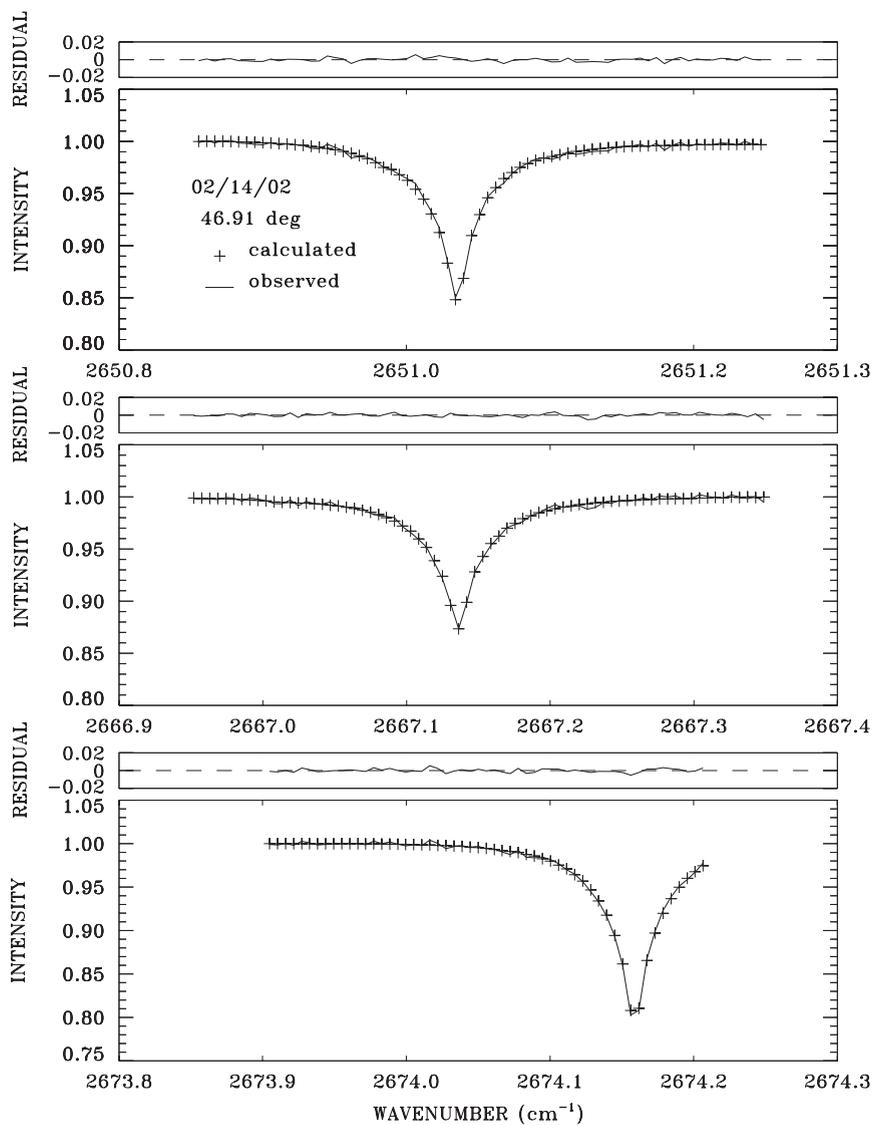


Fig. 3. Sample spectral fits from the Kitt Peak time series for the three intervals analyzed in this study. Residuals (measured minus calculated signals) are shown above each on an expanded vertical scale.

where C_A is the daily average tropospheric VMR at time t , a_0 , a_1 , and a_2 are coefficients for modeling the trend of the tropospheric VMR, a_3 is the amplitude of the seasonal cycle, and ϕ is the phase corresponding to the seasonal maximum. The same expression was used to fit the NWR data set. Resulting best fits to the full 27 year KP and 20 year NWR time series are, respectively, reproduced as dashed and solid curves. Both show a continuous long-term CH_4 increase with a slowdown in the accumulation rate in recent years. For Kitt Peak, we calculate a trend that corresponds to an increase of $8.255 \pm 2.197 \text{ ppbv yr}^{-1}$, one sigma, in 1983 declining to $1.945 \pm 3.695 \text{ ppbv yr}^{-1}$ in 2003, not significant at the one sigma level. The seasonal cycle was

Table 1

Random (R) and systematic (S) error sources and their estimated relative uncertainties for retrievals of CH₄ 2.09–10 km daily mean mixing ratios

Source of error	Type	Relative error (%)
Finite signal-to-noise	R	2
Zenith angle uncertainty	R	2
Channeling in spectrum	S	<1
Interferences	S	1
Forward model approximations	S	2
A priori relative contribution	S	13
CH ₄ spectroscopic parameters	S	2
Zero-level offsets	S	<1
Retrieval algorithm	S	3
Total random error		3
Total systematic error		14

See Ref. [12, Section 6] for the method used and parameters considered for the error analysis.

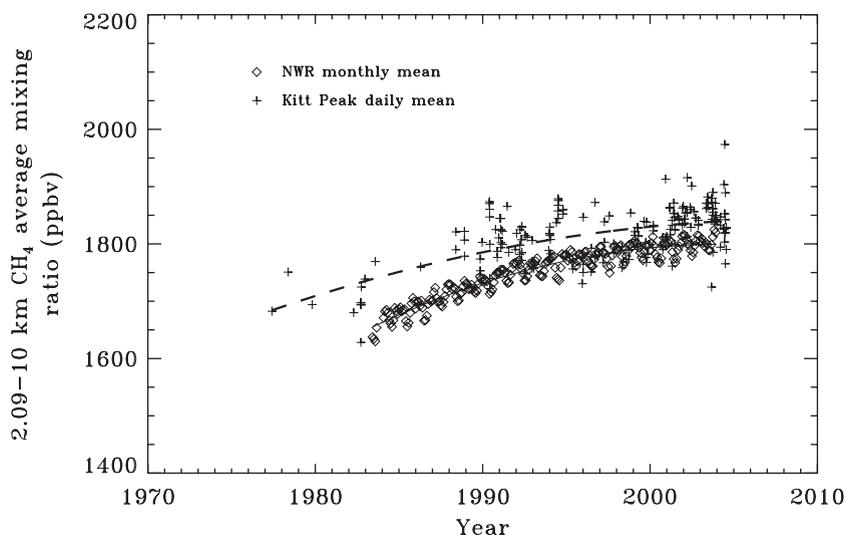


Fig. 4. Measured daily average 2.09–10 km mean volume mixing ratios versus time for Kitt Peak CH₄ (plus symbols) and monthly mean Niwot Ridge VMRs (diamond symbols) with fits to both assuming Eq. (1).

found not to be statistically significant in either sets and is not displayed. It is important to recognize the limited sampling of the Kitt Peak measurement time series. Prior to 1983, there are only 10 daily means, and the uncertainty in the CH₄ increase rate is likely to be larger than indicated by the formal uncertainty in our trend.

The Kitt Peak and CMDL measurements in general do not occur on the same days, nor is the frequency of the sampling the same. The mean ratio of Kitt Peak/CMDL VMRs has been calculated based on the fits to the time series for the coincident time period. The ratio of the

average Kitt Peak 2.09–10 km mixing ratio to the CMDL surface VMR the overlapping time period is 1.038 ± 0.034 . The relative difference in the mixing ratios is within the systematic error estimated for the Kitt Peak daily average measurements (Table 1) and suggests the error is overestimated.

3. Summary and conclusions

The Kitt Peak CH₄ time series can be compared with previously reported measurements. Washenfelder et al. [28] analyzed a time series of near infrared measurements of CH₄ recorded between 1977 and 1995 from the same station at 0.02 cm⁻¹ resolution. Column-averaged measurements between 1977 and 1995 show a seasonal peak-to-peak seasonal cycle with an amplitude of 30 ppbv and were fitted to estimate an average increase rate of 18.0 ± 0.8 ppbv yr⁻¹ over the time span, consistent with the trend of 18 ± 2 ppbv for the same time period [29,30].

A continuous rise in the CH₄ tropospheric mixing ratio is observed both above Kitt Peak over the past 27 years and at the surface from a northern hemisphere CMDL stations with overlap over 1983–2003. The Kitt Peak time series covers May 1977 to July 2004 with a best-fit increase rate of 8.255 ± 2.197 ppbv yr⁻¹, one sigma in 1983 declining to 1.945 ± 3.695 ppbv in 2003 for the 2.09–10 km mean VMR. The ratio of the Kitt Peak to the CMDL mixing ratios for the overlapping October 1987 to December 2003 time period equals (1.038 ± 0.034) , indicating the CMDL measurements are consistent with those from Kitt Peak within the error estimated for the ground-based remote sensing results (Table 1). This consistency is encouraging and suggests the infrared spectral parameters [23] and the SFIT2 algorithm [12] are valid within the estimated errors assuming the northern hemisphere CMDL results are also valid, there is no significant offsets due to the difference in station location. The solar absorption and surface measurement results indicate a significant slowdown in the CH₄ accumulation rate at northern mid-latitudes over the continental US. Our observation is consistent with ground-based solar absorption measurements, obtained from the Jungfraujoch for the 1951–2000 time period [5]. There is a continued need to monitor CH₄ levels both with the Kitt Peak FTIR and at NWR as they provide databases useful for understanding mid-latitudinal continental sources of CH₄ over the US, their variability, and changes as a function of time.

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