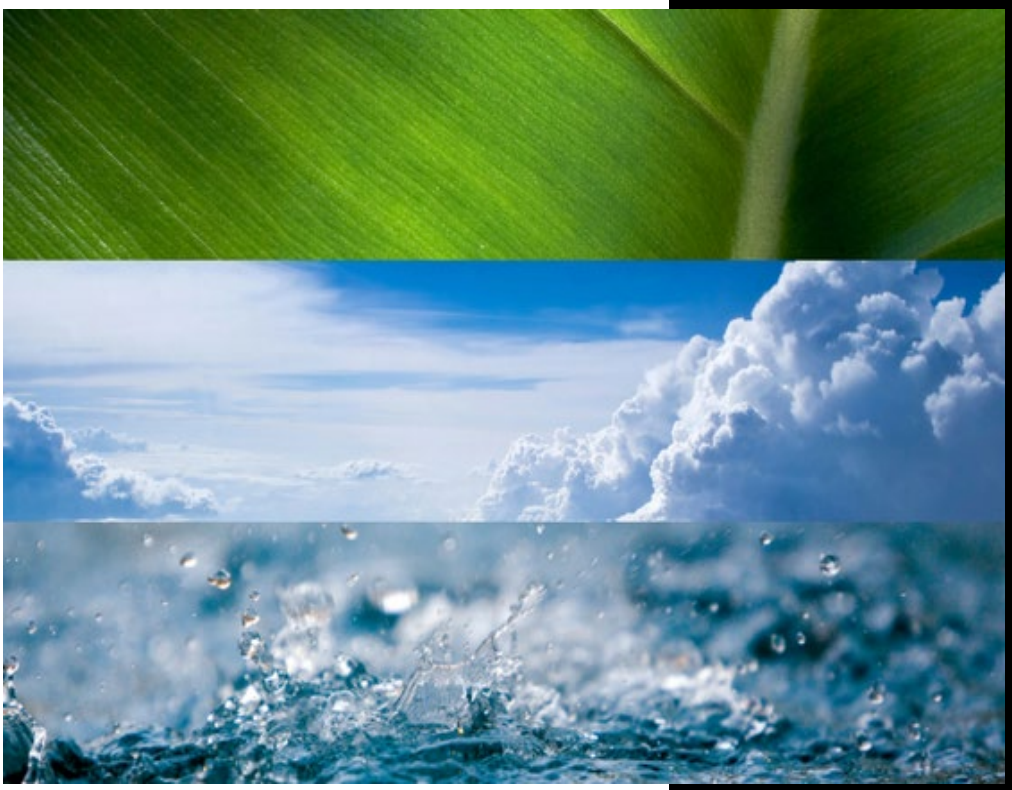
RINGO | Readiness of ICOS

Readiness of ICOS for Necessities of integrated Global Observations

D3.1

Specification for high accuracy in situ vertical profile measurements



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Deliverable: Specification for high accuracy in situ vertical profile measurements

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ABSTRACT

Within the EU-funded Readiness of ICOS for Necessities of integrated Global Observations (RINGO) of Integrated carbon observation system (ICOS) project, vertical profile measurements using AirCore have been explored to enhance the link between ICOS ground-based in situ measurement network, the Total Carbon Column Observing Network (TCCON), and satellite measurements.

In June 2018, an intensive AirCore comparison campaign took place at the TCCON site in Sodankylä, Finland. A total of 10 balloon flights and 26 vertical profiles were made, with combinations of different AirCores and/or the Lightweight Stratospheric Air (LISA) sampler per balloon flight. The measured species include CO_2, CH_4, CO, O_2, H_2O by continuous cavity ring-down spectrometers (CRDS) at Sodankylä, and subsequent isotopic compositions of CO_2, CH_4 and halogenated trace gases by delayed analyses of collected stratospheric air samples conducted later in several individual home laboratories. In June 2019, a second intensive AirCore comparison campaign was performed in Trainou, France. A total of 27 balloon flights were made, with a payload of less than 4 kg per balloon flight.

The results show that the uncertainties of AirCore mole fraction measurements are 0.15 – 0.2 ppm and 4 – 7 ppb for CO_2 and CO, respectively. When no chemical dryer was used during sampling, we observed small and insignificant stratospheric CO_2 difference of 0.06 – 0.11 ppm. Furthermore, variations of AirCore CO_2 and CH_4 measurements at individual heights are dominated by spatial resolution differences, and AirCore tubing with and without surface coating can cause a large difference of up to ~ 5ppm for CO_2. With these, we recommend that AirCores shall be carefully designed to obtain desired spatial resolution, AirCore tubing must be properly coated to achieve high-accuracy CO_2 observations, and no chemical dryer during sampling may be an option at least for the stratospheric part, but is still recommended for tropospheric sampling to preserve the AirCore coating from deterioration due to water vapor on surface areas, and/or to preserve the quality of the tropospheric portion of the AirCore sample .

For CO_2, we have achieved the accuracy target for high-accuracy observations. However, there is certainly room to improve the uncertainties of CO observations. Furthermore, we observed a difference in the altitude registration of 2-3 hPa for the stratospheric part among different AirCore retrievals, indicating the need to further develop and improve the altitude registration in future projects.

We worked on a full-physical CH_4 profile retrieval algorithm (SFTIR4NIR) for near-infrared (NIR) spectra recorded at TCCON sites using ground-based Fourier transform spectrometers. We obtained a degree of freedom of about 2.4 indicating that we get two distinct pieces of information as the tropospheric and the stratospheric columns in addition to the total column of CH_4. Applying our retrieval strategy at six TCCON sites (Ny-Ålesund, Sodankylä, Bialystok, Bremen, Orléans and St Denis) and comparing to the standard TCCON XCH_4 we ascertain systematic uncertainty to be within 0.35% and random uncertainty to be within 0.5% for our product. The SFIT4NIR tropospheric and stratospheric columns were compared to surface in-situ, satellite, AirCore and aircraft reference measurements. The comparison between our SFIT4NIR retrievals and AirCore/aircraft measurements indicate that the uncertainties of our retrieved tropospheric partial columns are 1.0±0.2% and the stratospheric partial columns are 4.0±2.0%. Finally, we have compared the SFIT4NIR CH_4 partial and total column retrievals from the NIR TCCON measurements performed during the RINGO campaigns at Sodankylä, Finland and Orléans, France to the AirCore measurements from the different groups. The difference was found to be within the uncertainty estimates of the SFIT4NIR results. The small differences among the AirCore results are better understood. Our method to retrieve CH_4 profile showed robust results for six TCCON sites and can be further applied to TCCON type of measurements from other locations and offer partial column CH_4 products for further use.

A method separating tropospheric from stratospheric methane using TCCON spectra has been established and evaluated against vertical resolved measurements by AirCores. The method is based on N_2O as a proxy for stratospheric CH_4 using the standard TCCON data product. The comparison against AirCore measurements has been performed at the TCCON sites Orléans and Sodankylä and shows promising results.

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1 INTRODUCTION

ICOS has implemented an extensive network of atmospheric monitoring of GHG mole fractions, which is, however, entirely based on surface stations and ships, and is lacking vertical profile measurements. However, vertical profile measurements provide a unique means to validate the vertical mixing in transport models, and are essential in bridging remote sensing with in situ measurement networks.

Within the RINGO project, Task 3.1, we have explored two new ways of observing vertical profile measurements of GHG mole fractions, which may be potentially implemented in the future ICOS network: 1) High accuracy in situ vertical profile measurements of GHG mole fractions using AirCore; 2) vertical profile retrievals of CH_4 using TCCON spectrometers.

AirCore is an atmospheric sampling system which uses a long tube to sample the air from the surrounding atmosphere and to preserve profiles of the trace gases of interest from the surface (few hundred meters) to the middle stratosphere (about 30 km; Karion et al., 2010). The Total Carbon Column Observing Network (TCCON) network uses the ground-based FTIR measurement system to obtain atmospheric column measurements of trace gases. The measurement system is composed of an automatic weather station, a sun tracker and a FTIR instrument. All these sites use a Bruker IFS 120/125HR instrument to record near-infrared (NIR) spectra for TCCON measurements.

AirCore provides vertical profile measurements of GHGs from near the surface up to an altitude of ~30 km. Validation of AirCore GHG profile observations is very challenging, especially for parts of the profiles above the altitude ceiling of a typical aircraft, i.e. 10-30 km (Karion et al., 2010). Possible measurements to validate AirCore observations are high altitude (up to ~21 km) aircraft measurements by Geophysica or ER-2 or by balloon-borne whole air sample measurements. However, it is very costly and logistically challenging to obtain the above-mentioned two types of observations along with AirCore observations. Furthermore, vertical profile retrievals of CH_4 are obtained continuously at TCCON sites. AirCore provides a cost-effective tool to regularly evaluate the TCCON profile retrievals. Therefore, our strategy is to develop and validate AirCore GHG measurements using comparison campaigns of different types of AirCores and to evaluate TCCON profile retrievals using regularly launched AirCore vertical profiles. The aim of the campaigns was to develop the readiness of in situ vertical profile measurements at ICOS stations in five European countries (Finland, Netherlands, Germany, France, and Switzerland) and of vertical profile measurements of CH_4 from TCCON.

Two intensive AirCore comparison campaigns have been performed, i.e. the Sodankylä campaign in 2018 and the Trainou campaign in 2019. The two locations are complementary in terms of the different latitudes (high latitude Sodankylä vs. mid-latitude Trainou) and the different complexity to obtain flight permission (relatively easy in Sodankylä vs. typically stringent in Trainou). The first intensive campaign took place in June 2018 at the TCCON site in Sodankylä, Finland (Kivi and Heikkinen, 2016). A total of 10 balloon flights and 26 vertical profiles were made, with mostly three AirCores and a total of ~10 kg payload per balloon flight. While the first campaign focused on comparisons of different AirCore measurement techniques by direct comparisons of various AirCores during same flights, the second campaign in Trainou launched AirCores in a similar way to a standard operation in most European countries, i.e. with an individual payload of below 3 kg. The second campaign prioritized the comparison of AirCore retrievals from balloon flights with individual AirCore payloads.

The deliverable shows the uncertainties of AirCore observations based on the comparison results, and then discuss the factors that influence the measurements, e.g. spatial resolution, drying of air samples, and the altitude registration during AirCore profile retrievals.

2 Specification for high accuracy AirCore observations

2.1 Comparisons of CO_2, CH_4, and CO profiles

Since multiple AirCores were flown on same balloon flights during the 2018 Sodankylä campaign and their inlets were positioned next to each other, air samples were collected from nearly identical air mass during descent. The differences in sampling caused by atmospheric variabilities are to the first order negligible, which is particularly the case for the relatively stable stratosphere. The observed variations in the profile measurements therefore indicate the differences in the measurement characteristics of various AirCore systems (see Table 1), e.g. vertical resolutions, measurement accuracy, and altitude registration. The comparison results are performed per gas species.

Table 1. A list of AirCores (configuration, volume, and weight) flown during the measurement campaign.

Institutions	AirCore tubing length	Volume	Weight
1. RUG/FMI	40 m 1/4" O.D. + 60 m 1/8" O.D.	~ 1400 cm^3	3.5 kg
2. LSCE/LMD	23 m 8 mm O.D. + 46 m 4 mm O.D.	~ 1600 cm^3	2.9 kg
3. GUF	20 m 8 mm O.D. + 40 m 4mm O.D. + 40 m 2 mm O.D.	~ 1000 cm^3	2.5 kg
4. UBERN	105m 3.4 mm O.D.	~700 cm^3	3.0 kg
5. NOAA	100 m 1/8" x 2	~600 cm^3 x 2	1.4 kg

2.1.1 Comparisons of CO_2 profiles

The CO_2 profiles are shown per individual days in Figure 1. All payloads in each panel were flown on the same balloon flights except that on June 21 the GUF AirCore was flown on a separate flight. The differences at individual altitudes vary in the range of -4.2 – 2.8 ppm, and the mean column differences vary in the range of -0.18 – 0.32 ppm.

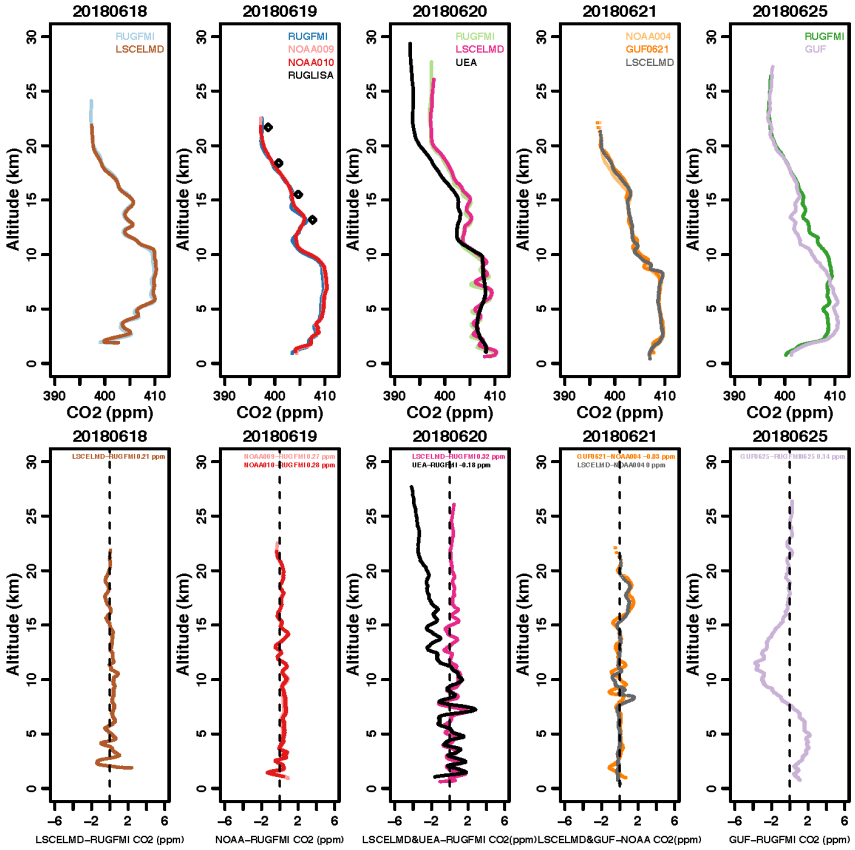


Figure 1. *Comparisons of CO_2 profiles from multiple AirCores/LISA on individual flight days. All payloads in each panel were flown on the same balloon flights except that the GUF AirCore was flown separately on 20180621. The mole fraction profiles are shown in the top, and the difference profiles are shown in the bottom.*

The large range of variations is mainly due to two profiles: UEA on June 20 and GUF on June 25. The deviation of UEA CO_2 from the other two profiles at above ~10 km on the same flight is likely due to uncoated tubing of the stratospheric part of the UEA AirCore. The GUF CO_2 profile below ~16.5 km is an outlier in the CO_2-CH_4 scatter plot compared to other profiles (not shown); however, the column mean CO_2 difference between GUF and RUGFMI is rather small, suggesting that CO_2 may have been smeared in the GUF AirCore although there is no sign of visible smearing for CH4. When the two AirCore profiles are excluded, the range of the differences at individual altitudes and the range of the column mean differences are reduced to -1.4 – 2.4 ppm and -0.03 – 0.32 ppm, respectively. The remaining variations in the differences at individual altitudes are most likely caused by the different resolutions of the AirCore profiles, which is primarily determined by the diameter and the length of the tubing of the AirCores (Membrive et al., 2017). This is mostly apparent in the differences below ~10 km between UEA (1/2 in. O.D.) and LSCELMD (1/4 in. O.D.), i.e. the tropospheric part of the UEA AirCore profile is largely smoothed compared to the other two profiles.

The CO_2 differences of LISA minus weighted averages of AirCore measurements are 1.28 ± 0.07 ppm, 1.42 ± 0.22 ppm, and 1.39 ± 0.22 ppm for RUGFMI and NOAA AirCore pairs (009 and 010), respectively. A difference of CO_2 of ~ 1 ppm between LISA and AirCore observations has been observed in previous measurements (Hooghiem et al., 2018). The positive bias of LISA CO_2 measurements is likely due to contamination during sampling, which is to be followed up after RINGO by the University of Groningen.

2.1.2 Comparisons of CH_4 profiles

The CH_4 profiles seem to be in a better agreement than the CO_2 profiles due to its relatively large range of the measurements: ~ 40 % CH_4 vs. ~ 4 % CO_2. The mean column differences vary in the range of 0.5 – 8.7 ppb. The CH_4 differences are clearly visible around 20 km on June 19 and between 20 km and 25 km on June 25. These differences are due to measurement spatial resolutions and are confirmed by strong correlations between CO_2 and CH_4 of the RUGFMI profiles on June 19 and of the GUF profiles on June 25. Besides the differences caused by spatial resolutions, there exists a significant bias for the comparison of the profiles on June 21. The differences of the column mean above 15 km between GUF and NOAA (75.2 ppb), and between LSCELMD and NOAA (60.1 ppb) are significantly larger than those below 15 km, 2.4 ppb and -0.2 ppb, respectively. The large differences are mainly caused by the different altitude registration of the profiles.

The CH_4 differences of LISA minus weighted averages of AirCore measurements are 27.9 ± 20.1 ppb, 28.0 ± 17.2 ppb, and 28.8 ± 15.6 ppb for RUGFMI and NOAA AirCore pairs (009 and 010), respectively.

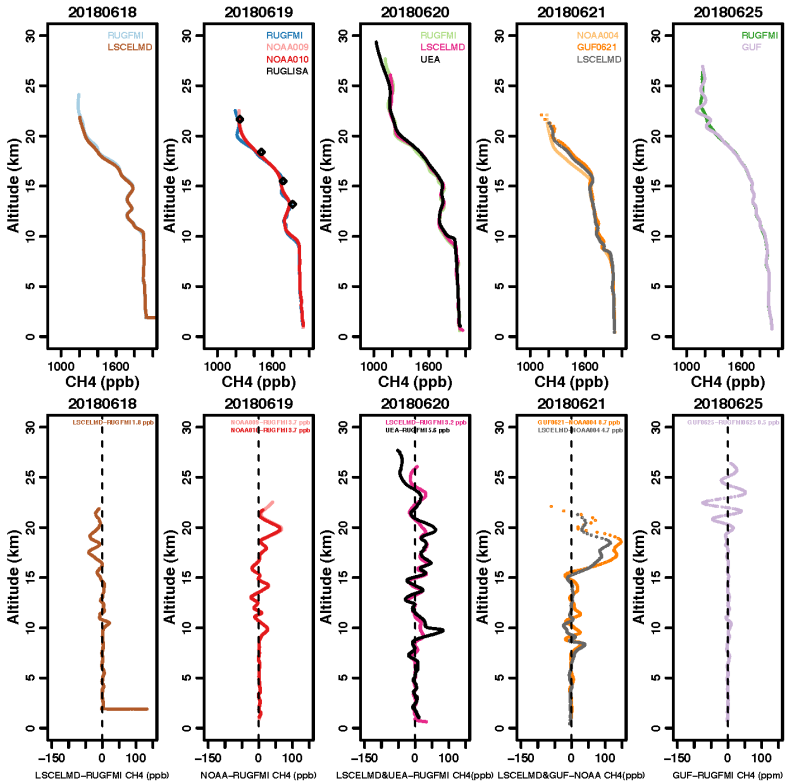


Figure 2. *Comparisons of CH_4 profiles from multiple AirCores/LISA on individual flight days. All payloads in each panel were flown on the same balloon flights except that the GUF AirCore was flown separately on 20180621. The mole fraction profiles are shown in the top, and the difference profiles are shown in the bottom.*

2.1.3 Comparisons of CO profiles

The CO profile measurements are relatively noisy compared to the range of the signal of 0 – 150 ppb due to the low precisions of the CO measurements by the CRDS analyzers. All profiles show a sharp decrease near the tropopause heights at ~ 10 km, except for the UEA profile on June 20. The CO spike of the UEA profile corresponds to the connection between 1/2 in. tubing and 1/8 in. tubing, and is likely caused by CO emissions of the connector. A second CO spike occurs at ~19.5 km of the GUF profile and correspond to the connection between 2 mm and 4 mm tubing. The findings may refer to an issue concerning the connections of the AirCore GUF004.

The mean column differences vary in the range of -8.6 – 9.7 ppb, with a mean absolute column difference of 6.2 ppb, which corresponds to ~7.5% of the average column mean of 80 ppb.

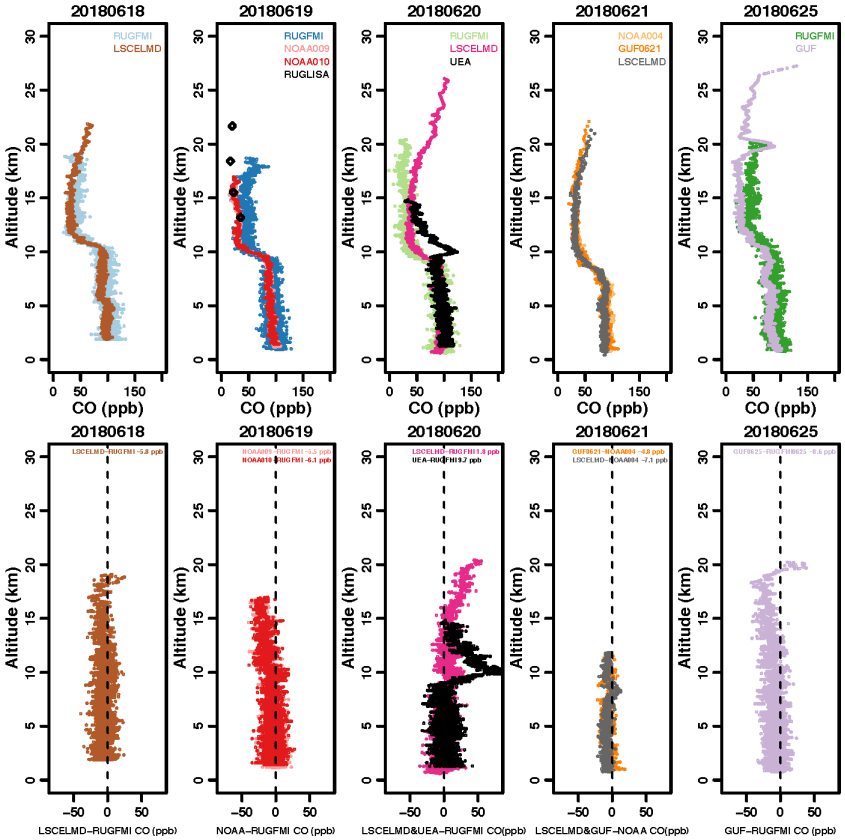


Figure 3. *Comparisons of CO profiles from multiple AirCores/LISA on individual flight days. All payloads in each panel were flown on the same balloon flights except that the GUF AirCore was flown separately on 20180621. The mole fraction profiles are shown in the top, and the difference profiles are shown in the bottom.*

2.2 Uncertainties of CO_2 and CO mole fraction measurements

The uncertainties of AirCore CO_2 and CO mole fraction measurements can be caused by air sampling and storage bias and by sample analyses and instrument calibrations. The uncertainties associated with air sampling and storage for real atmospheric measurements cannot be directly assessed, except that extensive laboratory AirCore slug tests have been performed to identify any significant surface effects prior to the field campaign. Furthermore, sample analyses were performed using CRDS analyzers by individual institutions and were calibrated to the WMO scales through various laboratory standards. Therefore, instead of estimating directly the various uncertainties, we assess the overall uncertainties based on comparisons of parts of the profiles with relatively steady mole fractions.

2.2.1 Uncertainties of CO_2 mole fraction measurements

Although all profiles were made during a short period between June 18 and June 29, CO_2 below ~15 km varies in the range of 5 - 10 ppm from day to day (Figure 4a&d). Since the profiles were made on different days and at different locations (descent profiles), the variations can mostly be explained by real atmospheric variabilities, e.g. due to atmospheric transport and signatures of land surface fluxes (Gerbig et al., 2003;

Shirai et al., 2012; Sweeney et al., 2015), which makes it difficult to compare all vertical profiles. However, the profiles above 20 km vary very little (Engel et al., 2009), and are suitable to assess the reproducibility of CO_2 measurements by different AirCores (Figure 4b&e). Furthermore, CO_2 and CH_4 are correlated in the overworld stratosphere (above 380 K and below 20 km) and CO_2 in the CH_4 domain are directly comparable, see Figure 4c&f. We assume that the composition of air masses above 380 K does not change significantly within the campaign period of 12 days, which is a reasonable assumption as the mean age of air is 1 - 5 years. Although the altitude of the air masses may change due to the variations of tropopause heights, mole fractions of CO_2 are not affected in the CH_4 domain. The CO_2 differences from the average profile for both above 20 km, and above 380 K and below 20 km vary within ~0.5 ppm.

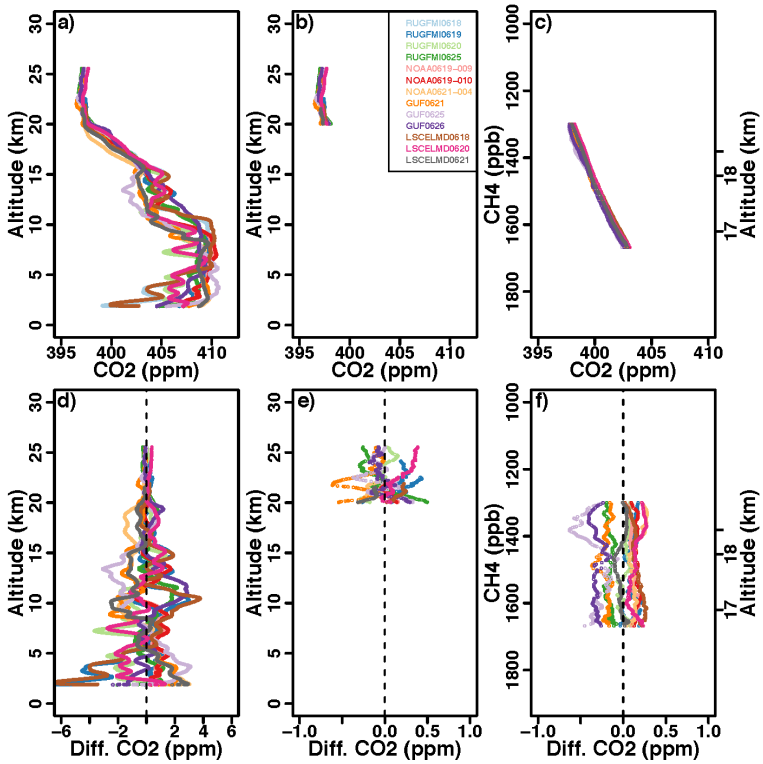


Figure 4. *Comparisons of 13 AirCore CO2 profiles made during the RINGO campaign June 18 – 29: a) full profiles; b) above 20 km; c) the scatter plot of CO2 vs. CH4; d) the difference of individual profiles from the average of the profiles; e) same as d, but only above 20 km; f) the difference of individual profiles from the average of the profiles in the CH4 domain.*

A summary of the mean CO2 differences from the average profiles is shown for above 20 km (Figure 5a) and above 380 K and below 20 km (Figure 5b). The standard deviation of the mean differences for both cases are ~0.2 ppm. However, GUF shows a larger difference of -0.3 ppm for above 380 K and below 20 km than for above 20 km. This is caused by a higher spatial resolution of GUF measurements above 380 K (Engel et al., 2017) that other measurements. The correlation between AirCore CO_2 and CH_4 is largely conserved, however, the correlation is slightly affected by the difference in the molecular diffusivities of CO_2 and CH_4.

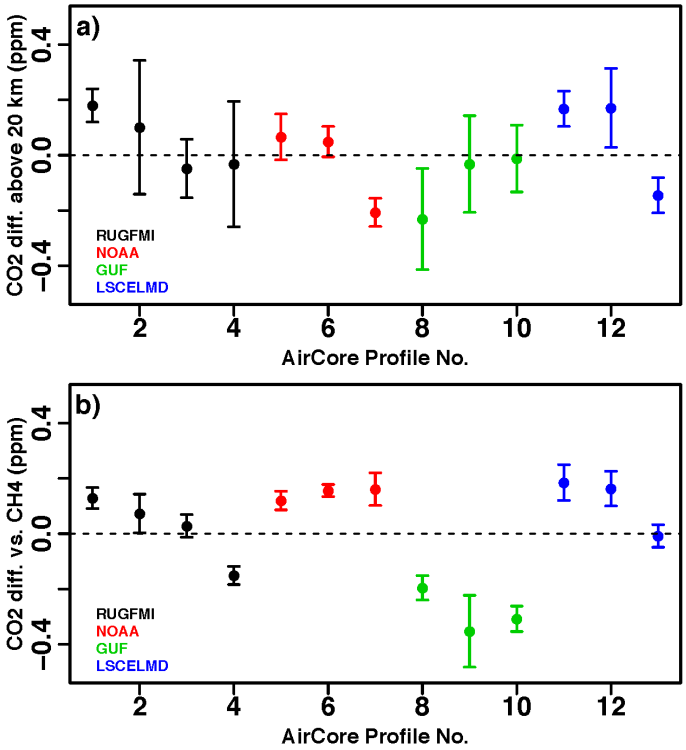


Figure 5. *Mean CO2 differences of part of individual AirCore profiles from their corresponding average profile: a) for profiles above 20 km; b) calculated in the CH4 domain for part of the profiles with between 1300 and 1700 ppb CH4 (16 – 19 km). Different colors indicate AirCore profiles from different groups.*

2.2.2 Uncertainties of CO mole fraction measurements

The CO profiles during the campaign show a general pattern of a sharp gradient near the tropopause, and a slight increase at above 15 km (Figure 6a). Since the profiles of 13 -17 km in the stratosphere and 5 -8 km in the troposphere are relatively stable, we use the two parts of the profiles to assess the reproducibility of CO measurements by different AirCores (Figure 6b&c).

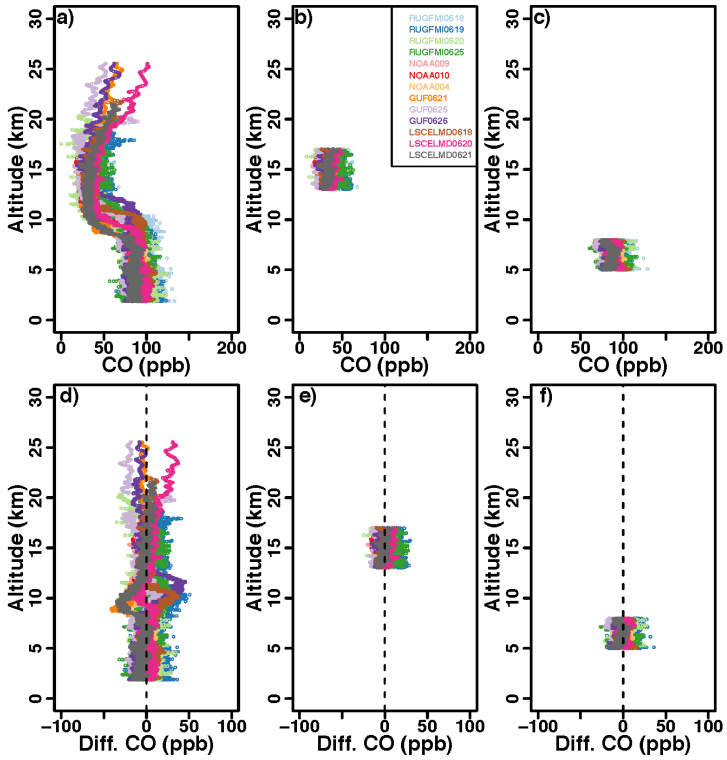


Figure 6. *Comparisons of AirCore CO profiles made during the RINGO campaign June 18 – 29 for 13 CO profiles 0 – 30 km (a), 13 – 17 km (b) and 5 – 8 km (c) and the difference of individual profiles from their corresponding average profiles for 13 CO profiles 0 – 30 km (d), 13 – 17 km (e) and 5 – 8 km (f).*

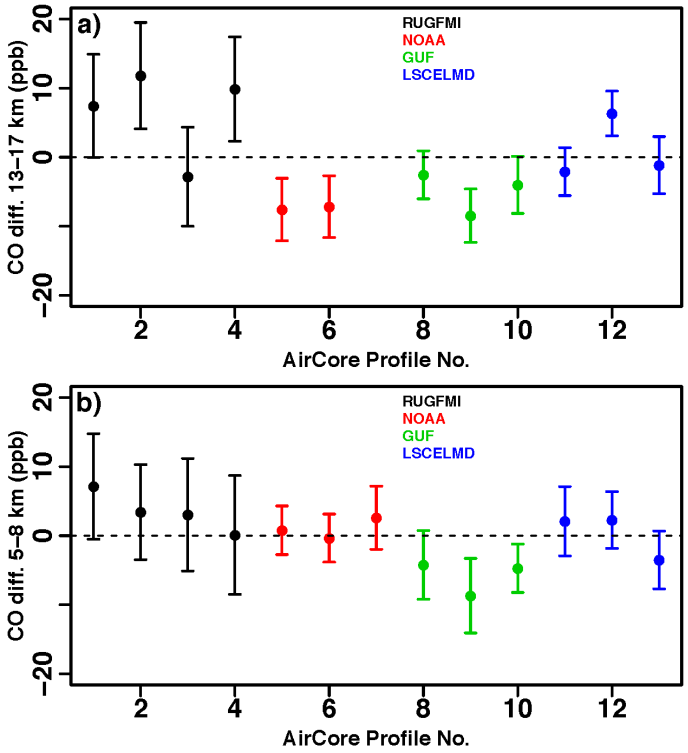


Figure 7. *Mean CO differences of part of individual AirCore profiles from their corresponding average profile: a) for profiles 13 – 17 km; b) for profiles 5 – 8 km. Different colors indicate AirCore profiles from different institutions.*

2.3 Altitude registration

2.3.1 Uncertainty analysis based on the Sodankylä results

The altitude registration of AirCore samples is realized by assigning a pressure value to each trace gas mole fraction. Several factors contribute to the altitude registration: 1) the neglection of the pressure drop across the tube or the uncertainty in simulating the pressure drop; 2) the choice of the starting point of the sample analysis; 3) the uncertainty in the measurements of the coil temperature; 4) the possible variation or drift of the flow rate during sample analysis. The uncertainty in the measurements of the ambient pressure will contribute to the altitude registration as well; however, it does not contribute to the comparison when the same ambient pressure profile is used in each multiple-payload flight.

Since altitude registration is mostly sensitive for the stratospheric part of the profile, we focus on evaluating the uncertainties in the altitude registration of stratospheric profiles, i.e. higher than 13 km. For each pair of CH_4 profiles in the pressure domain, we create a series of profiles by shifting one profile upward and downward within 10 hPa, and find the one that maximizes its correlation with the reference profile. Accordingly, CO_2 and CO profiles are shifted in the same amount as for CH_4 profiles. From Table 2, we can see that the vertical shifts are mostly below 3 hPa, except for two profiles on 20180621, 10 hPa and 13 hPa, respectively.

Table 2. the uncertainty of AirCore altitude registration estimated based on vertical matching of various AirCore profiles

Flight dates	AirCore Comparisons	Mean stratospheric profile differences (> 13 km)			Vertical coordinate shifts	Mean stratospheric profile differences after vertical coordinate shifts		
		CH_4 (ppb)	CO_2 (ppm)	CO (ppb)	Pressure (hPa)	CH_4 (ppb)	CO_2 (ppm)	CO (ppb)
20180618	LSCELMD - RUGFMI	-9.6	-0.02	-7.8	-2	-0.5	0.11	-8
20180619	NOAA009-RUGFMI	10.4	0.15	-19.7	0	10.4	0.15	-19.7
	NOAA010-RUGFMI	9.0	0.2	-19.1	1	4.4	0.13	-19.4
	RUGFMI - RUGLISA	-31.1	-1.30	27.8	-2	-26.7	-1.27	29.5
20180620	LSCELMD-RUGFMI	11.5	0.32	12.1	2	3.4	0.22	16.8
	UEA - RUGFMI	10	-2.33	12.1	3	-4.3	-2.53	11.6
20180621	LSCELMD-NOAA004	37.5	0.37	-	10	-3.9	-0.16	-
	GUF003-NOAA004	50.8	0.35	-	13	0.4	-0.28	-
20180625	GUF004-RUGFMI	-0.3	-0.75	-16.4	-2	7.3	-0.69	-17.1

2.3.2 Uncertainty analysis based on the altitude marker

The altitude registration was evaluated for two AirCore flights from GUF during the Traînou campaign using a newly developed CO-spiking method (Wagenhäuser et al., submitted to AMT November 2020). The CO-spiking system allows for releasing small amounts of signal gas with high CO in the inlet of the AirCore during descent at predefined GPS altitudes, therefore marking the air sample at the release altitude. When assigning the trace gas measurements to the sampling altitude by applying the retrieval procedure of a conventional AirCore flight, the CO-spike signals are assigned to a modelled altitude as well. Figure 8 shows the resulting vertical distribution of CO mole fractions for the two flights.

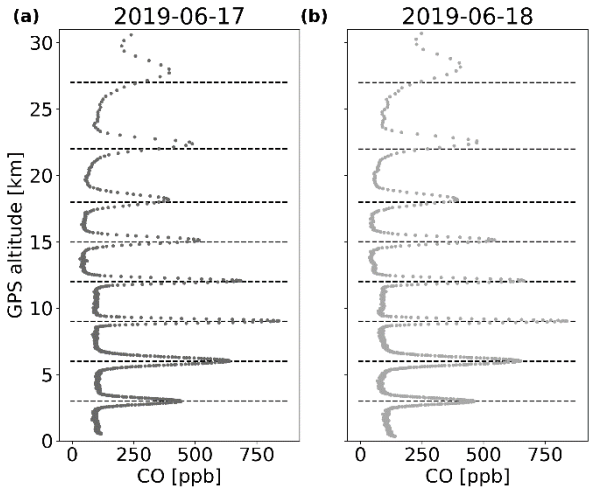


Figure 8. *CO vertical profiles with signal gas spikes from GUF003 measurements. Flight on* ***(a)*** *June 17 and* ***(b)*** *June 18, Traînou 2019. The dashed lines indicate the signal release altitudes. An instantaneous pressure equilibrium between AirCore and ambient air was assumed in context of the altitude retrieval. (Wagenhäuser et al., submitted to AMT November 2020)*

The difference between the registered CO-spike altitudes and the release altitudes Δh is an in situ measure for the quality of the altitude registration. Below 12 km, Δh was less than 100 m for both flights. Below 20 km, Δh was comparable for both flights with less than 250 m. Between 20 km and 27 km Δh was up to approximately 900 m regarding the first flight, and up to 1200 m with respect to the second flight. Differences in descent velocity profiles were identified to have a major impact on differences in Δh between both flights. The quantities are strictly bound to the GUF AirCore geometry (i.e. tubing diameter, dryer) and the altitude registration procedure applied by Wagenhäuser et al. (2020), which assumes an instantaneous pressure equilibrium between ambient air and the AirCore. The altitude registration may be improved by applying an empirical altitude correction (Wagenhäuser et al., 2020) or by modeling the flow of air into the AirCore.

The vertical resolution was modeled using the same approach as Membrive et al. (2017) and Engel et al. (2017) for both CO-spiking flights. In addition, the vertical resolution of the empirically corrected trace gas profiles was derived from the individual signal widths. The modelled and the observed vertical resolution agree well within less than 220 m throughout the profile, being better than 1 km below 22 km and reaching approximately 1.5 km at 27 km (Wagenhäuser et al., 2020, Figure 8).The uncertainty analysis based on the altitude marker proofs, that trace gas profiles can be obtained from AirCores deployed to weather balloons with a highly accurate altitude registration at least up to 27 km and a fine vertical resolution, which is close to the calculations of a widely used simple model for characterizing AirCores (Wagenhäuser et al., 2020).

3 Specification for accurate TCCON profile retrievals

3.1 TCCON SFIT4 profile retrievals

Contribution from BIRA-IASB:

A full-physical methane (CH_4) profile retrieval algorithm is established for ground-based Fourier transform spectrometer (FTS) near-infrared (NIR) spectra recorded at TCCON sites.

Summary

In order to obtain pieces of vertical information in addition to the total column, the SFIT4 retrieval algorithm is applied to retrieve the CH_4 mole fraction vertical profile from the FTS NIR spectra measured at the TCCON sites in Ny-Ålesund, Sodankylä, Bialystok, Bremen, Orléans (Trainou) and St Denis. The retrieval strategy for the CH_4 profile retrieval from ground-based FTS NIR spectra using the SFIT4 code (SFIT4NIR) has been investigated:

- The retrieval strategy, e.g. spectroscopy, spectral windows, a priori profile, regularization, has been optimized.
- The degree of freedom for signal (DOFS) of the SFIT4NIR retrieval has been found to be about 2.4, with two distinct pieces of information in the troposphere and in the stratosphere.
- The retrieved profile uncertainty has been evaluated, based on the optimal estimation method, including the smoothing error, the model parameters error and the measurement error.

After finalizing the SFIT4NIR retrieval algorithm, the SFIT4NIR retrievals are compared to other reference data:

- The dry-air column-averaged mole fraction of CH_4 (XCH_4) derived from SFIT4NIR retrievals are compared to the standard TCCON XCH_4 data product.
- The CH_4 seasonal variations in the troposphere and stratosphere observed by SFIT4NIR retrievals are compared to surface in situ measurements and ACE-FTS satellite measurements.
- The SFIT4NIR retrieved CH_4 profiles are compared with aircraft and AirCore measurements.

The SFIT4NIR retrievals are applied to the TCCON measurements recorded during the RINGO campaigns:

- The SFIT4NIR retrievals are compared with the AirCore measurements during the RINGO campaigns at Sodankylä (2018), and Orléans (2019) to better understand the performance of AirCore measurements.

Retrieval algorithm

The SFIT4NIR retrieval strategy is investigated based on the TCCON spectra at St Denis (a humid site) using the SFIT4_v9.4.4 retrieval code. After that, the optimized retrieval strategy, with the key parameters listed in Table 3, is applied at six TCCON sites.

Table 3. the important settings in the SFIT4NIR retrieval strategy

Retrieval window (cm^{-1})	5996.45 – 6007.55
Interfering species	CO_2, H_2O
Spectroscopy	Atmospheric line list (ATM; Toon, 2014)
Regularization	Tikhonov L1
A priori profile	WACCM v4
Signal to noise ratio	~250

Figure 9 shows a typical averaging kernel (AVK) of SFIT4NIR retrieval with a solar zenith angle (SZA) of 63◦ at St Denis. The retrieved CH4 profile is sensitive to the altitude range from the surface to the middle stratosphere (about 40 km). The AVK shows that the SFIT4NIR-retrieved profile contains independent information in the troposphere and in the stratosphere (DOFS close to 1.0 for these two layers). In addition, the column averaging kernels indicate that the retrieved CH4 total column has a good sensitivity in the whole atmosphere, with a value close to 1.0 at all altitudes. The column-averaging kernels slightly vary with the

SZAs, which is more constant than the AVK variability for the SZAs of the standard TCCON products (Wunch et al., 2011).

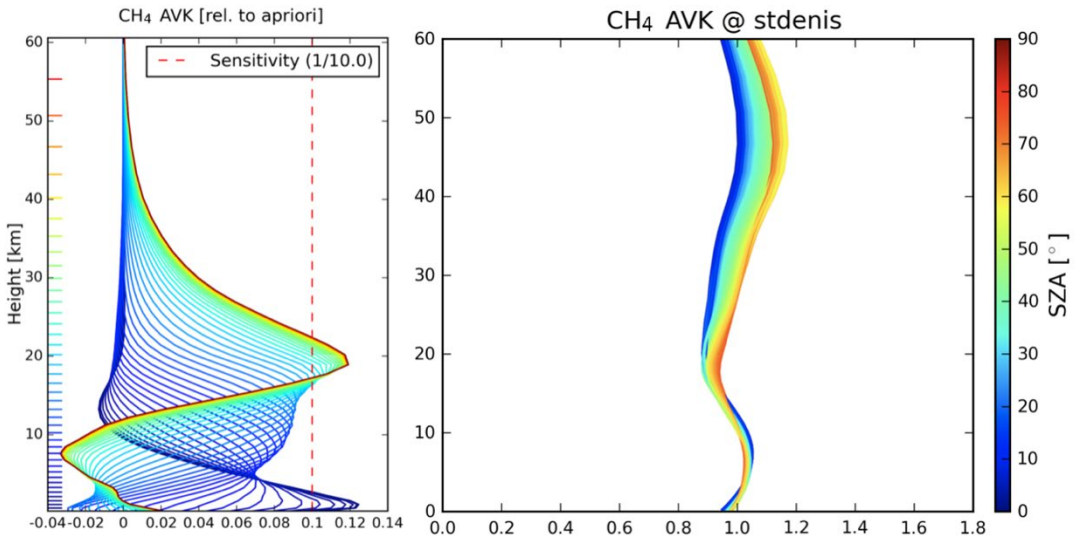


Figure 9. Left: a typical CH_4 averaging kernel matrix of the SFIT4NIR retrieval with the SZA of 63◦ at St Denis, in units of the mole fraction profile with respect to the a priori. Right: CH_4 column-averaging kernels (in unit of 1; applying for the partial column profile) with different solar zenith angles.

According to the OEM (Rodgers, 2000), the measurement uncertainty of the SFIT4NIR retrieval is estimated from three components: the smoothing error covariance matrix (S_s), the forward model parameters error covariance matrix (S_f) and the measurement error covariance matrix (S_m).

$$S_s = (A - I)S_a(A - I)^T,$$

$$S_f = G_y K_b S_b (G_y K_b)^T,$$

$$S_m = G_y S_e {G_y}^T,$$

where G_y is the contribution matrix, representing the sensitivity of the retrieval to the measurement. S_a, S_b and S_e are the covariance matrices of the a priori retrieval state vector, the forward model parameter and the measurement respectively.

The relative standard deviation of the CH_4 monthly means from the WACCM model in 1980–2020 is calculated as the random uncertainty of the CH_4 profile. For the systematic uncertainty, we have chosen a value of 5% (about 90 ppb in the troposphere), based on the difference between the a priori CH_4 mole fraction near the surface and the local in situ measurements. The systematic and the random uncertainties for H_2O and CO_2 are set to 5 %. The systematic and random uncertainties of ILS parameters are set to 1 %. The other retrieved parameters do not contribute significantly to the CH_4 uncertainty. According to the HITRAN2012 (Rothman et al., 2013), the uncertainty of CH_4 absorption in the selected retrieval window is about 2%–5%. Here, the systematic uncertainty of the spectroscopy is set to 3%, and the random uncertainty of the spectroscopic data is assumed to be negligible. The systematic and random uncertainties are set to 1% for the temperature. The systematic uncertainty is set to 0.1% and the random uncertainty is set to 0.5% for the SZA. S_e is assumed to be diagonal where the diagonal elements are the inverse square of the SNR.

The systematic and random uncertainties of the SFIT4NIR retrieved CH_4 total column are 3.2% and 0.5% respectively. The dominating component of the systematic uncertainty comes from the spectroscopy. The uncertainties of the partial column in the troposphere are closer to those of the total column, while the

uncertainties of the partial column in the stratosphere are relatively large. The systematic and random uncertainties for the SFIT4NIR retrievals are listed in Table 4.

Table 4. The systematic and random uncertainties for the SFIT4NIR retrieved CH_4 total column, partial columns in the troposphere and in the stratosphere. The uncertainties are shown in percentages (%). The empty field shows where the uncertainty is negligible, with a value of less than 0.1 %. Note that the retrieved parameters are the state vector but subtracting the CH_4 profile.

Error	Total column		Troposphere		Stratosphere	
	Systematic	Random	Systematic	Random	Systematic	Random
Smoothing	±0.2	0.2	±0.2	0.2	±1.2	1.6
Measurement		0.1		0.1		0.9
Retrieved parameters	±0.2	0.2	±0.1	0.1	±2.5	2.5
Temperature	±1.1	0.4	±1.0	0.4	±1.8	0.5
Spectroscopy	±3.1		±3.1		±6.0	
SZA	±0.1	0.2	±0.1	0.2	±0.2	0.9
Total	±3.2	0.5	±3.1	0.5	±6.8	3.3

Comparison SFIT4NIR retrievals with other reference data

- **Standard TCCON measurements**

Figure 10 shows the time series of the hourly means of XCH_4 from SFIT4NIR and TCCON retrievals and their differences for measurements performed in 2016–2017. The mean and standard deviation of the XCH_4 difference between SFIT4NIR and TCCON (SFIT4NIR–TCCON) at the six sites are in the range between −2.3 ppb (−0.14%) and 2.5 ppb (0.15%) and between 4.7 ppb (0.3%) and 9.9 ppb (0.5%). The standard deviations of the differences at all sites are within 0.5%, which is consistent with the combined random uncertainties from SFIT4NIR and TCCON retrievals. The systematic bias between the SFIT4NIR and TCCON retrieved XCH_4 is much lower than 3.2%, indicating that the systematic uncertainty of the SFIT4NIR total column from the spectroscopy (see Table 4) is overestimated. Since the systematic uncertainty of the TCCON XCH_4 retrieval is better than 0.2%, it is inferred that the systematic uncertainty of the SFIT4NIR XCH_4 retrieval is within 0.35%.

Surface in situ measurements

The ground-based in situ measurements at the individual sites are compared with the tropospheric XCH4 retrieved using SFIT4NIR. Ground-based in situ measurements are more sensitive to the local sources and sinks as compared to the FTS measurements. The Traînou tower at the Orléans site takes in situ measurements at four heights (180, 100, 50 and 5 m). The measurements at 180m are used here as they are less affected by the boundary layer (Schmidt et al., 2014). In situ measurements for the St Denis site are taken from the measurements taken at Maïdo (2155 m) located at about 20km away from St Denis (Zhou et al., 2018).

Figure 11 shows the monthly means and standard deviations of the co-located ground-based in situ and the SFIT4NIR tropospheric XCH4 hourly means at Orléans and St Denis in 2016. In general, the seasonal cycle from the in situ measurements is similar to the one from the SFIT4NIR tropospheric XCH4 retrievals at these two sites. However, the in situ tower measurements (180 m) at Orléans are still influenced by the boundary layer, and several high spikes are observed in March, June and December 2016. The in situ measurements at Orléans are found to be about 36 ppb larger than the SFIT4NIR tropospheric XCH4. Schmidt et al. (2014) showed that the CH4 mole fractions at the four layers of the Orléans tower measurements are decreasing with increasing altitude. There is a strong CH4 anthropogenic emission around Orléans, which remains mainly at the surface. This might explain the bias between the SFIT4NIR tropospheric XCH4 and the in situ tower measurements at Orléans. The in situ measurements at St Denis are found to be about 24 ppb lower than the SFIT4NIR tropospheric XCH4. Zhou et al. (2018) pointed out

that the air near the surface above St Denis (0–2 km) mainly comes from the Indian Ocean and partly from the southern African region, whereas the air mass in the middle and upper troposphere (4–12 km) mainly comes from Africa and South America. As CH4 emission on land is much larger than that from the ocean, it is reasonable that SFIT4NIR tropospheric XCH4 is systematically larger than the CH4 mole fraction at the surface.

The phases and amplitudes of the seasonal cycles from the SFIT4NIR tropospheric XCH4 and the ground-based in situ CH4 measurements are found to be in good agreement. CH4 mole fraction is high in December–March and low in July–September at Orléans (located in the Northern Hemisphere), and high in July–September and low in December–March at St Denis (located in the Southern Hemisphere). The CH4 seasonal variations in the troposphere are driven by the OH variation, which is the major sink of CH4 in the atmosphere.

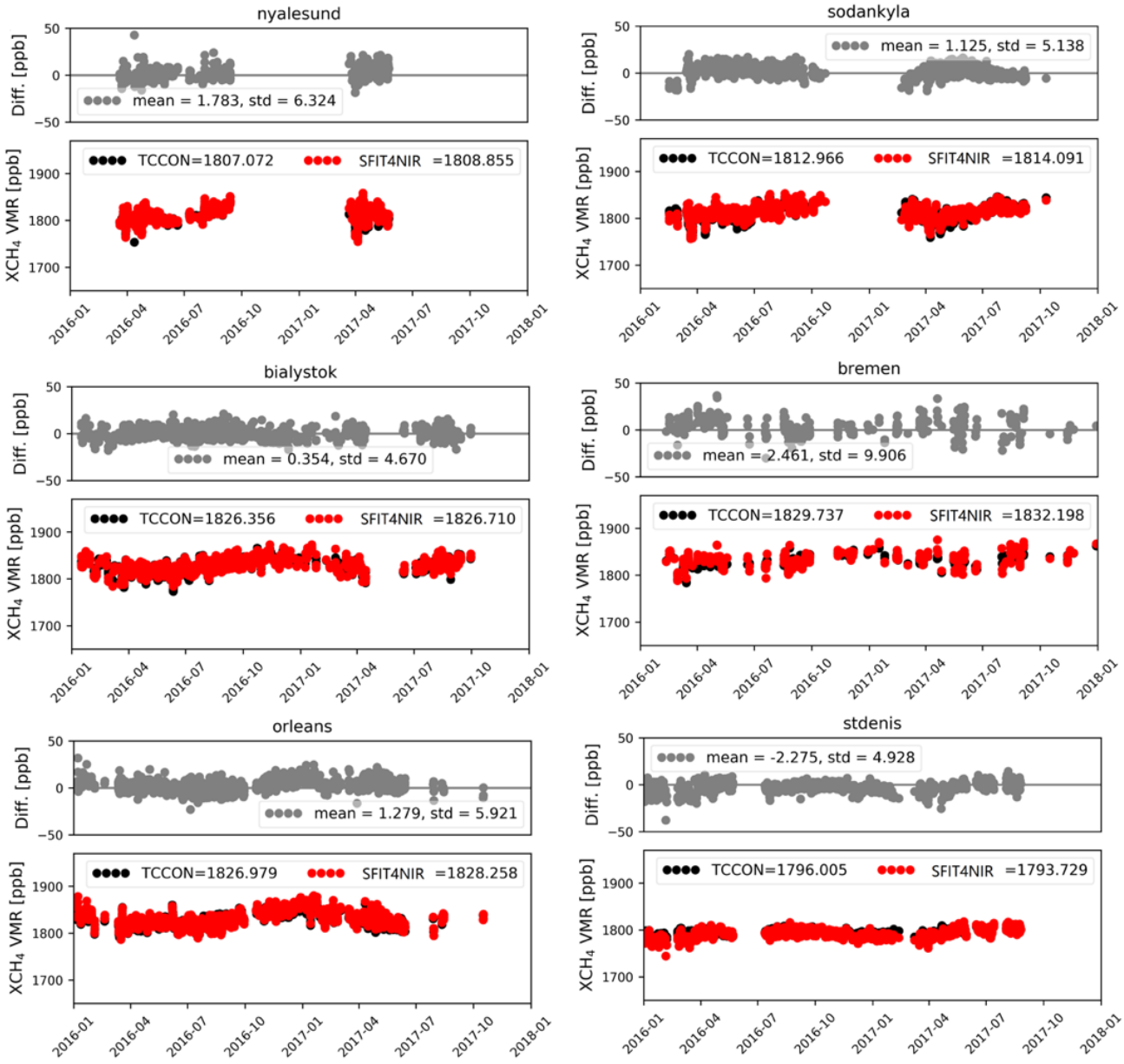


Figure 10. The time series of hourly means of XCH_4 from the SFIT4NIR and the TCCON retrievals at six TCCON sites during 2016–2017, together with their differences. For each site, the lower panel shows the time series of SFIT4NIR and TCCON measurements, and the upper panel shows the absolute difference between them (SFIT4NIR–TCCON; in ppb units). The values in the legend of the lower panel are the means of the TCCON and SFIT4NIR retrievals.

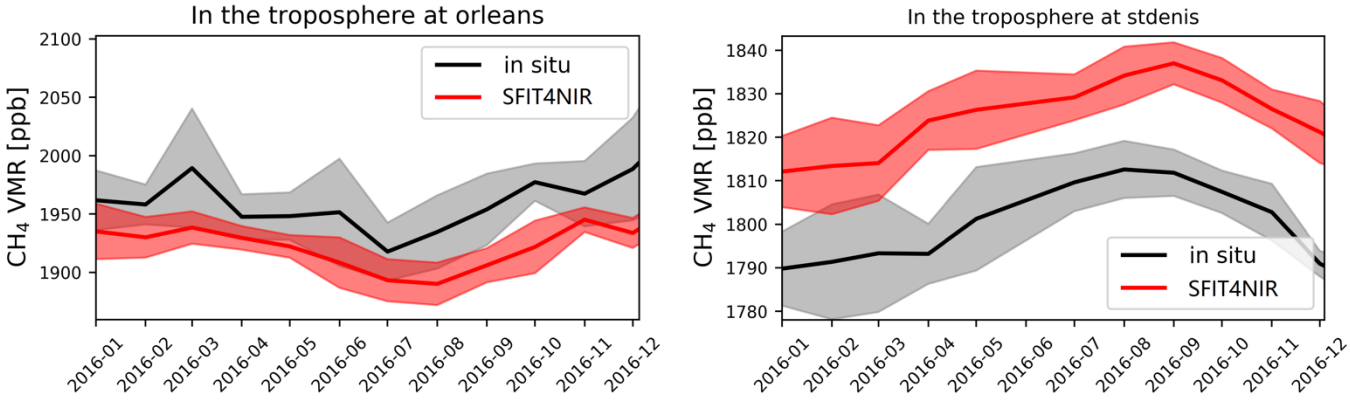


Figure 11. The time series of the monthly means (solid line) and standard deviations (shading) from the SFIT4NIR tropospheric XCH_4 and the ground-based in situ CH_4 measurements at Orléans (a) and at St Denis (b). At Orléans, the in situ measurements are recorded at 180 m on a tower at the same place. The in situ measurements at St Denis are recorded at 2155 m on Maïdo mountain, which is about 20km away from St Denis.

- **ACE-FTS satellite measurements**

The ACE-FTS satellite measurements are compared to the SFIT4NIR stratospheric XCH_4. The vertical range from the tropopause height up to 50 km is treated as the stratosphere in this study. The ACE-FTS satellite has been monitoring the atmospheric CH_4 concentration mainly in the stratosphere since 2004 in solar occultation mode (Bernath et al., 2005). The latest level 2 version 3.6 data with data quality flag equal to 0 (without any known issues) are selected from the ACE/SCISAT data set (Sheese et al., 2015). The ACE-FTS CH_4 profile is retrieved at target altitudes with a vertical resolution of 3–4 km, and then it is interpolated onto a 1 km grid. The older version v2.2 data of the ACE-FTS CH_4 data have been compared to space-based satellite, balloon-borne and ground-based FTS data (De Maziere et al., 2008). The accuracy of the version 2.2 data is within 10% in the upper troposphere–lower stratosphere, and within 25 % in the middle and higher stratosphere up to the lower mesosphere. The uncertainty of the new version of the ACE-FTS data has a reduction of about 10 % near 35–40 km and a slight reduction at 23 km, as compared to the v2.2 version (Waymark et al., 2014).

Figure 12 shows the SFIT4NIR and ACE-FTS co-located daily means of the stratospheric XCH_4 at Bialystok, Orléans and St Denis. The ACE-FTS measurements are selected within ±3×30° (latitude by longitude) around each FTS site. Limited co-locations are found for Ny-Ålesund, Sodankylä and Bremen sites and so the results are not shown here. Figure 12 shows that the seasonal cycles (both phase and amplitude) of the stratospheric XCH_4 from SFIT4NIR and ACE-FTS are similar. The stratospheric XCH_4 shows a minimum in February–April and a maximum in August–October for the Bialystok and Orléans sites located in the Northern Hemisphere, whereas the stratospheric XCH_4 shows a minimum in August–October and a maximum in February–April for the St Denis site, located in the Southern Hemisphere. The mean and the standard deviation of the differences in stratospheric XCH_4 between the SFIT4NIR and ACE-FTS measurements at these three sites are in the range between −0.27 % and 2.06 % and between 1.92 % and 3.21 %, respectively, which are within the combined uncertainties.

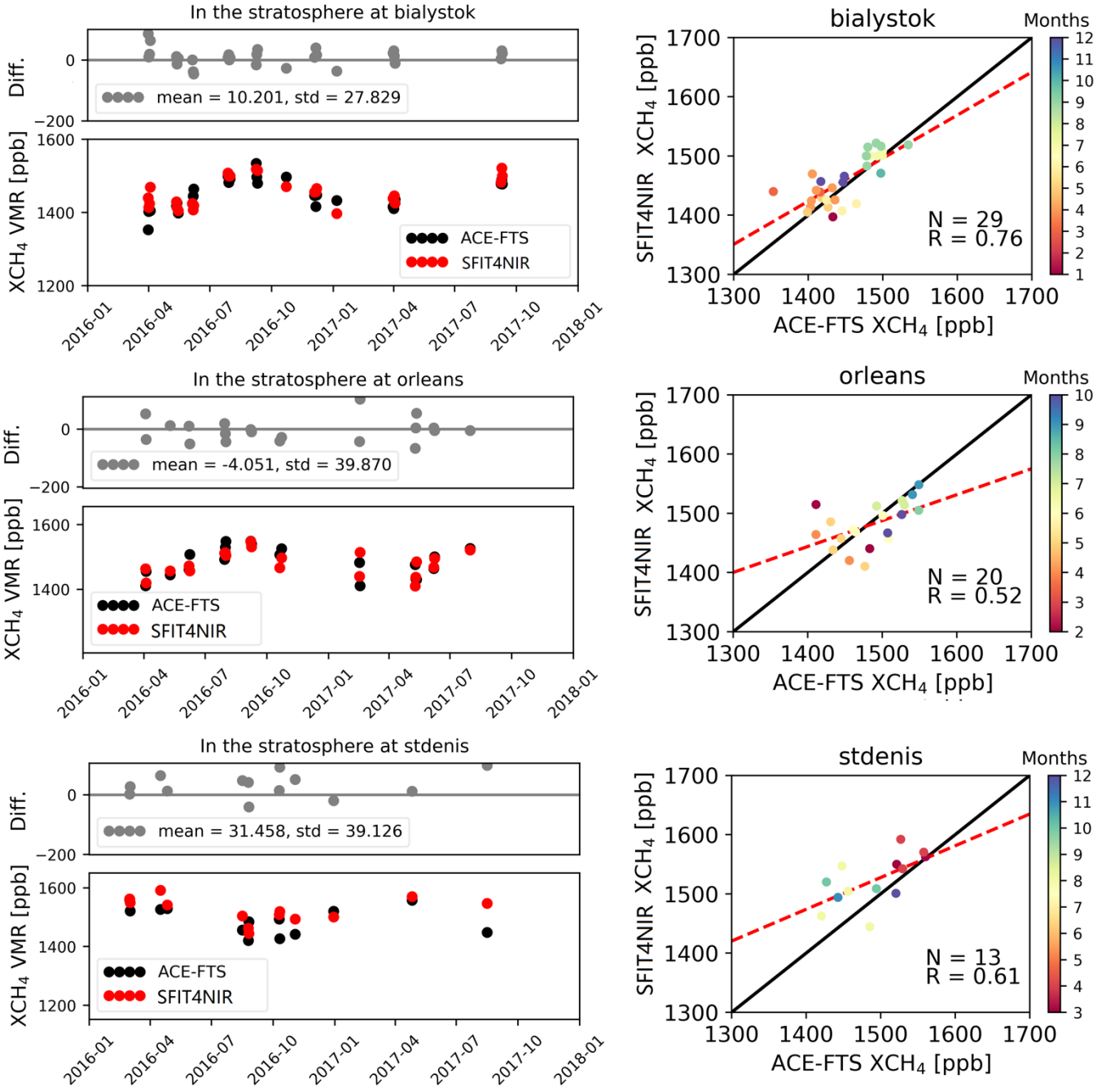


Figure 12. Left panels: the time series of the daily mean of the co-located SFIT4NIR and ACE-FTS stratospheric XCH_4 daily mean measurements, together with the absolute differences (unit: ppb) between them for Bialystok, Orléans and St Denis. Right panels: the correlation plots between the co-located SFIT4NIR and the ACE-FTS stratospheric XCH_4 daily means.

- **Aircraft and AirCore measurements**

The Infrastructure for Measurement of the European Carbon Cycle (IMECC) aircraft equipment passed over several European TCCON sites in September and October 2009, including Orléans, Bremen and Bialystok. We refer to Geibel et al. (2012) for a detail description of the IMECC aircraft data. The aircraft equipment covers a vertical range from about 300 to 13 000 m, mainly in the troposphere. Therefore, in this section, we use the co-located aircraft measurements for comparison with the SFIT4NIR tropospheric XCH_4. The location, date and time of the overflight, SZA and the profile code are listed in Table 3 in Geibel et al. (2012). There are four aircraft vertical profiles over Bialystok (BI-OF1a, BI-OF1b, BI- OF2a, BI-OF2b), four profiles over Orléans (OR-OF1a, OR- OF1b, OR-OF2a, OR-OF2b) and two profiles over Bremen (BR-OF1a, BR-OF2a).

In order to take the vertical sensitivity of the FTS retrieval into account (Rodgers, 2003), the aircraft profile is smoothed with the co-located SFIT4NIR retrieval. To this end, the aircraft profiles need to be extended for comparison with FTS retrievals. For the near ground part, ground-based in situ data from the co-located tall-tower stations are used to extend the aircraft data to the ground at Orléans and Bialystok, and the values measured at the lowermost altitude by the aircraft are linearly extrapolated to the surface at Bremen. For the upper part, the TCCON a priori profile multiplied by the retrieval scaling factor is used. The uncertainties of extended aircraft profiles have been shown in Table 4 in Geibel et al. (2012). The SFIT4NIR retrievals within a time window of ± 1 h around the aircraft overflight are chosen. The standard deviation of the co-located SFIT4NIR retrievals is used as the random uncertainty of the FTS retrieval.

Regular AirCore measurements of CH4 have been carried out at Sodankylä since September 2013. During 2016–2017, we selected seven AirCore profiles which are within 1 h of SFIT4NIR measurements. Similar to the aircraft data, the AirCore measurement also needs to be extended for comparison with the FTS data. For the extrapolation, a scaled SFIT4NIR a priori profile is applied to extend the AirCore CH4 profile above, and the local surface CH4 mole fraction observations (Kilkki et al., 2015) are applied to extend the AirCore CH4 profile below.

The smoothed aircraft tropospheric XCH4 is 1.0 ± 0.2 % larger than the SFIT4NIR tropospheric XCH4, which is consistent with the result from the comparison between the AirCore measurements and SFIT4NIR retrievals (1.1 ± 0.4 %). Combining the AirCore measurements at Sodankylä and aircraft measurements at Orléans, Bremen and Bialystok, Figure 13 shows that there is a systematic overestimation of 1.0 ± 0.3 % in the SFIT4NIR tropospheric XCH4.

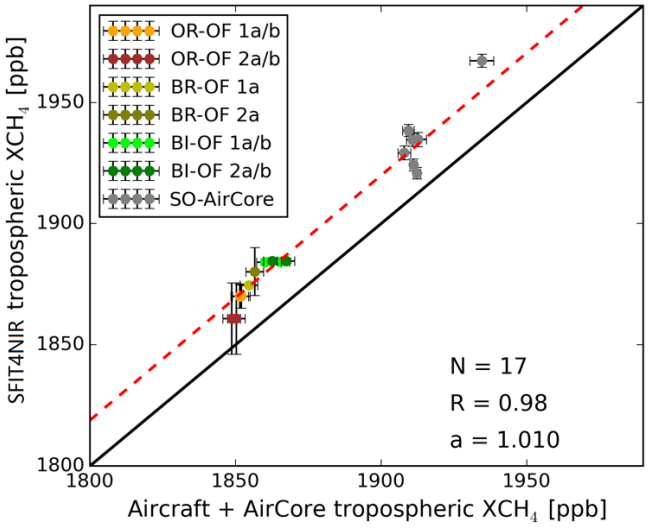


Figure 13. The scatter plots of XCH_4 between the SFIT4NIR and the IMECC aircraft measurements together with the AirCore measurements for the tropospheric components. The black line is the one-to-one line and the dashed red line is the regression line with the intercept to zero ($y = a \cdot x$). N is the co-located measurement number, R is the correlation coefficient and a is the slope.

As AirCore can measure CH_4 profiles up to about 30 km, the SFTIR4NIR retrieved stratospheric XCH_4 are also compared with AirCore measurements at Sodankylä. Figure 14 shows the scatter plots of XCH_4 between the co-located SFIT4NIR retrievals and the AirCore measurements for the whole atmosphere, and for the stratospheric component. The error bars are the random uncertainties of the SFIT4NIR retrievals and the AirCore measurements. It is assumed that the random uncertainty of the AirCore profile is about 0.1 % between the surface and its maximum measurement altitude (~ 30 km), and it is about 2 % above the maximum measurement altitude. The slope of the regression line (a = 1.001) in the whole atmosphere indicates that there is almost no systematic difference between the SFIT4NIR and the AirCore XCH_4, which is consistent with the result in the comparison between SFIT4NIR and TCCON XCH_4 measurements. The SFIT4NIR stratospheric XCH_4 is about 4.0±2.0% less than the AirCore measurements.

These differences between the SFIT4NIR retrievals and AirCore or aircraft measurements are within the systematic uncertainties of the SFIT4NIR partial columns in the troposphere and in the stratosphere, and it is inferred that the systematic uncertainty of the SFIT4NIR partial column mainly comes from the uncertainty of the spectroscopy (see Table 4).

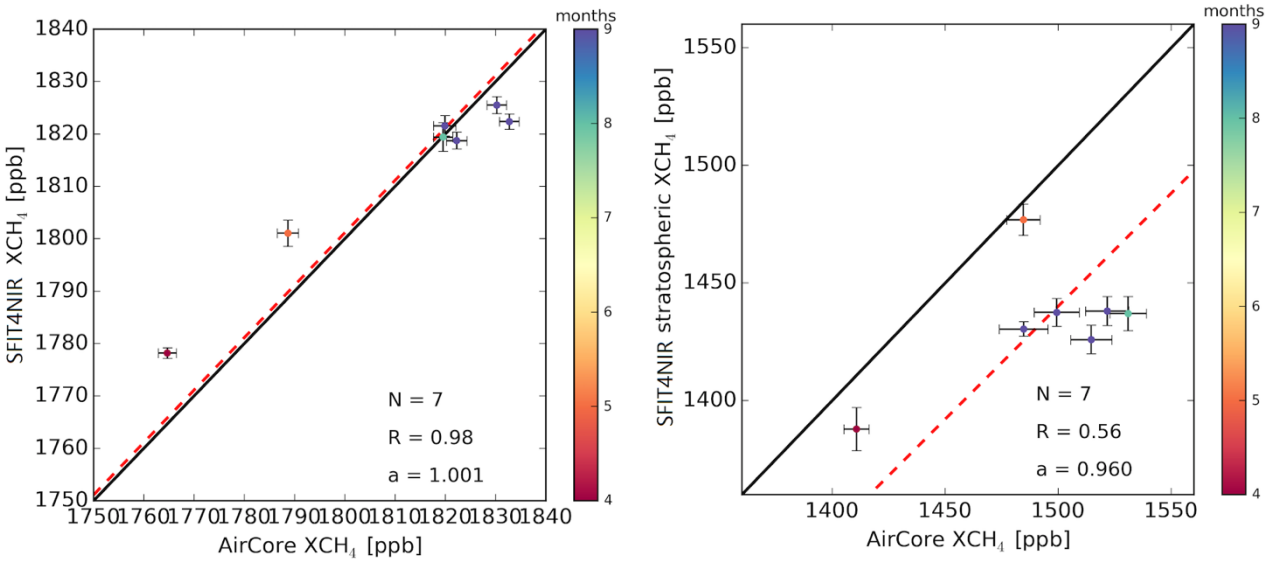


Figure 14. The scatter plots of XCH_4 between the SFIT4NIR and the AirCore measurements for the total column (left) and stratospheric component (right). The black line is the one-to-one line and the dashed red line is the regression line with the intercept to zero ($y = a \cdot x$). N is the co-located measurement number, R is the correlation coefficient and a is the slope.

SFIT4NIR retrievals applied for the RINGO AirCore campaigns

- **2018 Sodankylä**

The SFIT4NIR retrievals are compared with AirCore measurements during the Sodankylä June 2018 RINGO campaign:

Figure 15 shows the comparison between the SFIT4NIR retrievals and three AirCore measurements from GUF, LMD and NOAA on 21 June 2018. The SFIT4NIR retrieved vertical CH_4 profile cannot be regarded in the same way as a high resolution in situ profile, but it does capture the overall transition from the troposphere to the stratosphere quite accurately. The differences between the SFIT4NIR retrievals and AirCore measurements in the troposphere are within 2%. In addition, differences between the SFIT4NIR retrievals and AirCore measurements from three groups in the troposphere are very close to each other. The AirCore profile from GUF group can measure the CH_4 mole fraction above 22 km, while other two AirCore profiles stopped. The difference between the SFIT4NIR retrieval and GUF AirCore measurement in the stratosphere is within 2% too, but the differences between the SFIT4NIR retrievals and LMD or NOAA AirCore measurement in the stratosphere are relatively large, which is probably due to the limited vertical coverage of these two AirCore profiles.

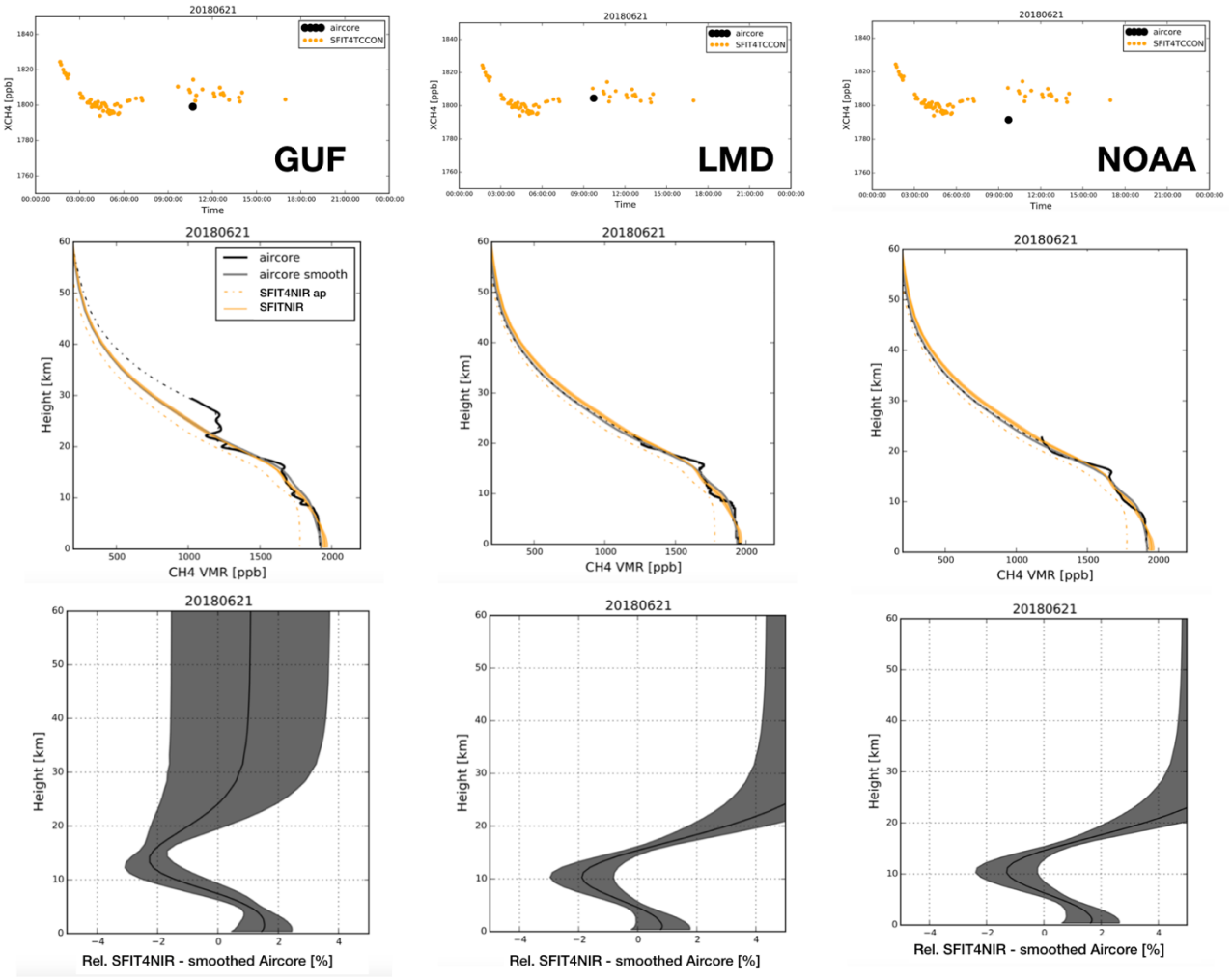


Figure 15. The comparison between the SFIT4NIR retrievals with three AirCore measurements from GUF, LMD and NOAA on 21 June 2018 during the RINGO campaign at Sodankylä. The upper panels are the SFIT4NIR retrieved XCH_4 together with the AirCore XCH_4. The middle panels are the SFIT4NIR a priori and retrieved profiles and AirCore profile (with and without smoothing). The lower panels are the relative differences between SFIT4NIR retrieved profile and smoothed AirCore profile.

- **2019 Orléans**

Between June 11 and June 21 2019, there are 27 AirCore launches at Trainou, France from 7 groups: FRA(LSCE/LMD), NOAA, RUG, GUF, UBern, FMI, and Forschungszentrum Jülich. Besides, one ground-based FTIR instrument is operated on 17 and 18 June, nearby. Here, we compare the SFIT4NIR CH4 profile with the co-located AirCore measurements from NOAA, RUG, FRA(LSCE/LMD) and FRA/RUG (see Fig. 8). The FRA/RUG means that the AirCore is launched by the FRA(LSCE/LMD) group but analysed by the RUG group after landing. In general, the SFIT4NIR retrieval can well capture the CH4 vertical profile observed by AirCore measurements. The maximum differences between SFIT4NIR XCH4 and AirCore are 0.35% for NOAA, 0.17% for RUG, 1.04% for FRA(LSCE/LMD) and 0.67% for FRA/RUG. The differences between SFIT4NIR XCH4 and AirCore are consistent in the troposphere with values between 0.43% and 0.86%, and the differences between SFIT4NIR XCH4 and AirCore are variable in the stratosphere with values between -2.89% and 2.46%.

Figure 16 shows that the tropospheric parts from AirCore measurements are similar, and the SFIT4NIR is about 0.7±0.4% overestimated in the troposphere. The difference between the SFIT4NIR XCH4 and AirCore measurements in the total column is within 0.3%. However, the stratospheric portion of the AirCore sample has a higher uncertainty than the tropospheric portion. If we only take the CH4 profile from FRA(LSCE/LMD) AirCore measurement below 21 km, then the stratospheric XCH4 from AirCore measurement become closer

to the SFIT4NIR retrieval. The stratospheric CH4 observed by AirCore is strongly dependent on the accuracy of the pressure measurement, and has been investigated among the AirCore groups.

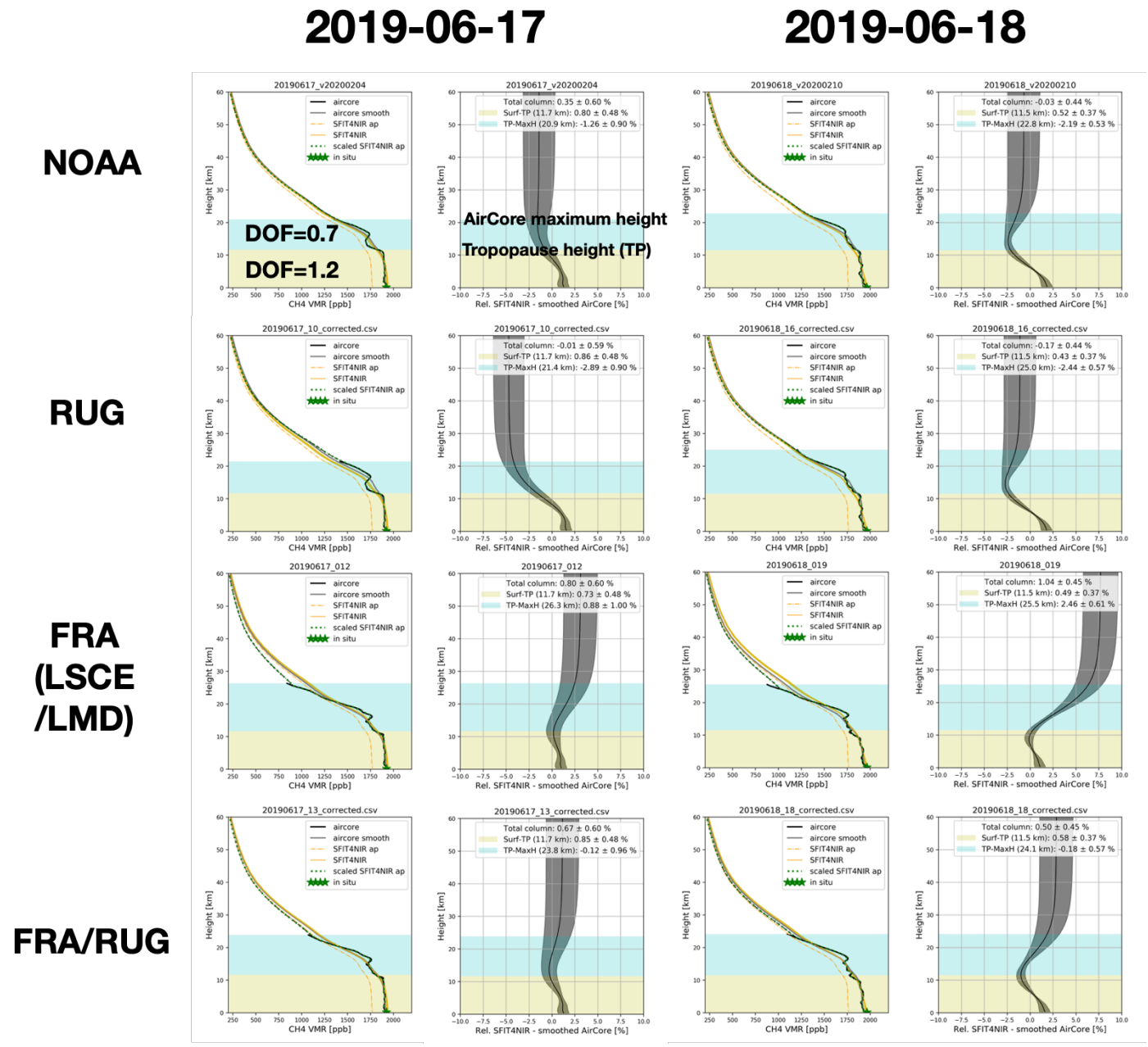


Figure 16. The comparison between the SFIT4NIR retrievals with three AirCore measurements from NOAA, RUG, FRA(LSCE/LMD) and FRA/RGU on 17 and 18 June 2019 during the RINGO campaign at Orléans. For each comparison, the left side is the CH_4 profile and the right side is the relative difference between the SFIT4NIR and smoothed AirCore profile.

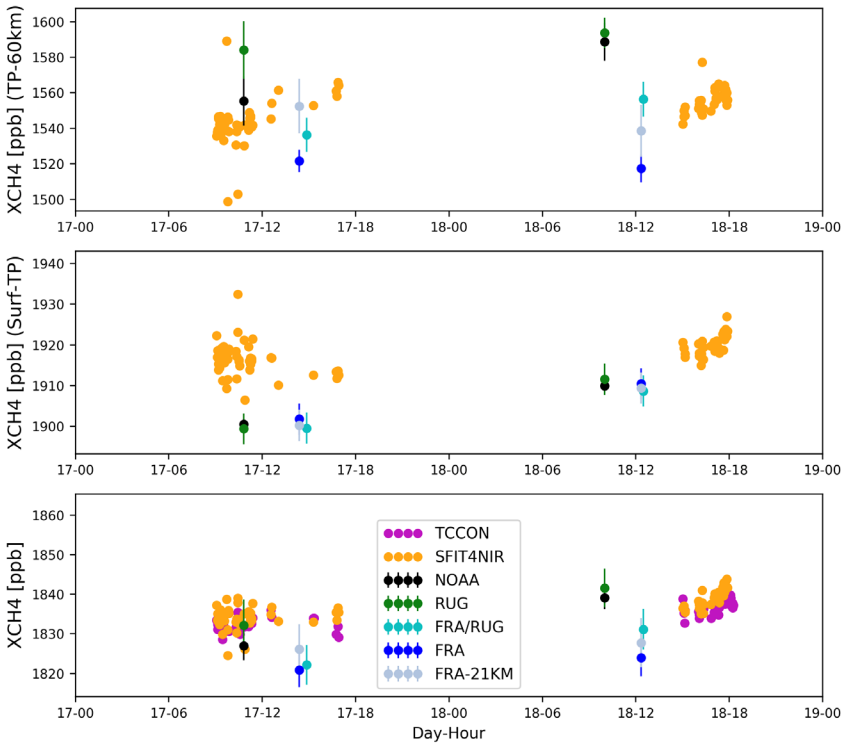


Figure 17. The time series of XCH_4 in the total column (bottom), in the troposphere (middle) and in the stratosphere (upper) from the standard TCCON measurements, the SFIT4NIR retrievals and three AirCore measurements from NOAA, RUG, FRA(LSCE/LMD) and FRA/RGU on 17 and 18 June 2019 during the RINGO campaign at Orléans.

Contribution from IUP Bremen:

A method separating tropospheric from stratospheric methane using TCCON spectra has been established and evaluated against vertical resolved measurements by AirCores. The method is based on N_2O as a proxy for stratospheric CH_4. The comparison against AirCore measurements has been performed at the TCCON sites Orléans and Sodankylä.

Summary

The column averaged mole fraction of methane is impacted by tropopause altitude variations. Inverse models are often optimised for the troposphere. Satellite CH_4 data only provide the total column and systematic errors in the inverted fluxes could occur when using these data by the inverse models. Therefore, it is desired to have the tropospheric as well as the total column from the satellite validation network.

The mole fraction of N_2O is almost constant with respect to altitude in the troposphere. In addition, the seasonal and long-term variations of the N_2O mole fraction are quite small, and therefore highly predictable. Using a correlation between CH_4 and N_2O in the stratosphere, the tropospheric column of CH_4 can be determined from simultaneous vertical column measurements of CH_4 and N_2O (e.g. the standard TCCON data products).

The resulting tropospheric columns of CH_4 have been compared to AirCore measurements during the RINGO campaigns at Sodankylä (2018) and Orléans (2019).

Retrieval algorithm

The used vertical column measurements have been retrieved using the standard TCCON retrieval algorithm GFIT 2014. In contrast to the profile retrieval algorithm SFIT, GFIT is a profile scaling algorithm. In order to get the vertical total column, during the retrieval process GFIT scales a given a-priori profile referring to each gas until the residual of the measured spectrum minus the calculated spectrum becomes minimal. Within the GFIT retrieval, a standard priori is used and scaled with NCEP data for individual measurements.

Table 5: Retrieval Windows within GFIT

Retrieval windows (cm-1)	5880 – 5996	5996.45 – 6007.55	6007 – 6145
Interfering species	CO_2, H2O, N_2O	CO_2, H_2O, HDO	CO_2, H_2O, HDO
Spectroscopy	Atmospheric line list (ATM; Toon, 2014)		
A priori profile	Scaled TCCON standard a-priori		
Signal to noise ratio	~250		

Method

The tropospheric column of CH_4 can be derived using the column HF or the column N_2O as a tracer. The HF method is described in Washenfelder et al. (2003) and Saad et.al. (2014). The Method using N_2O as a tracer was developed at the University of Bremen by Wang et.al. (2014).

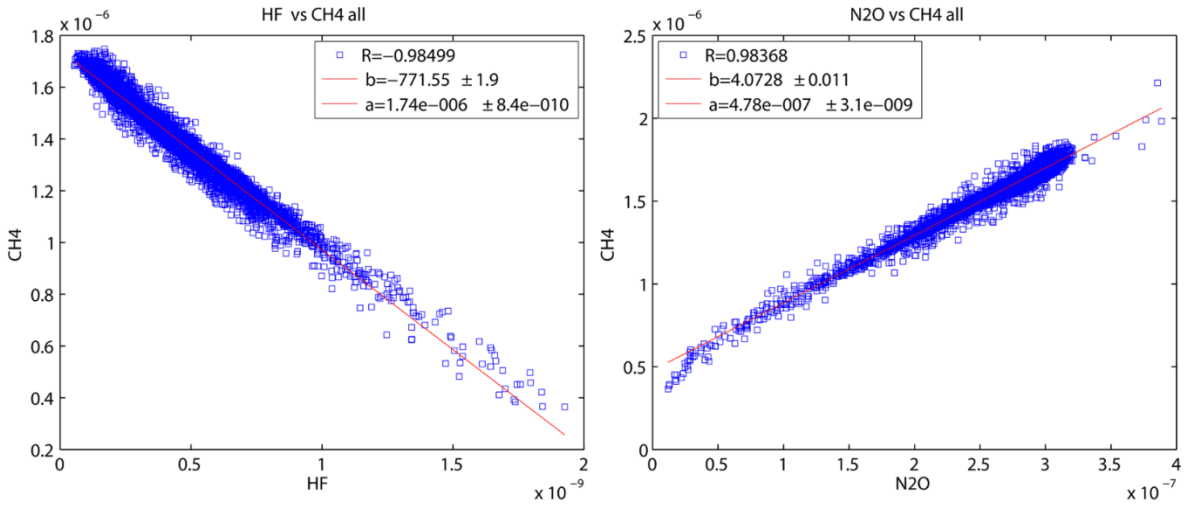


Figure 18. Correlations between the stratospheric mole fractions of N_2O (right) and HF (left) with CH_4 on a global scale. The data are from the ACE-FTS satellite. Plot by Wang et.al.(2014)

There is a strong correlation between HF and CH_4 and a strong anticorrelation between N_2O and CH_4 in the stratosphere. While the tropospheric column of HF is zero, the tropospheric N_2O is well known and must be considered in the calculation of the tropospheric column of CH_4. It is almost constant with respect to altitude in the troposphere and in addition the seasonal and long-term variations of the N_2O mole fraction are small, and therefore highly predictable. The tropospheric column of CH_4 can then be calculated by subtracting the stratospheric column from the total column (with xCH_4 as dry air mole fraction and VC as vertical column)

$$X_{CH_4}^{trop} = \frac{VC_{CH_4} - VC_{CH_4}^{strat}}{VC_{air}^{trop}}.$$

The stratospheric column of CH_4 can be calculated as a linear function of the stratospheric column of N_2O. Inserting this gives the tropospheric column of CH_4 as

$$X_{CH_4}^{trop} = \frac{VC_{CH_4} - b\left(VC_{N_2O} X_{N_2O}^{trop} VC_{O_2}/0.2095\right)}{VC_{O_2}/0.2095}.$$

The scatter of the N_2O method is similar to the HF method.

AirCore comparison

In order to compare measurements of different instrument types, a smoothing with the averaging kernels has to be applied. Exemplary averaging kernels for the standard TCCON measurements are shown in Figure 19. In this study, the AirCore measurements are smoothed using TCCON standard averaging kernels for specific solar zenith angles

xs = xa + A(xh - xa).

AirCores measure mixing ratios during the drop down from an altitude of 25 to 35 km. To compare these measurements with column measurements, the individual layers have to be added up to a column. The lowest measured AirCore level is usually in the range of 300m above ground. The lowest measurement level is extrapolated to the surface and supplemented with the surface pressure, measured at the TCCON site. For the total column comparison, the high altitude levels which are not covered by the AirCores have to be supplemented. As the contribution of the high altitude levels is low, this can be approximated using the scaled TCCON standard a-priori. An example is shown in Figure 20. In order to get the tropospheric column, the levels from the ground level to the tropopause height have to be added up. Each layer is weighted using the pressure weighting function (e.g. Connor et. al. 2008)

$$h_i = \left| \left(-p_i + \frac{p_{i+1} - p_i}{\ln(p_{i+1}/p_i)} \right) + \left(p_i - \frac{p_i - p_{i-1}}{\ln(p_i/p_{i-1})} \right) \right| \frac{1}{p_{surf}}$$

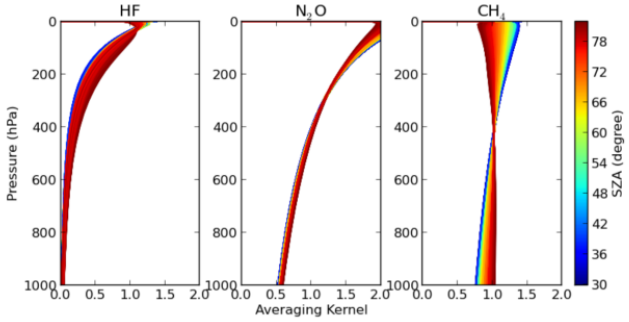


Figure 19. Exemplary averaging kernels for TCCON measurements depending on solar zenith angle.

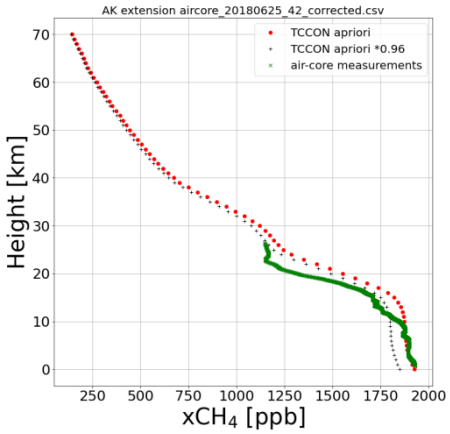


Figure 20. Exemplary TCCON a-priori (red dots). To supplement the AirCore measurements for high altitudes in order to get the total column, the TCCON a-priori is scaled to fit the highest value of the AirCore.

Results for the comparison of the total column can be seen in Figure 21 to 28. Deviations of more than 2% (36ppb) are handled as outliers, which could be due to experimental problems. Over all days with AirCore measurements and corresponding FTIR measurements at Sodankylä a bias of 9.1 ppb and a standard deviation of 9.8 ppb are found. For Orleans a bias of 11.7 ppb and a standard deviation of 10.2 ppb are found.

Results for the comparison of the tropospheric column are shown in Figure 25. and 26. for Orléans and Figure 27. and 28. for Sodankylä. Corresponding bias is -13.2 ppb with a standard deviation of 10.3 ppb for Sodankylä and a bias of 1.8 ppb with a standard deviation of 10.7 ppb for Orléans, see Table 6.

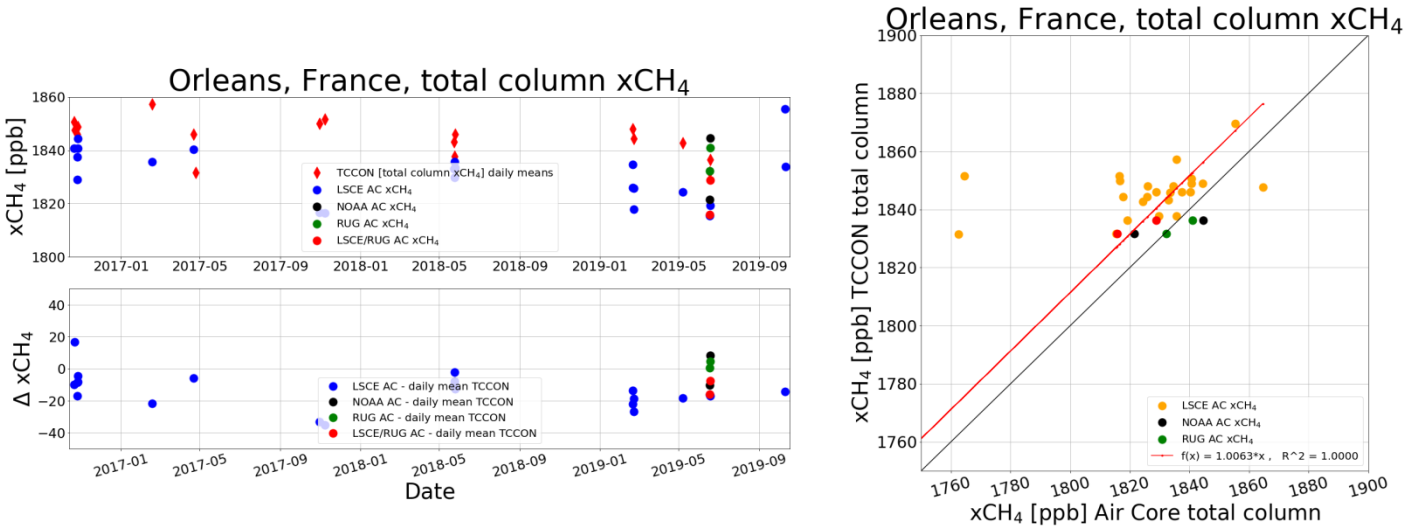


Figure 21. and 22.Total column measurements from TCCON instrument and the AirCores at the TCCON site Orléans.

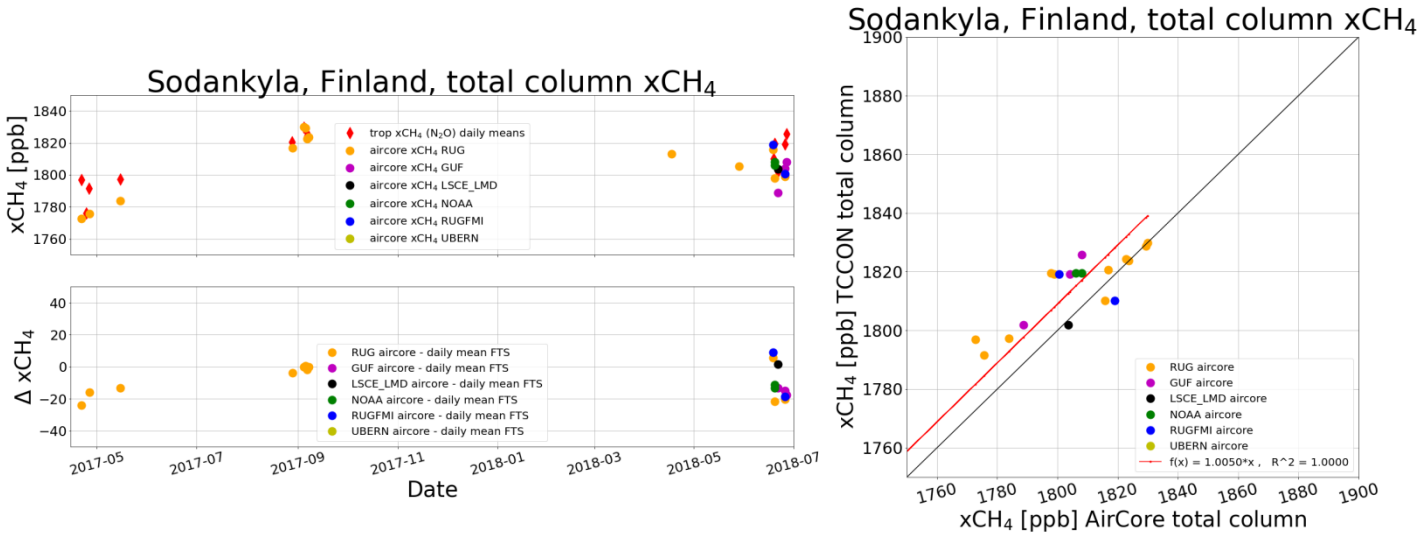
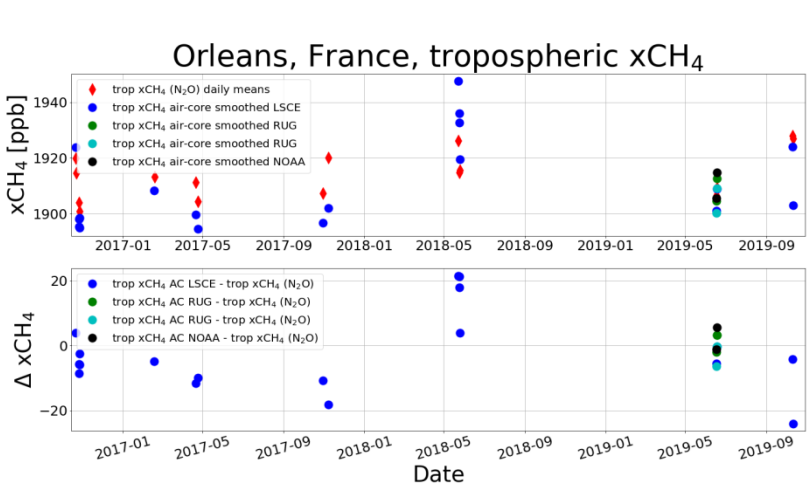


Figure 23. and 24.Total column measurements from TCCON instrument and the AirCores at the TCCON site Sodankylä.



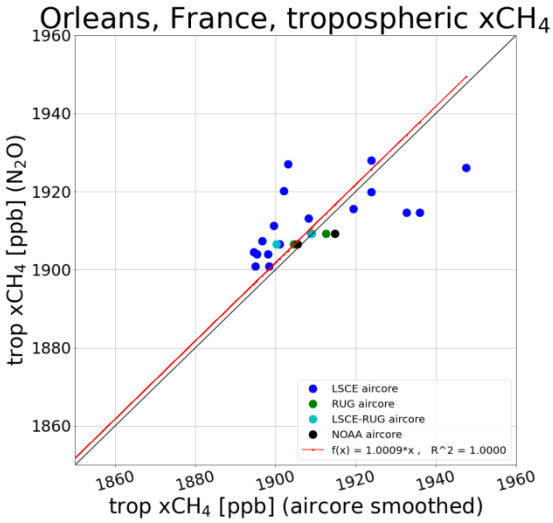
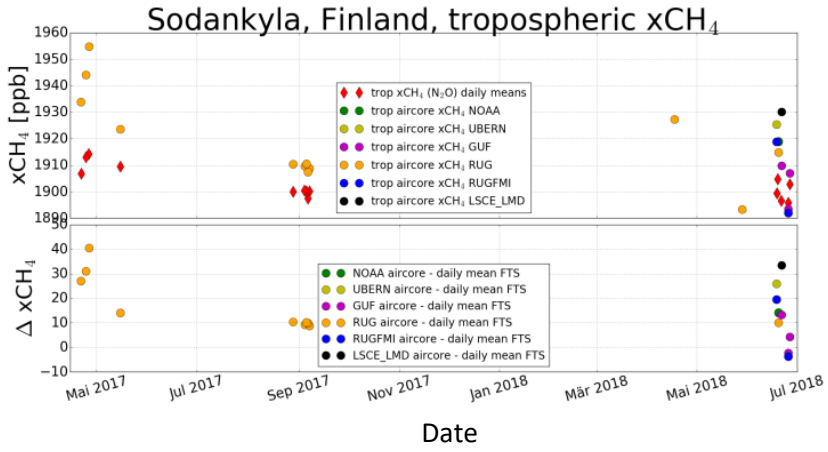


Figure 25. and 26.Tropospheric column measurements from TCCON instrument and the AirCores at the TCCON site Orléans.



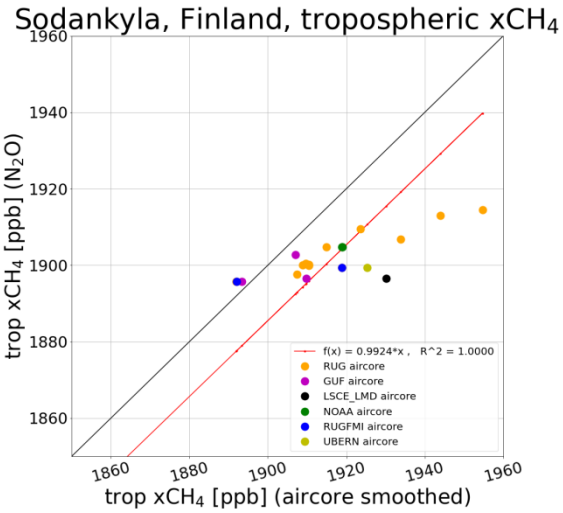


Figure 27. and 28.Tropospheric column measurements from TCCON instrument and the AirCores at the TCCON site Sodankylä.

Table 6: Mean bias and standard deviations. Deviations of more than 2% have been handled as outliers and are not included in the calculation.

Site	Mean bias AirCore –TCCON xCH_4 total column (ppb)	Standard deviation AirCore – TCCON xCH_4 total column (ppb)	Mean bias AirCore – TCCON xCH_4 tropospheric column (ppb)	Standard deviation AirCore –TCCON xCH_4 tropospheric column (ppb)
Orleans	11.7	10.2	1.8	10.7
Sodankylä	9.1	9.8	-13.2	10.3

The general agreement of the AirCore measurements and the corresponding FTIR TCCON measurements for the total column is within ~20ppb. We find a bias and a scatter in the order of 10 ppb each, see Table 2. At the AirCore campaign at Orleáns we see an agreement of 10ppb. At Sodankylä, the outliers in April 2017 have been investigated and are assigned to increased uncertainties of the FTIR measurements due to increased variations of the tropopause altitude. The investigation showed that on these days a strong subsidence of the troposphere occurred and there is a strong deviation of the standard TCCON a-priori and the AirCore measurements. Such strong deviations lead to higher uncertainties within the GFIT 2014 retrieval. A new version of the GFIT retrieval algorithm GFIT 2020 is in the final test phase. GFIT 2020 uses 3-hourly calculated a-priori inputs instead of daily a-priori inputs. This investigation will be repeated using GFIT 2020 as soon as it is final.

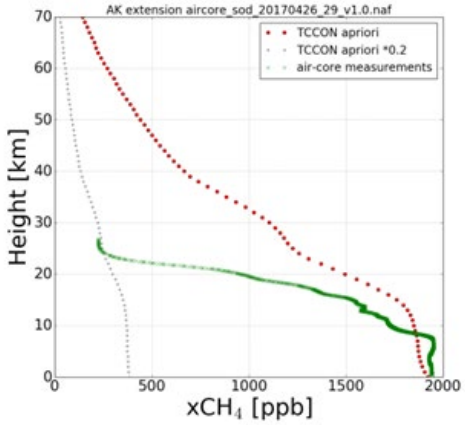


Figure 29 . TCCON a-priori and AirCore measurements of xCH4 at Sodankylä for the 26th of April 2017. The AirCore measurements show a strong subsidence of the troposphere compared to the expected standard TCCON a-p29riori due to the polar vortex. Furthermore, increased values at ~7km altitude might come from a long range transport of CH4.

Furthermore we applied the method of deriving the tropospheric column of xCH_4 to 'TCCON-like' measurements of our tropical wet site Paramaribo (Suriname) and compared them to the HF method. Results are in good agreement as expected. The results further show an increasing scatter of the HF method plotted over the H_2O column, shown in Fig 13. The N_2O method is not affected by high humidity, so the N_2O method has an advantage over the HF method at sites with a high humidity.

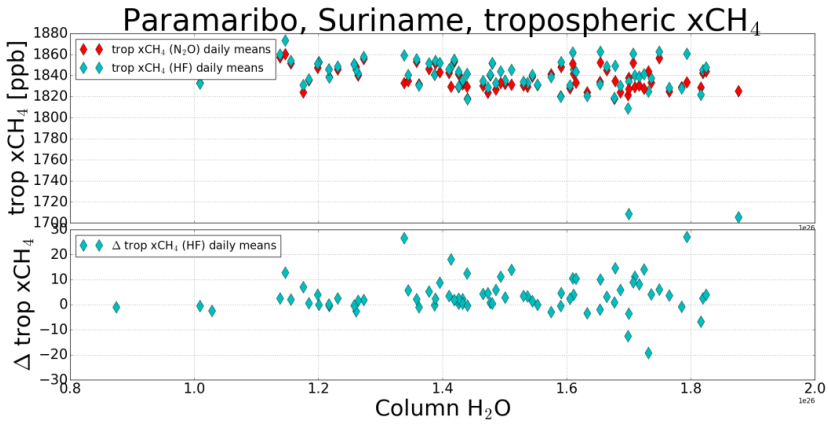


Figure 30. The methods of deriving the tropspheric column of xCH_4 from HF and from N_2O have been compared examplarily at tropical wet site Paramaribo (Suriname). It is clearly to be seen that the scatter for th HF method increases with the column of H_2O while the N_2O method is not affected.

Uncertainties

The uncertainties of the GFIT retrieval are a combination of statistical errors (measurement noise) and systematic artifacts (e.g. errors/omissions in the spectroscopy, the modeling of the instrument response, and pointing-induced solarline shifts) (Wunch et al., 2011). The TCCON measurement precision (2σ) for xCH_4 is<0.3 % (<5 ppb) for a single measurement. The measurement errors for total column measurements of the different gases from the same measurement are affected in the same way. This leads to comparable uncertainties of the tropospheric column of xCH_4.

Conclusion

A method of deriving the tropospheric column of xCH_4 has been established and evaluated against vertical resolved measurements by AirCores. The separation of tropospheric and stratospheric xCH_4 using N_2O as a tracer has been applied to the standard TCCON data product of xCH_4 and compared to AirCore measurements at the sites Orléans and Sodankylä. The results agree within ~20ppb, for the AirCore campaign 2019 within 10ppb. The outliers at Sodankylä can partly be explained by an increased uncertainty of the FTIR TCCON measurements due to high deviations of the atmosphere from the TCCON standard a-priori. A new version of the retrieval algorithm GFIT (GFIT2020) is in the final test phase and likely to further improve these results.

For tropical wet sites, using N_2O as a tracer in order to derive the tropospheric column of xCH_4 gives less scatter than using HF.

4 CONCLUSIONS

Two intensive AirCore comparison campaigns were successfully performed, the 2018 Sodankylä campaign with a total of 10 balloon flights and 26 vertical profiles and the 2019 Trainou campaign with a total of 27 balloon flights. The measured species include CO_2, CH_4, CO, O_2, H_2O by continuous cavity ring-down spectrometers (CRDS) at Sodankylä, and subsequent isotopic compositions of CO_2, CH_4 and halogenated trace gases by delayed analyses of collected stratospheric air samples conducted later in several individual home laboratories. Furthermore, additional vertical profiles of COS and N_2O were obtained during the Trainou campaign.

The intensive AirCore comparison results show that the uncertainties of AirCore mole fraction measurements are 0.15 – 0.2 ppm and 4 – 7 ppb for CO2 and CO, respectively. When no chemical dryer was used during sampling, we observed small and insignificant stratospheric CO2 difference of 0.06 – 0.11 ppm or column means compared to other collocated AirCore profiles. Furthermore, variations of AirCore CO_2 and CH_4 measurements at individual heights are dominated by spatial resolution differences, and AirCore tubing with surface coating can cause a large difference of up to ~ 5ppm for CO_2. From a comparison of multiple stratospheric vertical profiles, we found that the AirCore altitude registration has an uncertainty of ~3 mbar.

For AirCore CO_2 measurements, we have achieved the accuracy target for high-accuracy observations. However, there is certainly room to improve the uncertainties of CO observations and a need to further develop and improve the altitude registration in future projects.

Furthermore, we have developed a full-physical CH_4 profile retrieval method for ground-based solar absorption measurements performed in the near-infrared spectral region following the TCCON recommendations. The SFIT4 retrieval algorithm has been used for this purpose with several optimizations.

We achieved to get a degree of freedom of 2.4, indicating distinct information for the tropospheric column and the stratospheric column in addition to the total column of CH_4. We provided uncertainty estimates for our results based on the optimal estimation, including the contribution from smoothing error, model parameter error and measurement error. A direct comparison of our dry-air column averaged mole fractions of CH_4 (XCH_4) retrieval results (SFIT4NIR) to the standard TCCON XCH_4 for six sites shows that our systematic uncertainty is within 0.35% and random uncertainty is within 0.5%. The SFIT4NIR tropospheric and stratospheric columns were compared to surface in-situ measurements, ACE-FTS satellite measurements, Aircraft and AirCore measurements to evaluate the individual products. The difference between the reference measurements and our SFIT4NIR retrievals of partial columns are within the uncertainty estimates of our retrieval. The comparison between the SFIT4NIR retrievals and AirCore/aircraft measurements indicate that the uncertainties of SFIT4NIR partial columns are 1.0±0.2% in the troposphere and 4.0±2.0% in the stratosphere. Finally, we applied our retrieval method to the FTS NIR measurements performed at the TCCON sites in Sodankylä and Orléans during the two RINGO AirCore campaigns in 2018 and 2019, respectively. We compared our tropospheric and stratospheric columns as well as the total column CH_4 to the respective columns derived from the AirCore measurements provided by the participating research groups. The differences between the SFIT4NIR and the AirCore CH_4 values are found to be within the uncertainty estimates of the SFIT4NIR results. The small differences among the AirCore results are better understood. Comparing our SFIT4NIR partial columns and total columns against other remote sensing and in-situ measurements at several locations with varying measurement conditions showed the robustness of our results. We have successfully demonstrated the vertical profile retrievals of CH_4 from measurements performed at the ground-based TCCON network at several sites (Ny-Ålesund, Sodankylä, Bialystok, Bremen, Orléans and St Denis). This method is now ready and can be further applied to the TCCON type of measurements from other locations and offer new partial column CH_4 products for further use.

5 DEFINITIONS, ACRONYMS AND ABBREVIATIONS

ICOS	Integrated Carbon Observation System
RINGO	Readiness of Integrated carbon observation system (ICOS) for Necessities of integrated Global Observations
TCCON	Total Carbon Column Observing Network
LISA	Lightweight Stratospheric Air
CRDS	Cavity ring-down spectrometers
FTS	Fourier transform spectrometer - Fourier Transform Spectrometer
NR	Near-infrared
DOFS	Degree of freedom for signal
SFIT4NIR	Ground-based FTS NIR spectra using the SFIT4 code
ACE-FTS	Atmospheric Chemistry Experiment -
AVK	Averaging kernel
SZA	Solar zenith angle
SNR	Signal to noise ratio
HITRAN	High-resolution transmission molecular absorption database
ILS	Instrumental Line Shape
WACCM	The Whole Atmosphere Community Climate Model
GUF	Goethe University Frankfurt
LMD	Le Laboratoire de Météorologie Dynamique
NOAA	National Oceanic and Atmospheric Administration
LSCE	Laboratoire des sciences du climat et de l'environnement
UBern	University of Bern
RUG	University of Groningen
FMI	Finnish Meteorological Institute
UEA	University of East Anglia
O.D.	Outer diameter

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