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Z. Wang, N. Deutscher, T. Warneke, J. Notholt, B. Dils, et al.. Retrieval of tropospheric column-averaged CH₄ mole fraction by solar absorption FTIR-spectrometry using N₂O as a proxy. *Atmospheric Measurement Techniques*, 2014, 7 (10), pp.3295-3305. 10.5194/amt-7-3295-2014 . hal-03116026

HAL Id: hal-03116026

<https://hal.science/hal-03116026>

Submitted on 20 Jan 2021

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Retrieval of tropospheric column-averaged CH₄ mole fraction by solar absorption FTIR-spectrometry using N₂O as a proxy

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Received: 30 December 2013 – Published in Atmos. Meas. Tech. Discuss.: 13 February 2014

Revised: 7 May 2014 – Accepted: 6 June 2014 – Published: 6 October 2014

Abstract. Tropospheric column-averaged CH₄ mole fractions were derived from ground-based column absorption measurements. The method uses stratospheric N₂O columns to correct for the stratospheric contribution to the CH₄ total column. The method was applied to four Total Carbon Column Observing Network (TCCON) sites covering locations from the Northern Arctic to the tropics. It performs well for all sites. The derived tropospheric CH₄ concentrations were compared with profiles measured by aircraft at three sites. The results indicate an inter-site consistency within 6 ppb (~0.3%). With aircraft profiles up to 3 km, the seasonal behavior of the derived tropospheric CH₄ concentration was also checked, revealing a difference of around 20 ppb. The mean relative uncertainty of the four sites, as estimated from the daily standard deviations, is 0.23 %.

The atmospheric mole fraction of methane has increased from about 700 ppb to the current atmospheric background of about 1800 ppb since 1770. Despite this dramatic increase, the observed global annual mean atmospheric abundance was nearly constant from 1999 to 2006, before it began to increase again in 2007 (Rigby et al., 2008; Dlugokencky et al., 2009). This behavior is a subject of open scientific discussion (Bousquet et al., 2011; Pison et al., 2013).

Atmospheric CH₄ concentration measurements can be linked quantitatively to regional sources and sinks by inverse modeling. Improving both the quality and quantity of measurements is a way to better constrain source and sinks, since this is an under-constrained problem. The Total Carbon Column Observation Network (TCCON) was founded to remotely measure column abundances of CO₂, CH₄, CO, N₂O and other molecules that absorb in the near infrared (NIR) (Wunch et al., 2011). The Network for the Detection of Atmospheric Composition Change (NDACC) ground-based solar absorption spectrometry in mid infrared (MIR) spectral regions can provide a total column measurement for many gases (Sussmann et al., 2013). Such column data are essential for the validation of greenhouse gas measurements from satellites and as either input or independent validation for inverse model studies. The column-averaged dry-air mole fraction (DMF) of CH₄ (known as X_{CH_4}) can be determined by creating a ratio to the retrieved column of the reference gas O₂ whose atmospheric abundance is well known. The tropospheric column-averaged mole fraction of CH₄ can be derived using methods based on the following: (i) a posteriori

1 Introduction

Methane (CH₄) is the second most important anthropogenic greenhouse gas in the atmosphere (Montzka et al., 2011). The main sources of CH₄ to the atmosphere are natural wetlands, anthropogenic activities (livestock production; rice cultivation; production, storage, transmission, and distribution of fossil fuels; waste waters and landfills) and biomass burning. Destruction by OH in the troposphere is the dominant atmospheric sink of CH₄. Both anthropogenic and natural emissions of CH₄ are likely to increase in the twenty-first century as global population increases and climate warms.

correction to the total column using a proxy for variations in the stratospheric contribution, such as the HF total column as an estimator for the stratospheric CH₄ contribution (Washenfelder et al., 2003; Warneke et al., 2006), as well as (ii) direct determination of the tropospheric mole fraction of CH₄ via retrieval of CH₄ profiles (Sepulveda et al., 2012). Currently the second method is only applied to NDACC high-resolution MIR solar absorption spectra, not to the NIR TCCON spectra. The first method is based on the fact that a linear relationship exists in the stratosphere between the DMFs of the CH₄ and HF and that the tropospheric mole fraction of HF exhibits little variability, and is indeed approximately zero. The stratospheric column of CH₄ can therefore be inferred from the total column of HF via this linear relationship, and then subtracted from the total column of CH₄ to yield the tropospheric CH₄ column. Variations in the CH₄ column due to changes in surface pressure are determined from the O₂ column. Using this method, the tropospheric column-averaged DMF of CH₄ can be determined with a precision of 0.5 % (Washenfelder et al., 2003).

In the stratosphere, a compact correlation exists between species of sufficiently long lifetime (Plumb et al., 1992). Species whose local lifetimes are longer than quasi-horizontal transport time scales share surfaces of constant mixing ratio, and a scatter plot of the mixing ratio of one versus that results in a compact curve. These correlations have been demonstrated by data sets from both chemical transport models and in situ measurements, such as observations taken from an aircraft platform (Avalone et al., 1997), Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) observations (Michelson et al., 1998) and balloon observations (Herman et al., 1998). This is true in the case of CH₄ and N₂O in the stratosphere. Hence, using N₂O to infer the stratospheric contribution of the total column of the CH₄ is an alternative approach. This approach is, however, complicated by the fact that N₂O is also present in the troposphere. In this work, we describe a method to derive the tropospheric column-averaged DMF of CH₄ in which the stratospheric N₂O column is used to estimate the stratospheric column of the CH₄. We apply the method to TCCON spectra at four sites, one tropical, two extra-tropical and one polar, and compare it with the results derived with the method using HF. In the following, Sect. 2 introduces the measurement sites and data. Section 3 describes the method, while Sect. 4 presents the results and discussion. In Sect. 5 we give an uncertainty analysis and summarize the merits of our proposed method in Sect. 6.

2 Measurements site and data analysis

2.1 FTIR data

Here we use solar absorption Fourier transform infrared spectroscopy (FTIR) measurements at four TCCON sta-

tions: Ny-Ålesund (78.9° N, 11.9° E) at Spitsbergen (Palm et al., 2010), Orléans, France (47.97° N, 2.113° E), Bialystok, Poland (53.23° N, 23.025° E) (Messerschmidt et al., 2010, 2012), and Darwin, Australia (12.424° S, 130.892° E) (Deutscher et al., 2010). The observations in the near infrared cover the spectral range between 4000 cm⁻¹ and 10 000 cm⁻¹ and were carried out with a CaF₂ beam splitter and a room-temperature InGaAs photodiode.

The spectra were analyzed using the non-linear least-squares spectral fitting algorithm code GFIT, developed at NASA/JPL (Toon et al., 1992). Atmospheric absorption coefficients are calculated line-by-line for each gas in a chosen spectral window, and for each retrieval level using the assumed temperature, pressure and a priori DMF profile in the forward model. All these absorption coefficients together produce the atmospheric transmittance spectrum. The temperature, pressure and water vapor profiles are obtained from National Centers for Environmental Prediction (NCEP) re-analysis data provided by the NOAA/ESRL Physical Sciences Division (Kalnay et al., 1996), and interpolated in time and space from six-hourly data to local solar noon and site latitude/longitude. The simulated spectrum is compared with the measured spectrum and DMF profiles are iteratively scaled to minimize the least-squares differences between the calculated and measured spectra. The spectral regions used in this study are the TCCON-standard regions given in Wunch et al. (2010).

2.1.1 In situ measurements

To validate the tropospheric CH₄ derived from FTIR measurements, in situ data from several sources are used. At Ny-Ålesund (78.9° N, 11.9° E) in situ CH₄ data are available from NOAA surface flask measurements (Dlugokencky et al., 2012) measured at Zeppelin mountain, which has an elevation of 474 m.a.s.l. compared to the TCCON site elevation of 30 m.a.s.l. The relatively high elevation and absence of strong local sources means that these measurements could approximately represent the free troposphere, and are used here in the absence of other more appropriate validation data for this site. Low altitude aircraft flight data are available at Orléans, taken twice per month since 1998 up to 3 km, corresponding to approximately 700 hpa in the pressure coordinate. Over Bialystok there has been regular profiling with semi-monthly to monthly observations using flask sampling at multiple levels up to 3 km for CO₂, CH₄, N₂O and other tracers since 2002. These measurements are extended through the entire atmosphere via a linear interpolation between 3.0 km and the tropopause altitude and assuming the GFIT a priori above that. The tropospheric column-averaged CH₄ abundances obtained are used to check the seasonal behavior of the FTIR-derived tropospheric column-averaged CH₄ mole fraction.

In addition, data from the HIAPER Pole-to-Pole Observations (HIPPO) of Carbon Cycle and Greenhouse Gases Study and Infrastructure for the Measurement of the Europe Carbon Cycle (IMECC) aircraft campaigns are used to calibrate the derived tropospheric column-averaged CH₄ mole fractions. HIPPO of Carbon Cycle and Greenhouse Gases Study measured cross sections of atmospheric concentrations approximately pole-to-pole, from the surface to the tropopause (Wofsy et al., 2011). A comprehensive suite of atmospheric trace gases pertinent to understanding the Carbon Cycle were measured. The measurements were taken using the High-performance instrumented Airborne Platform for Environmental Research. In this work, the measurements near the TCCON site at Darwin are used. The IMECC project aimed to build the infrastructure for a coordinated, calibrated, integrated and accessible data set for characterizing the carbon balance of the European. The aircraft campaign conducted within the IMECC project was organized by the Max Planck Institute for Biogeochemistry. A Learjet 35 aircraft was equipped with a cavity ring-down spectroscopy instrument (Picarro Inc.) for CO₂ and CH₄ mixing ratio measurements and with a vacuum UV fluorescence analyzer for mixing ratio measurements of CO. Profiles were taken from 300 m to 12 000 m over the European TCCON stations, including Bialystok and Orléans, during September and October, 2009 (Geibel et al., 2012).

2.1.2 Method

For both HF and N₂O, assuming there is a linear relationship between their stratospheric mole fractions, f , and that of CH₄ in the stratosphere, then

$$f_{\text{CH}_4}(z) = a + b \cdot f_y(z) \quad (1)$$

where, y represents HF or N₂O. Figure 1 presents the correlation of the stratospheric mole fractions of HF (left) and N₂O (right) with CH₄ based on retrievals from the ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer) satellite (Bernath et al., 2005). The deviation of the N₂O-CH₄ relationship from the global fit occurs only in the -80 to -60° latitude bin, and represents a small contribution to the column. For the derivation of a and b , the retrieved stratospheric profiles of HF, N₂O and CH₄ are separated into several 20 degrees wide latitude bands. In case of HF, the latitudinal variation of the slope b ranges from 740 to 870 ppb ppb⁻¹, and from 3.6 to 4.4 ppb ppb⁻¹ for N₂O. Between 2004 and 2010 no discernable time-dependency could be detected. For the four TCCON sites: Spitsbergen, Bialystok, Orléans and Darwin the slopes, b , for their corresponding latitude bands are 4.34, 4.39, 4.39 and 3.53, respectively, for N₂O, and -749.05 , -751.21 , -751.21 and -876.03 for HF.

Multiplying both sides of Eq. (1) with air density and integrating through the stratosphere yields:

$$\text{VC}_{\text{CH}_4}^{\text{strat}} = a \cdot \text{VC}_{\text{air}}^{\text{strat}} + b \cdot \text{VC}_y^{\text{strat}}, \quad (2)$$

where VC denotes the vertical column. The stratospheric column of y can be obtained by subtracting the tropospheric column from the total column, so Eq. (2) can be rewritten as follows:

$$\text{VC}_{\text{CH}_4}^{\text{strat}} = a \cdot \text{VC}_{\text{air}}^{\text{strat}} + b \left(\text{VC}_y - \text{VC}_y^{\text{trop}} \right). \quad (3)$$

The tropospheric column-averaged mole fraction of the CH₄ is then calculated as follows:

$$X_{\text{CH}_4}^{\text{trop}} = \frac{\text{VC}_{\text{CH}_4} - \text{VC}_{\text{CH}_4}^{\text{strat}}}{\text{VC}_{\text{air}}^{\text{trop}}}. \quad (4)$$

In Eq. (3) the tropospheric column of HF is zero. The mole fraction of N₂O is almost constant with respect to altitude in the troposphere. In addition, the seasonal and long-term variations of the N₂O mole fraction are quite small, and therefore highly predictable. So the tropospheric column of N₂O can then be calculated as the product of its mole fraction and the dry air column in the troposphere. The mole fraction of N₂O in the troposphere can be obtained from either in situ measurements or a model simulation. The distribution of N₂O is fairly uniform with relatively small variability (3–5 ppb) (Kort et al., 2011). In this paper a simple linear model is applied, an N₂O growth rate of 0.75 ppb yr⁻¹ is assumed from a background concentration of 315 ppb at the start of the year 2000 (<http://www.esrl.noaa.gov/gmd/hats/combined/N2O.html>).

In the case of the HF, when approaching the tropopause, the HF mole fraction approaches zero and so the constant a in Eq. (1) represents the CH₄ mole fraction in the troposphere. Washenfelder et al. (2003) consider a as the tropospheric column-averaged CH₄ mole fraction, and use O₂ to infer the dry air column. Under these conditions, inserting Eq. (3) into Eq. (4) yields the equation used by them:

$$X_{\text{CH}_4}^{\text{trop}} = a = \frac{0.2095(\text{VC}_{\text{CH}_4} - b \cdot \text{VC}_{\text{HF}})}{\text{VC}_{\text{O}_2}}. \quad (5)$$

This method can be used for N₂O as well. Since in the troposphere, the N₂O mole fraction is almost constant and its value can be quite well predicted, we then subtract the tropospheric N₂O mole fraction from its mole fraction profile in the whole atmosphere. Such a derived “species” will also be present completely in the stratosphere and Eq. (1) also holds as long as the constant a is replaced by a value equal to a plus the tropospheric N₂O mole fraction multiplied by the slope b . The resulting quantity can then be considered as the tropospheric column-averaged CH₄ mole fraction. We obtain the following equation:

$$X_{\text{CH}_4}^{\text{trop}} = \frac{\text{VC}_{\text{CH}_4} - b \left(\text{VC}_y - X_y^{\text{trop}} \text{VC}_{\text{O}_2} / 0.2095 \right)}{\text{VC}_{\text{O}_2} / 0.2095}. \quad (6)$$

In this equation, X_y^{trop} is replaced by $X_{\text{N}_2\text{O}}^{\text{trop}}$ for N₂O or set to zero for HF.

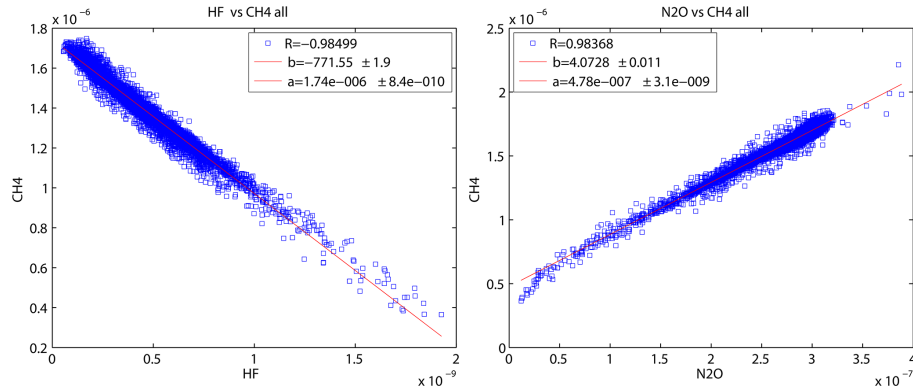


Figure 1. Correlations between the stratospheric mole fractions of N₂O (right) and HF (left) with CH₄ on a global scale. Correlation coefficient, slope and intercept are indicated in the legend. The data are from the ACE-FTS satellite.

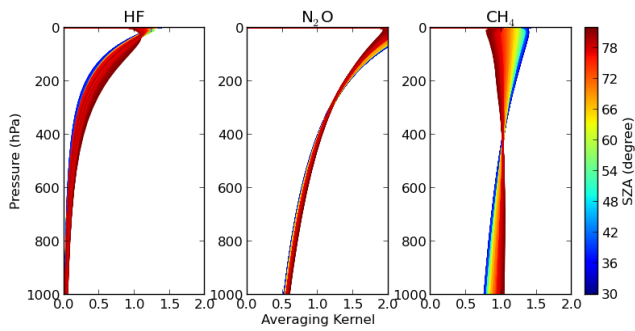


Figure 2. The averaging kernels of HF, N₂O and CH₄ at Bialystok for all spectra from 2010. The colors indicate the solar zenith angle of the corresponding measurements.

Due to the effect of the averaging kernels the straightforward equation above (Eq. 6) needs to be modified. The total column retrieved by GFIT is a weighted summation of partial columns at different altitudes. The weights are represented by the averaging kernel and a pressure weighting function that usually differs from one. Figure 2 presents the averaging kernels of HF, N₂O and CH₄ for Bialystok from all spectra during 2010. The averaging kernel depends largely on the solar zenith angle. In the case of N₂O, the averaging kernel has a large weight in stratosphere and small weight in troposphere, so variations in the stratospheric column of N₂O will be amplified in the retrieved total column compared to the true atmospheric variability, and tropospheric variations will be dampened. For CH₄, the averaging kernel is close to unity at all altitudes, so the effect of the averaging kernel is small.

From Rodgers (2000) and Wunch et al. (2010) the mole fraction profile retrieved by a profile-scaling retrieval, such as that performed by GFIT, is as follows:

$$f_r = f_a + A(f_t - f_a), \quad (7)$$

where the f_r , f_t and f_a are the retrieved, true and a priori mole fraction profiles, respectively, and A is the averaging

kernel. Integrating Eq. (7) and rearranging yields:

$$\int_0^{P_s} f_r \frac{dp}{mg} = \int_0^{P_s} (I - A) f_a \frac{dp}{mg} + \int_0^{P_s} A f_t \frac{dp}{mg}, \quad (8)$$

where m is the molecular mass of moist air (i.e., $m = (1 - x_{\text{H}_2\text{O}}) m_{\text{dry}}^{\text{air}} + x_{\text{H}_2\text{O}} \cdot m_{\text{H}_2\text{O}}$), g is the gravitational acceleration, I is the identity matrix, and P_s is surface pressure. Because GFIT performs a profile scaling retrieval and produces the column averaging kernel vector (Connor, 2009) instead of a full averaging kernel matrix, when using a column averaging kernel Eq. (8) can be rewritten as follows:

$$\int_0^{P_s} f_r \frac{dp}{mg} = \int_0^{P_s} (1 - a(p)) f_a \frac{dp}{mg} + \int_0^{P_s} a(p) f_t \frac{dp}{mg}, \quad (9)$$

where $a(p)$ is the column averaging kernel vector, which is a function of pressure (altitude). It can be seen from the equation above that the retrieved total column includes contributions from the a priori and true profiles and the averaging kernel.

After taking the averaging kernel effect into account Eq. (6) is changed to the following equations:

$$X_{\text{CH}_4}^{\text{trop}} = \quad (10)$$

$$\frac{\text{VC}_{\text{CH}_4} - \gamma_{\text{CH}_4} - b\mu_y (\text{VC}_y - \gamma_y - \varphi_y \cdot X_y^{\text{trop}} \cdot \text{VC}_{\text{O}_2}/0.2095)}{\varphi_{\text{CH}_4} \cdot \text{VC}_{\text{O}_2}/0.2095},$$

$$\varphi = \int_0^{P_s} a \frac{dp}{mg} / \int_0^{P_s} \frac{dp}{mg}, \quad (11)$$

$$\mu = \int_0^{P_t} a_{\text{CH}_4} (f_t - X_t^{\text{trop}}) \frac{dp}{mg} / \int_0^{P_t} a (f_t - X_t^{\text{trop}}) \frac{dp}{mg}, \quad (12)$$

$$\gamma = \int_0^{P_s} (1 - a(p)) f_a \frac{dp}{mg}, \quad (13)$$

where, P_t is tropopause pressure. For calculation of the coefficients φ and μ , the true mole fraction profiles of N₂O and HF are replaced by the GFIT a priori profile, and in the case of N₂O, the a priori profile is scaled to fit the tropospheric N₂O mole fraction assumed previously.

To compare the derived tropospheric column-averaged CH₄ mole fraction with in situ measurements, the measured CH₄ profiles need to be integrated. At the same time, the averaging kernel of the FTS measurements needs to be taken into account. For our purpose only the tropospheric profile is important. After replacing the total column on the right hand side of Eq. (10) by the right hand side of Eq. (9), assuming the coefficient defined by Eq. (12) accurately replaces the averaging kernels of N₂O or HF with ones of CH₄, and applying Eq. (1) in the stratosphere, it can then be seen that the effect of averaging kernel can be represented as follows:

$$X_{\text{CH}_4}^{\text{trop}} = \frac{\int_{P_t}^{P_s} a_{\text{CH}_4} f_t \frac{dp}{mg}}{\int_{P_t}^{P_s} a_{\text{CH}_4} \frac{dp}{mg}} \quad (14)$$

to integrate the aircraft data, with x_t simply replaced by the measured in situ profile.

The derivations above are based on the total columns of CH₄, N₂O and HF, but the total columns directly retrieved from the spectra include errors arising from spectroscopic imperfections and instrumental effects. The final TCCON products are the dry air column averaged mole fractions X_{CH_4} , $X_{\text{N}_2\text{O}}$ and X_{HF} , which have been corrected by air-mass independent and air-mass dependent calibration factors to account for such errors. These corrections should be taken into account for this work and the Eq. (10) can be written as follows:

$$X_{\text{CH}_4}^{\text{trop}} = \frac{1}{\varphi_{\text{CH}_4}} \left[X_{\text{CH}_4} - \frac{\gamma_{\text{CH}_4}}{\text{VC}_{\text{air}}} - b \cdot \mu_y \left(X_y - \frac{\gamma_y}{\text{VC}_{\text{air}}} - \varphi_y \cdot X_y^{\text{trop}} \right) \right]. \quad (15)$$

The air-mass independent calibration factors are taken as those used throughout TCCON (Wunch et al., 2010). These factors have been re-evaluated by Geibel (2012) based on European sites, but this re-evaluation is not taken into account because it has not been applied to the current TCCON release.

3 Results

To test the method described in Sect. 3, data from four TCCON sites at Spitsbergen, Orléans, Bialystok and Darwin are used.

3.1 Comparison between the N₂O and HF methods and in situ data

Figures 3–6 show the results for Spitsbergen, Orléans, Bialystok and Darwin. We compare to in situ data from NOAA

at Spitsbergen, and the low aircraft data at Orléans and Bialystok. These profiles have been extended into whole troposphere as described in Sect. 2.2, and then integrated to produce a tropospheric column-averaged CH₄ mole fraction. For each site with available in situ data the results using N₂O are in better agreement with the in situ measurements than when using HF. The difference between the results using N₂O and HF has both seasonal and site dependence. At Spitsbergen the results using N₂O are about 30 ppb higher than that using HF, about 20 ppb at Bialystok and Orléans, and about 10 ppb lower at Darwin. Such a difference might result from the uncertainty in the HF column. The HF column used here is not calibrated through in situ profile measurements since HF is located completely in the stratosphere and there are no such measurements currently available. Inaccuracy in the spectroscopy of HF will force the retrieved HF column away from the truth. Such an effect also depends on the HF total column. A stronger signal is more sensitive to a spectroscopy parameter error. This might partly explain the site dependence of the difference between the results using N₂O and HF since the tropopause pressure and HF column generally decrease from Arctic to tropics.

Another difference is that the results using HF have more scatter at Darwin than at the other three sites, while the results using N₂O have similar scatter for all four sites. This difference also arises from HF column error. In the NIR the HF column is retrieved from a weak spectral absorption line that is located at the shoulder of a water line. Therefore, the retrieval of HF suffers from water vapor interference. Such influence depends on both the water amount and its vertical distribution, and results in more scatter. In the tropics the higher amount of water vapor in the atmosphere will significantly influence the retrieved HF column. Another factor is that HF is completely located in the stratosphere, and since generally the tropopause height increases from high to low latitude, the column amount of HF decreases. The retrieval of HF has better precision and worse accuracy for larger HF columns due, respectively, to a stronger signal and larger effect from spectroscopy error, and vice versa. The performance of the HF method should be more stable but have a larger offset for high-latitude sites like Spitsbergen owing to the dry conditions and more significant signals, and be less stable and have a smaller offset for tropical sites like Darwin because of the moisture conditions and relatively weaker signals.

The main uncertainty resulting from the N₂O approach comes from assuming a constant N₂O mole fraction throughout the troposphere. This is a reasonable approximation because of its long life time in the atmosphere (114 years). However, in the presence of local sources, like biomass burning and industrial sources, such an assumption might not be valid. As the same tropospheric N₂O mole fraction is used for all sites, the difference between different regions is also neglected. This can also cause problem for sites where there are strong local N₂O sources. A sensitivity test reveals that a

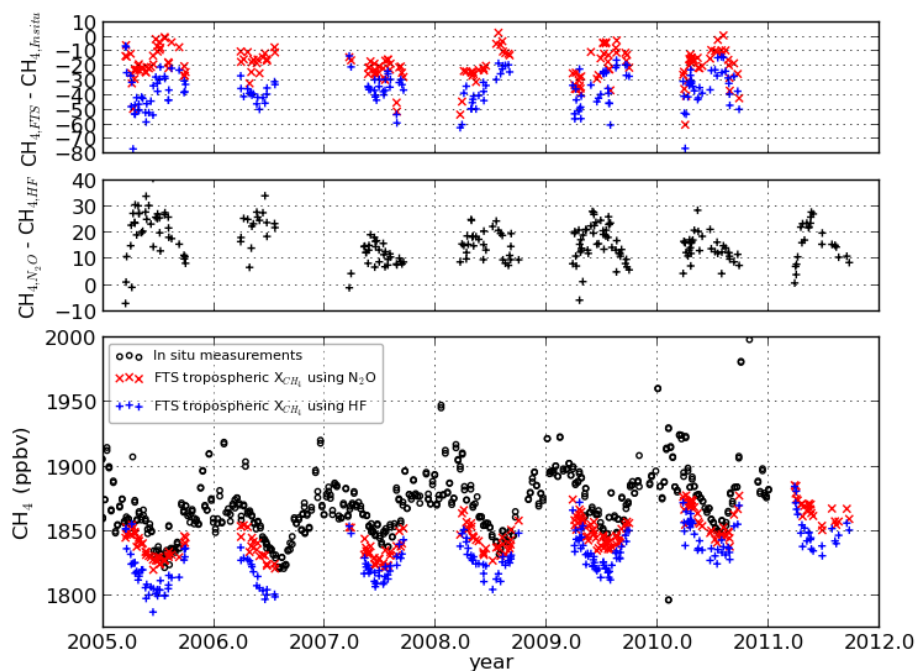


Figure 3. Results at Spitsbergen, the red points correspond to the tropospheric column-averaged CH₄ mole fraction derived from N₂O, the blue to those derived using HF and the open circles are in situ CH₄ data measured at Zeppelin mountain. The upper panel shows the difference between the in situ and tropospheric column-averaged CH₄ mole fractions, the middle panel is the difference between the results using N₂O and HF.

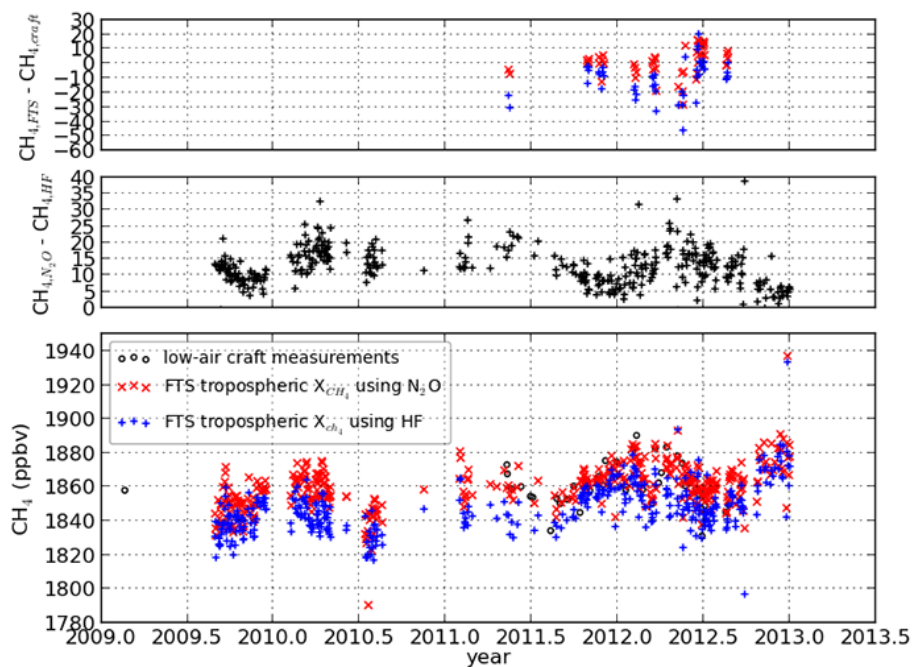


Figure 4. Same as Fig. 3 except for the Orléans site and with the black points in the lower panel representing tropospheric column-averaged CH₄ mole fractions derived from low altitude aircraft flights at this site.

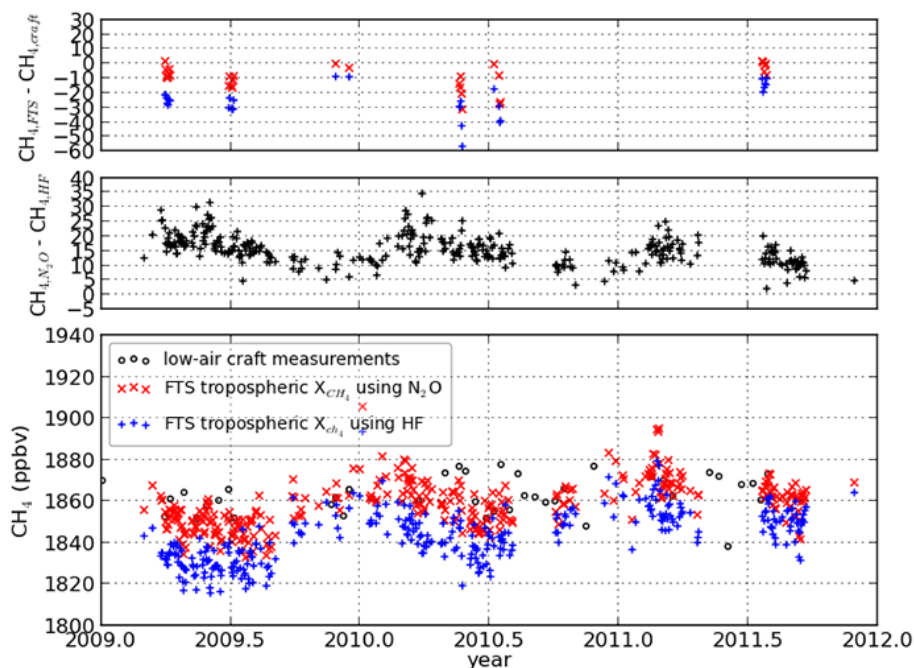


Figure 5. Same with Fig. 4 except for Bialystok.

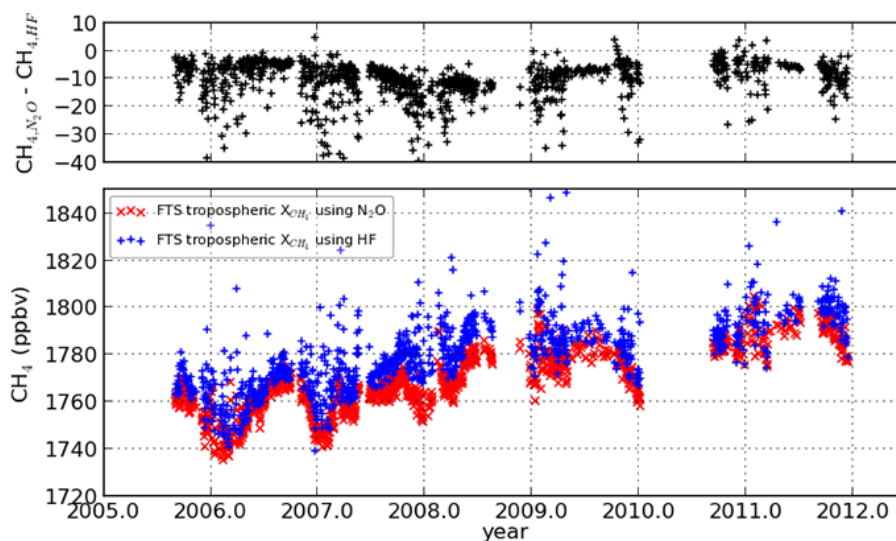


Figure 6. Results at Darwin.

2 ppb perturbation in assumed tropospheric N₂O mole fraction (an estimation of its seasonal cycle amplitude) results in perturbation in the derived tropospheric column-averaged CH₄ mole fraction of 4.0–4.4 ppb at Darwin, 4.2–5.6 ppb at Orléans and 4.5–5.5 ppb at Spitsbergen.

Figure 7 presents annual cycles derived through averaging all time series results given by Figs. 3–6. Generally the seasonal features of results from N₂O and HF are similar except an almost constant offset (with a variability of about 8 ppb) at

each site. As previously mentioned, these might come from the error in the HF total column.

3.2 Comparison with aircraft profile data

In situ profiles from the HIPPO and IMECC aircraft campaigns are used to compare to the derived tropospheric column-averaged CH₄ mole fractions and assess the inter-site consistency of the methods. The comparison between the integrated in situ profiles and the HF- and N₂O-derived tropospheric column-averaged CH₄s is shown in Fig. 8. The

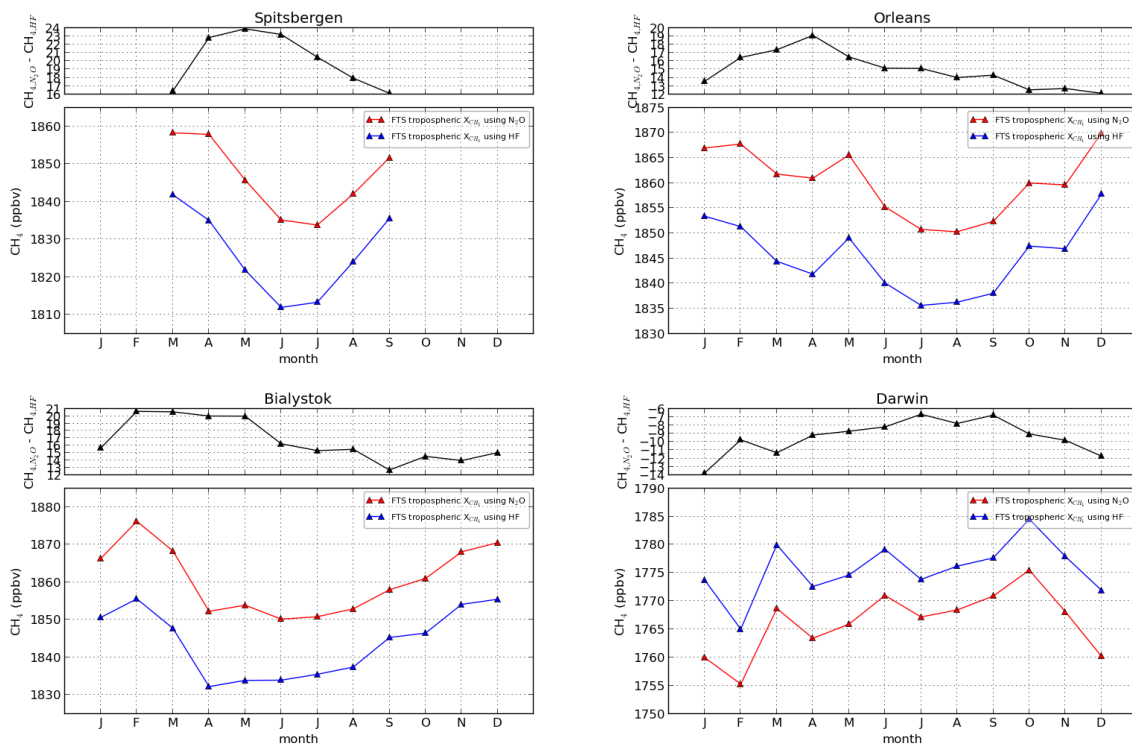


Figure 7. The multi-annual mean annual cycles of tropospheric column-averaged CH₄ mole fraction for four sites. The red points correspond to the results derived from N₂O and the blue to HF.

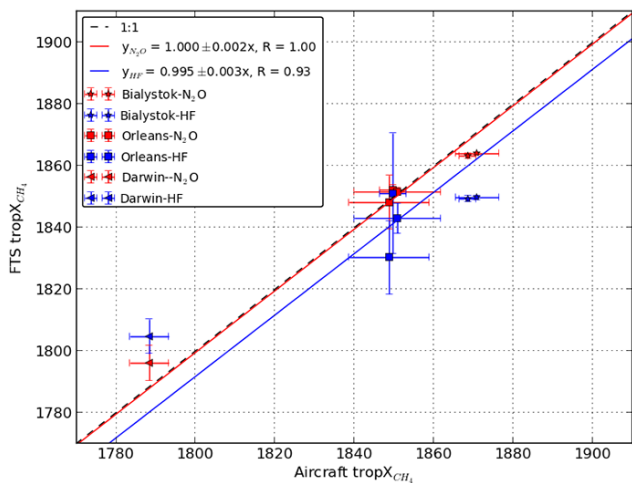


Figure 8. Comparison results with aircraft data. The aircraft profiles are smoothed using GFIT averaging kernels in troposphere using Eq. (14). The FTS data are averaged through aircraft measurements periods, and the error bars of FTS data are standard deviations of these averaged data.

aircraft data at Bialystok and Orléans are from the IMECC campaign, and at Darwin from the HIPPO-4 campaign. According to definition, the tropospheric column-averaged CH₄ mole fraction is the mean abundance between the surface and

the chemical tropopause. The aircraft profiles do not extend high enough to identify the chemical tropopause, so the thermal tropopause is used instead. The GFIT a priori profile is used for altitudes between the highest in situ measurement and the tropopause altitude. The a priori profile has been scaled to match the aircraft profile. The mole fraction at the lowest sample point is used to extrapolate to the surface to complete the profile below the lowest measured point during the aircraft flight.

The constructed profiles are then integrated using Eq. (14). Results from the FTIR during the aircraft measurement period are averaged, and the uncertainty of the FTIR data is estimated as the standard deviation of these results. The uncertainty of the tropospheric CH₄ integrated from the aircraft profile is calculated as the mean of the uncertainties at all sample points along the altitude axis, weighted by the partial air column at each point. Comparing the GFIT a priori and the in situ measurements reveals that the standard deviation of the ratios of the a priori to the measurement is 1.8%. Therefore, for the altitude range where the scaled GFIT a priori is used, an uncertainty of 1.8% is assumed. This represents the largest contribution to the total uncertainty. The uncertainties of the points above the aircraft ceiling are estimated from instrumental performance and the variation of CH₄ mole fraction along the aircraft path. In general the results using N₂O fall closer to the fitted line. The distances between the points and the fitted line are 3.5, 4.6, 2.1, 0.8,

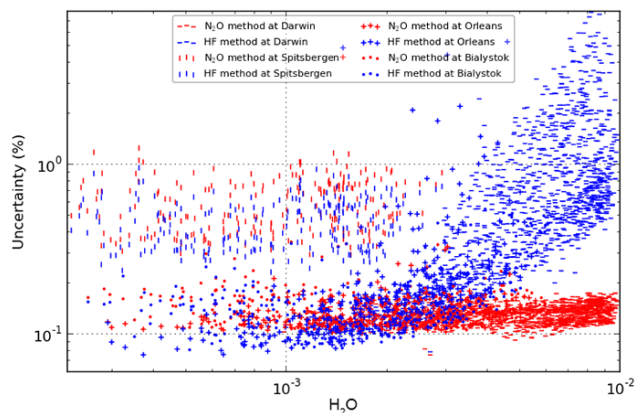


Figure 9. Relative error estimation of the tropospheric column-averaged CH₄ mole fraction using Gaussian error propagation equation for four sites, the blue corresponds to the error for the method using HF and the red to that of method using N₂O.

0.2, 5.7 ppb for the results derived using the N₂O method, and 7.6, 9.0, 6.9, 0.4, 7.1, 17.2 ppb for the HF method.

4 Uncertainty analysis

The Gaussian error propagation equation is used to estimate the uncertainty in calculating the tropospheric column-averaged mole fraction of CH₄ using Eq. (15). The variation of the tropospheric mole fraction of N₂O during one day is small and might cause biases that vary on a seasonal time scale. Here, we concentrate on the estimation of precision, so the errors in the assumed tropospheric mole fraction of N₂O were not taken into account. Also, the errors in the coefficients accounting for the averaging kernel effect are overlooked since they are unknown. The errors of the slope parameters (*b*) are estimated as 0.011 (N₂O) and 1.9 (HF). The errors of the XCH₄, XN₂O and XHF are taken as the uncertainties estimated in GFIT. As an alternative approach of estimating the uncertainty, we calculate the standard deviation of the derived tropospheric column-averaged CH₄ mole fractions during a day. To ensure the calculated standard deviation is meaningful and that only days with fine weather conditions are considered, only those days with more than 50 spectra available at Spitsbergen and 100 spectra available at other sites are used. Figure 9 presents the estimated relative uncertainty for all sites using the Gaussian error propagation equation method and Fig. 10 presents the results using the standard deviation method. The two methods produce results with similar behavior. The mean relative standard deviation of the tropospheric column-averaged CH₄ mole fractions using N₂O is 0.15 % (Darwin), 0.30 % (Spitsbergen), 0.28 % (Orléans) and 0.14 % (Bialystok), and 0.93 %, 0.45 %, 0.50 %, and 0.20 %, respectively, in the case of HF. So the method using HF produces larger uncertainties, especially at Darwin. Also the uncertainty of the method us-

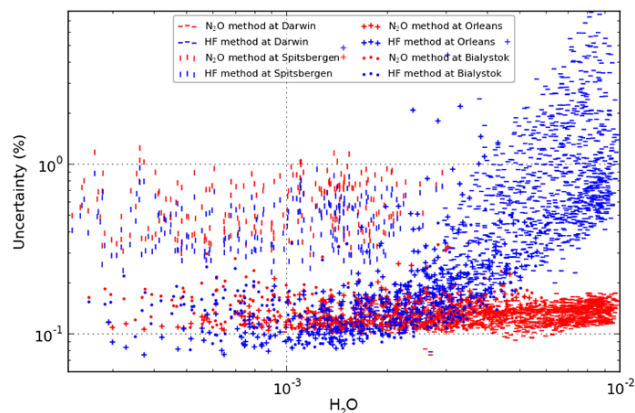


Figure 10. Same as Fig. 9, except for that the relative error is estimated as the standard deviation of daily mean tropospheric CH₄.

ing HF suffers from stronger H₂O interference, resulting in higher uncertainties with larger H₂O columns. At low H₂O, the two methods are comparable, and using the Gaussian error formulation, the HF method results in marginally lower uncertainties, while the relative daily standard deviations are smaller for the N₂O method.

5 Conclusions

In this paper, we propose using N₂O to correct for the stratospheric contribution to the total column of CH₄ in order to derive a tropospheric column-averaged CH₄ mole fraction. This method is applied to data from four TCCON sites. At Spitsbergen and Orléans, the tropospheric CH₄ derived using N₂O and HF are compared with surface flask measurements and low aircraft profiles data, respectively. At both sites, the results using N₂O agree better with in situ measurements than the HF derived results. The mean relative standard deviations are 0.23 % and 0.52 % for the methods using N₂O and HF, respectively. Especially, at Darwin the HF method produces much larger uncertainty (0.93 % compared with 0.15 % of N₂O method), which results from interference from H₂O that is absent for the N₂O method. Under drier conditions, the relative uncertainties of the two methods are comparable, however the N₂O method shows a clear advantage in more humid situations. The methods have also been compared with aircraft profiles at three sites, and the results reveal that the N₂O method has better inter-site consistency, however, this needs to be verified across a wider range of sites. The sensitivity of the derived tropospheric CH₄ to the assumed tropospheric N₂O mole fraction is around 4–5 ppb per 2 ppb. Further work could be done to represent N₂O mole fraction in troposphere more realistically.

Acknowledgements. This work was funded by the EU-project InGOS. Furthermore the authors acknowledge the EU-projects ICOS-INWIRE for support of the measurements, the EU-project IMECC for the aircraft data at Orleans and Bialystok, additional funding for IMECC aircraft data by the Max Plank Society, and the sponsors of the HIPPO project: the National Science Foundation, the National Oceanic and Atmospheric Administration and G-V “HIAPER”: National Center for atmospheric Research and Steven C. Wofsy for providing aircraft data at Darwin (the HIPPO data are also available to the public from the HIPPO website at <http://hippo.ornl.gov/>). We thank NOAA, Earth System Research Laboratory, Global Monitoring Division for providing surface CH₄ flask data.

Edited by: T. von Clarmann

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