Improved ozone monitoring by ground-based FTIR spectrometry

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Abstract. Accurate observations of atmospheric ozone (O_3) are essential to monitor in detail its key role in atmospheric chemistry. The present paper examines the performance of different O_3 retrieval strategies from FTIR (Fourier Transform InfraRed) spectrometry by using the 20-year time series of the high-resolution solar spectra acquired from 1999 to 2018 at the subtropical Izaña Observatory (IZO, Spain) within NDACC (Network for the Detection of Atmospheric Composition Change). In particular, the effect of two of the most influential factors have been investigated: **the inclusion of a simultaneous atmospheric temperature profile fit and spectral O_3 absorption lines used for the retrievals (the broad spectral region of 1000-1005 cm^{-1} and single micro-windows between 991-1014 cm^{-1}). Additionally, water vapour (H_2O) interference on O_3 retrievals has been evaluated, with the aim of providing an improved O_3 strategy that minimises its impact and, therefore, could be applied at any NDACC FTIR station under different humidity conditions.** The theoretical and experimental quality assessments of the different FTIR O_3 products (total column -TC- amounts and volume mixing ratio -VMR- profiles) provide consistent results. Combining a simultaneous temperature retrieval and an optimal selection of **single O_3 micro-windows** results in superior FTIR O_3 products, with a precision greater than 0.6-0.7% for O_3 TCs as compared to coincident NDACC Brewer observations **taken** as reference. However, this improvement can only be achieved provided the FTIR spectrometer is properly characterised and stable over time. For unstable instruments, the temperature fit has been found to exhibit a strong negative influence on O_3 retrievals **due to the increase in** the cross-interference between **the temperature retrieval and instrumental performance (given by the instrumental line shape function and measurement noise), which leads to the precision of FTIR O_3 TCs worsening up to 2%**. This cross-interference becomes especially noticeable beyond the upper troposphere/lower stratosphere as documented theoretically as well as experimentally by comparing FTIR O_3 profiles to those measured using Electrochemical Concentration Cell (ECC) sondes within NDACC. Consequently, it should be taken into account for the reliable monitoring of O_3 vertical distribution, especially in long-term timescales.

1 Introduction

Monitoring atmospheric composition is crucial for understanding present climate and foreseeing possible future changes and is, therefore, the basis for the design and implementation of efficient climate-change mitigation and adaptation policies. Among the

atmospheric gases with important climate effects, ozone (O_3) plays a vital role in **atmospheric chemistry**. In the stratosphere it absorbs a large part of the biologically damaging ultraviolet sunlight, allowing only a small amount to reach the Earth's surface. Likewise, absorption of the ultraviolet radiation heats, stratifies, and determines the vertical stability of the middle atmosphere. In the troposphere, O_3 absorbs infrared radiation, acting as an important greenhouse gas, affects the oxidising capacity of the atmosphere, and is a harmful phytotoxicant to public health (Cuevas et al., 2013; WMO, 2014a, 2018; Gaudel et al., 2018, and references therein).

Stratospheric O_3 abundances have shown a significant decrease in global levels from the 1980s to the 1990s, mainly attributed to the increase of anthropogenic emission of Ozone Depleting Substances (ODSs) during that period (WMO, 2014a, 2018). The implementation of the 1987 Montreal Protocol and its amendments and adjustments has stopped global O_3 decay by controlling the ODSs emissions, with O_3 concentrations having approximately stabilised since stratospheric ODSs abundances reached their maximum at the end of the 1990s. As a result, global O_3 content is expected to slowly increase and return to pre-1980 levels during the 21st century (e.g., Weatherhead et al., 2000; Austin and Butchart, 2003; Eyring et al., 2010; WMO, 2014a, 2018). However, O_3 concentrations are not only affected by the presence of ODSs, but also by a wide variety of factors (increase of greenhouse gases concentrations, changes in the Brewer-Dobson circulation and stratospheric temperatures, etc.), making it very challenging to predict how, when and where the O_3 recovery will take place. **In the troposphere, since O_3 is highly variable depending on time period, region, and proximity to fresh O_3 precursor emissions, there is no consistent picture of O_3 tropospheric changes around the world (Steinbrecht et al., 2017; Gaudel et al., 2018; WMO, 2018)**. Hence, high-quality and long-term O_3 measurements are essential for further improvement our understanding of O_3 response to natural and anthropogenic forcings, **as well as to estimate consistent trends at a global scale** (Vigouroux et al., 2015; Gaudel et al., 2018; GCOS, 2021).

Within NDACC (Network for the Detection of Atmospheric Composition Change, www.ndaccdemo.org), high-resolution solar absorption infrared spectra have been continuously recorded since the 1990s by ground-based FTIR (Fourier Transform InfraRed) spectrometers distributed at a global scale. By analysing the measured spectra, these instruments are capable of providing both high-quality O_3 total column (TC) amounts and low-resolution O_3 vertical volume mixing ratio (VMR) profiles **at about twenty sites nowadays** (e.g. Barret et al., 2002; Schneider and Hase, 2008; Schneider et al., 2008a; Schneider et al., 2008b; Vigouroux et al., 2008; Viatte et al., 2011; García et al., 2012, 2014; Vigouroux et al., 2015, and references therein). **In the last years, the NDACC Infrared Working Group (IRWG, www2.acom.ucar.edu/irwg) has made considerable efforts in order to standardise the data acquisition protocols and inversion strategies used to derive O_3 concentrations at the different NDACC stations and, hence, produce uniform and consistent O_3 datasets (Hase et al., 2004; IRWG, 2014; Vigouroux et al., 2015). Nonetheless, scientific discussion is still on-going seeking improvements in O_3 monitoring and network-wide consistency**.

In this context, the present paper examines the effect of using different retrieval approaches on the quality of the FTIR O_3 products, with the aim of providing an improved O_3 strategy that could be applied at any NDACC FTIR station. The influence of two of the most important settings is assessed: the spectral region used for O_3 retrievals and simultaneous fit of the atmospheric temperature profile. To our knowledge, so far this analysis has been approached separately in most of the studies

present in literature or has not addressed in detail yet. Previous studies have shown, for example, that an optimised selection of the O_3 absorption lines or the inclusion of an additional temperature fitting significantly improve the precision of FTIR O_3 TCs and VMR profiles (e.g., Schneider and Hase, 2008; Schneider et al., 2008b; García et al., 2012, 2014). Nonetheless, possible combined effects were not analysed by these works.

The analysis has been performed at the O_3 super-site Izaña Observatory (IZO), where since 1999 ground-based FTIR observations have been carried out coincidentally to other high-quality O_3 measurement techniques. By using those data, a comprehensive assessment of the precision and long-term consistency of new O_3 retrieval strategies from ground-based FTIR spectrometry can be carried out. To this end, the current paper is structured as follows: Section 2 describes the Izaña Observatory, FTIR measurements and ancillary data considered to assess the quality of the new FTIR O_3 products (Brewer TC observations and Electrochemical Concentration Cell -ECC- vertical sondes). Section 3 presents the different FTIR O_3 retrieval strategies and their theoretical characterisation in terms of vertical sensitivity and expected uncertainty. Section 4 examines the quality and long-term reliability of the different FTIR O_3 TCs and VMR profiles by comparing them to the independent O_3 datasets. Finally, Section 5 summarises the main results and conclusions drawn from this work.

2 Izaña Observatory and its Ozone Programme

Izaña Observatory is a high-mountain station located on the island of Tenerife (Spain) in the subtropical North Atlantic Ocean (28.3ºN, 16.5ºW) at an altitude of 2370 m a.s.l.. The observatory is managed by the Izaña Atmospheric Research Centre (IARC, https://izana.aemet.es), which belongs to the State Meteorological Agency of Spain (AEMet, www.aemet.es). IZO is located below the descending branch of the northern subtropical Hadley cell, under a quasi-permanent subsidence regime, and typically above a stable trade wind inversion layer that acts as a natural barrier for local and regional pollution. This strategic location ensures clean air and clear-sky conditions during most of the year, making IZO an excellent station for in-situ and remote-sensing observations (Cuevas et al., 2019, and references therein).

Since many years IZO has run a comprehensive O_3 monitoring programme by using different measurement techniques: FTIR, Brewer, and DOAS (Differential Optical Absorption Spectroscopy) spectrometers, as well as ECC O_3 sondes and in-situ ultraviolet photometric analysers. The first four techniques routinely contribute to NDACC, aiming at monitoring changes in the troposphere and stratosphere with an emphasis on the long-term evolution of O_3 layer, while the in-situ O_3 records are taken in the framework of the WMO/GAW (World Meteorological Organization/Global Atmospheric Watch) programme. Refer to Cuevas et al. (2019) for more details about IZO and its atmospheric monitoring programmes.

2.1 FTIR Measurements

The IZO FTIR programme has been gathering high-resolution solar spectra within NDACC since 1999, when a Bruker IFS 120M spectrometer was installed by a collaborative agreement between the IMK-ASF (Institute of Meteorology and Climate Research-Atmospheric Trace Gases and Remote Sensing of Karlsruhe Institute of Technology, KIT, www.kit.edu) and AEMet-IARC. In 2005, this instrument was replaced for an upgraded model, the Bruker IFS 120/5HR, which is one of the best

performing FTIR spectrometers commercially available. For the present study, the measurements taken from 1999 to 2018, encompassing the operation of the two FTIR instruments, have been used.

Within NDACC activities, the IZO FTIR spectrometer records direct solar absorption spectra in the middle infrared spectral region, i.e., between 740 - 4250 cm^{-1} (corresponding to 13.5 - 2.4 μm) by using a set of different fieldstops, narrow-bandpass filters and detectors. Nevertheless, for O_3 retrievals, only the 960-1015 cm^{-1} spectral region is considered, which is measured with the NDACC filter 6 using a potassium bromide (KBr) beam splitter and a cooled mercury cadmium telluride (MCT) detector. The solar spectra were taken at a high spectral resolution of 0.0036 cm^{-1} (250 cm maximum optical path difference, OPD, OPD$_{max}$) until April 2000, and at 0.005 cm^{-1} (OPD$_{max}$=180 cm) onward. The IFS 120M's field-of-view (FOV) angle was varied between 0.17° and 0.29° depending on the measurement period, while it was always limited to 0.2° for the IFS 120/5HR. In order to increase the signal-to-noise ratio eight single scans are co-added, thereby the acquisition of one spectrum takes about 10 minutes.

NDACC FTIR solar spectra are only recorded when the line of sight (LOS) between the instrument and the sun is cloud-free. Given the IZO location, the cloud-free conditions are very common and thus FTIR measurements are typically taken about two or three times a week. For the 1999-2018 period the total number of NDACC measurement days for O_3 retrievals amounts to 1975, with an annual average of ∼100 measurement days a year. For further details about the FTIR measurements at IZO, refer to **García et al. (2021)**.

In order to characterise the instrumental performance of the IZO FTIR spectrometers, the ILS function has been routinely monitored about every two months since 1999 using low-pressure N_2O-cell measurements and LINEFIT software (v14.5), as detailed in Hase (2012). This ILS treatment ensures the independence of the FTIR trace gas retrievals and instrumental characterisation, but it also allows instrumental alignment and its temporal stability to be verified. Figure 1 depicts the time series of the ILS's modulation efficiency amplitude (MEA) and phase error (PE) parameters, between 1999 and 2018, used for O_3 retrievals. Three periods with different features affecting the IZO FTIR measurements can be distinguished: (1) 1999-2004, in spite of N_2O-cell measurements were routinely carried out, the ILS estimation is imprecise due to the instability of the IFS 120M spectrometer; (2) 2005-May 2008, the IFS 120/5HR instrument exhibits a gradual temporal drift, but the ILS function is properly assessed; and (3) June 2008-2018, the IFS 120/5HR instrument is optically aligned and well (ILS is nearly nominal). Therefore, these three periods will be independently analysed in the present work in order to examine the influence of instrument status on FTIR O_3 products.

2.2 Ancillary Data: Brewer and ECC sondes

At IZO Brewer spectrometers, managed by AEMet, have been continuously operating since 1991. In 2001, these activities were accepted by NDACC and, two years later, the RBCC-E (Regional Brewer Calibration Centre for Europe, www.rbcc-e.org) of the WMO/GAW programme was established at IZO. By recording direct solar absorption spectra in the ultraviolet spectral region, **IZO RBCC-E reference instruments can provide O_3 TCs with a total uncertainty (standard uncertainty, k=1) between 1.2-1.5%** (Gröbner et al., 2017). The high quality and long-term stability of IZO Brewer observations make them a useful reference for validating ground- and satellite-based instruments (León-Luis et al., 2018).
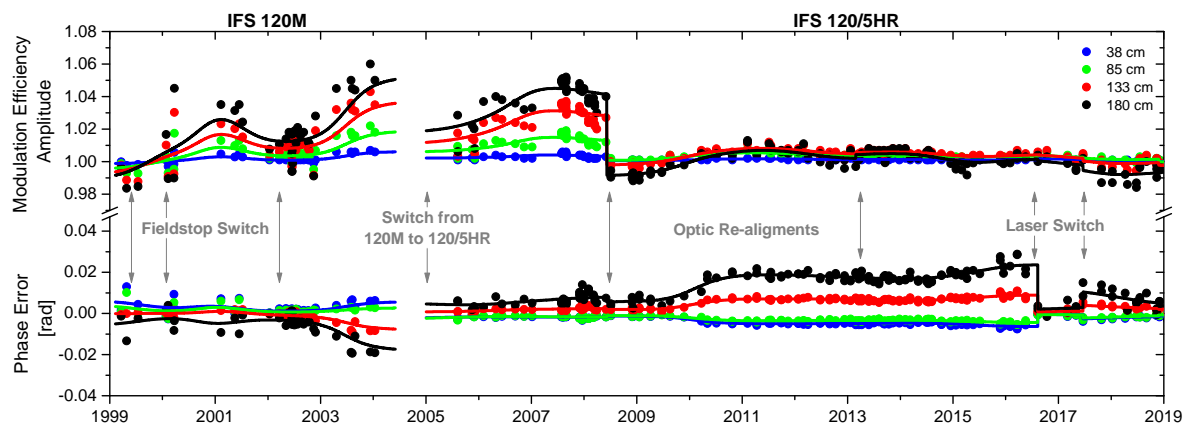
Figure 1. Time series of the normalised Modulation Efficiency Amplitude (MEA) and Phase Error (PE, rad) at four optical path differences (33, 85, 133, and 180 cm) for the NDACC O_3 measurement settings (filter 6 and MCT detector) of the IZO FTIR spectrometers between 1999 and 2018. Data points represent individual N_2O-cell measurements and solid lines depict smoothed MEA and PE curves. Grey solid arrows indicate punctual interventions on the instruments: different changes of fieldstops between 1999 and 2004, switch from the IFS 120M to the IFS 120/5HR system in 2005, optic re-alignments in June 2008 and February 2013, and internal laser replacements in August 2016 and June 2017.

125   The O_3 sonde programme on Tenerife started in November 1992, also run by AEMet, and since March 2001 it has operated in the framework of NDACC. The O_3 sounding is based on ECC that senses O_3 as it reacts with a dilute solution of potassium iodide (KI) to produce an electrical current proportional to atmospheric O_3 concentrations (Komhyr, 1986). The ECC sondes (Scientific Pumps 5A and 6A) were launched once weekly from Santa Cruz de Tenerife station (30 km north-east of IZO, 36 m a.s.l.) until 2010 and, since then, from Botanic observatory (13 km north of IZO, 114 m a.s.l.). The expected **total** uncertainty

130   of the ECC sondes is ±5–15% in the troposphere and ±5% in the stratosphere (WMO, 2014b), **which is a composite of different instrumental error contributions (i.e. sensor and background current, conversion efficiency, etc.)**.

    Note that for the purpose of the present work both Brewer and ECC sonde databases fully cover the entire FTIR 1999-2018 period.

3   FTIR Ozone Observations

135 **3.1   Ozone Retrieval Strategies**

To analyse the influence of the spectral region and simultaneous temperature fit on the quality of FTIR O_3 products, six different approaches have been defined. They combine three spectral regions and the possibility of performing or not a simultaneous temperature retrieval (referred to as retrieval set-ups 1000, 4MWs, 5MWs, 1000T, 4MWsT and 5MWsT hereafter, Figure 2). Set-up 1000 uses a broad spectral window covering from 1000 to 1005 cm^{-1}, which is the one recommended by the NDACC

140 IRWG (IRWG, 2014). This spectral region has been traditionally used by the FTIR community reporting high-quality O_3 products (e.g. Barret et al., 2002; Schneider et al., 2008a; Vigouroux et al., 2008; Lindenmaier et al., 2010; García et al., 2012; Vigouroux et al., 2015). Set-up 5MWs uses five single micro-windows between 991 and 1014 cm^{-1}, which is a simplification of the approach suggested by Schneider and Hase (2008). Schneider et al. (2008a) found that this strategy provides more precise O_3 estimations than those retrieved from the broad 1000-1005 micro-window when comparing to independent measurements.

145 Set-up 4MWs is the same as 5MWs, but the micro-window at the greatest wavenumbers is discarded in order to avoid any possible saturation of the strong O_3 absorption lines contained in this region, especially at high O_3 concentrations and low solar elevations. Set-ups 1000T, 4MWsT, and 5MWsT use the same micro-windows as set-ups 1000, 4MWs, and 5MWs respectively, but an optimal estimation of the atmospheric temperature profile is simultaneously carried out. To this end, four CO_2 micro-windows are added between 962.80-969.60 cm^{-1} according to **García et al. (2012)**.
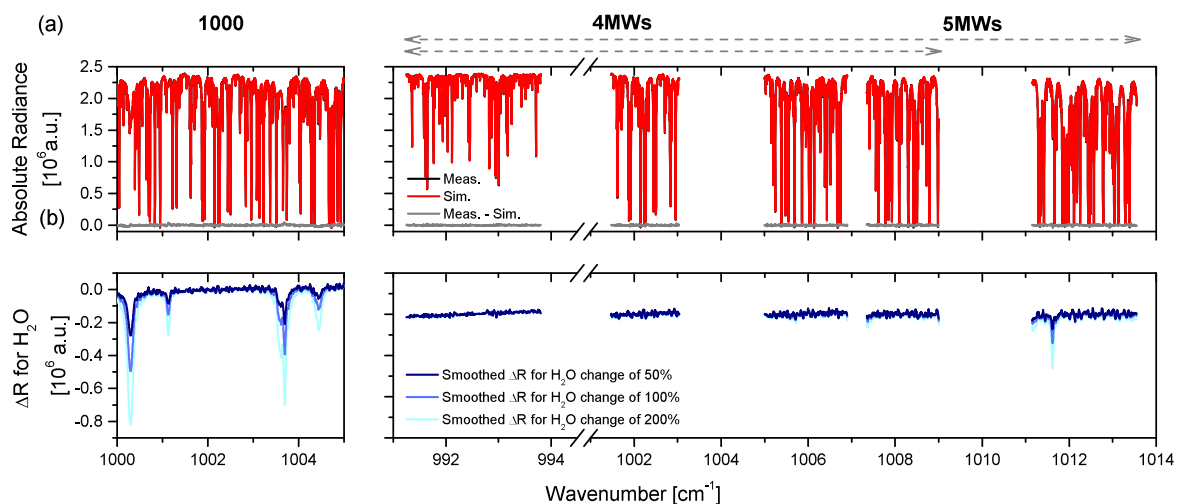
Figure 2. (a) Spectral regions considered in the different FTIR O_3 retrieval strategies: broad window used in the set-ups 1000/1000T, encompassing the 1000-1005 cm^{-1} spectral region, and the four and five micro-windows used in the set-ups 4MWs/4MWsT, between ~991 and 1009 cm^{-1}, and in 5MWs/5MWsT between ~991 and 1014 cm^{-1}, respectively. Red and black lines depict an example of the simulated and measured spectrum taken on 31st August 2007 (at solar zenith angle -SZA- of ≈50º, O_3 amount in the slant column -O_3 SC- of 390 DU, and H_2O TC of 10.7 mm). Grey lines show the difference between the measurement and simulation. (b) Spectral changes in the measured FTIR radiances ($\triangle R$) due to changes in H_2O content of 50% (TC of 16.1 mm), 100% (TC of 21.5 mm), and 200% (TC of 32.3 mm).

150 With the exception of the spectral region and temperature treatment, the retrieval strategy is identical for the six approaches. The O_3 VMR profiles are derived from the measured solar absorption spectra by means of PROFFIT code (PROFile FIT, Hase et al., 2004), using an ad-hoc Tikhonov-Philips slope constraint (TP1 constraint) on a logarithmic scale. Since O_3 concentrations are very variable around the tropopause, the logarithmic inversion has proved to be superior to the linear approach (e.g., Schneider and Hase, 2008; Schneider et al., 2008a; Schneider et al., 2008b). Then, the O_3 TCs are computed by integrating

155 the retrieved VMR profiles from the FTIR altitude up to the top of the atmosphere. The remaining settings are based on the NDACC IRWG recommendations (IRWG, 2014):

– **The interfering species considered are H_2O, CO_2, C_2H_4, and the main O_3 isotopologues ($^{666}O_3$, $^{686}O_3$, $^{668}O_3$, $^{676}O_3$, and $^{667}O_3$). Spectroscopic line parameters of these absorbers are taken from HITRAN 2008 (Rothman et al., 2009) with a 2009 update for H_2O (www.cfa.harvard.edu).**

160 – All set-ups use the same a-priori gas profiles, which are taken from the climatological model WACCM (Whole Atmosphere Community Climate Model, http://waccm.acd.ucar.edu)-version 6 generated by the NCAR (National Center for Atmospheric Research, J. Hannigan, personal communication, 2014).

– All set-ups apply the actual ILS time series evaluated from independent N_2O-cell measurements **(Figure 1)**.

– The pressure and temperature profiles for forward simulations are taken from the NCEP (National Centers for Environ-
165 mental Predictions) 12 UT daily database.

– For those approaches performing a simultaneous optimal estimation of atmospheric temperature profile, the NCEP 12 UT daily temperature profiles are used as the a-priori profiles. The a-priori temperature covariance matrix (S_{aT}) has been constructed following to Schneider et al. (2008a).

Given the importance of H_2O absorption across the infrared spectrum, the treatment of H_2O in O_3 retrievals should
170 **be carefully considered in the inversion strategy, as illustrated in Figure 2. This figure shows an example of the changes in the FTIR radiances for the spectral O_3 micro-windows due to changes in the H_2O content of 50%, 100% and 200%. These values, which correspond to extreme conditions at IZO, could account for typical H_2O content and variations at sites with greater humidity. As observed, the spectral signatures of H_2O variations are much stronger in the broad 1000 spectral region than in the narrow micro-windows (4MWs/5MWs), indicating that the quality of the O_3 products**
175 **in that region strongly depends on a correct interpretation of the spectroscopic H_2O signal. Therefore, in order to minimise interference errors due to H_2O, a two-step inversion strategy has been applied (García et al., 2012, 2014): firstly, the actual H_2O profile is derived using a dedicated H_2O retrieval (Schneider et al., 2012) and, then, the O_3 retrieval is simultaneously performed with an H_2O scaling fit, which uses the previously derived H_2O state. The remaining interfering gases are simultaneously estimated with O_3 in the second step. As discussed in detail in Appendix A, the H_2O**
180 **cross-interference is reduced by the two-step strategy, which leads to this approach being valid for humid FTIR sites.**

Once FTIR retrievals are computed, they are filtered according to (1) the number of iterations at which the convergence is reached, and (2) residuals of the simulated–measured spectrum comparison. This ensures that unstable or imprecise observations are not considered (which could likely be introduced, for example, by thin clouds) (García et al., 2016). These two quality flags are applied independently on the six O_3 datasets, and only those measurements available for all set-ups are con-
185 sidered in subsequent analysis. This leads to a total of 5393 O_3 observations between 1999 and 2018, which are coincident and quality-filtered ($\sim$90% of the original dataset).

3.2 Theoretical Quality Assessment

3.2.1 Vertical Sensitivity and Fitting Residuals

Because the vertical resolution of ground-based FTIR measurements is limited, a proper description of the relation between retrieved and true state must be provided together with the retrieved vertical profile. This information is theoretically characterised by the averaging kernel matrix ($\mathbf{A}$) obtained in the retrieval procedure (Rodgers, 2000). The rows of this matrix describe the altitude regions that mainly contribute to the retrieved profile and therefore the vertical distribution of the FTIR sensitivity, while its trace (also so-called "degrees of freedom for signal", DOFS) gives the number of the independent O_3 layers detectable by the remote-sensing FTIR instrument. As an example, Figure 3 (a) depicts the $\mathbf{A}$ rows for **the 5MWs set-up** for the measurement of Figure 2, while Table 1 summarises the DOFS' statistics for the six retrieval strategies considered.

Table 1. Summary of statistics of the DOFS and fitting residuals for the set-ups 1000/1000T, 4MWs/4MWsT, and 5MWs/5MWsT for the periods 1999-2004, 2005-May 2008, and June 2008-2018, and for the entire time series (1999-2018). Shown are median (M) and standard deviation (σ) for each period. The number of quality-filtered measurements is 519, 745, and 4219 for the three periods, respectively, and 5393 for the whole dataset. **The strategies showing the best performance, in terms of largest DOFS and smallest residuals, are highlighted in bold for each period.**

	DOFS				Residuals (x10^{-3})			
	1999-2004	2005-2008	2008-2018	1999-2018	1999-2004	2005-2008	2008-2018	1999-2018
Set-up	M, σ	M, σ	M, σ	M, σ	M, σ	M, σ	M, σ	M, σ
1000	3.76, 0.25	3.99, 0.21	3.98, 0.14	3.97, 0.18	3.56, 1.90	2.62, 0.93	2.75, 0.55	2.77, 0.93
4MWs	4.09, 0.28	4.34, 0.12	4.30, 0.12	4.30, 0.17	3.51, 1.90	2.57, 0.85	2.70, 0.54	2.71, 0.91
5MWs	**4.29**, 0.28	**4.56**, 0.15	**4.52**, 0.12	**4.51**, 0.17	3.53, 1.90	2.58, 0.87	2.70, 0.55	2.73, 0.92
1000T	3.66, 0.31	3.98, 0.26	3.92, 0.17	3.91, 0.22	3.50, 1.90	2.60, 0.91	2.73, 0.55	2.75, 0.92
4MWsT	3.91, 0.33	4.24, 0.18	4.17, 0.15	4.16, 0.20	3.46, 1.90	**2.55**, 0.86	**2.68**, 0.54	**2.70**, 0.91
5MWsT	4.10, 0.33	4.42, 0.20	4.35, 0.15	4.35, 0.21	**3.45**, 1.90	2.56, 0.87	**2.68**, 0.54	**2.70**, 0.91

The A rows are quite similar for all set-ups with a median total DOFS value of ∼4, meaning that the FTIR system is able to roughly resolve four independent atmospheric O_3 layers: the troposphere (2.37–13 km), the upper troposphere/lower stratosphere (UTLS) or tropopause region (12–23 km), the middle stratosphere around the ozone maximum (22–29 km), and the upper stratosphere (28–42 km). However, the total DOFS values are found to be greater for those set-ups using narrower micro-windows than for the broad spectral window (see Table 1), whereby the former configurations seem to offer a better vertical sensitivity (especially the 5MWs set-up). This pattern is independent on the FTIR instrument and consistent over time, as observed for the three periods analysed (1999-2004, 2005-May 2008, and June 2008-2018). The comparison between the instruments also reveals, as expected, the lower sensitivity to the O_3 concentrations of the IFS 120M spectra as compared to the IFS 120/5HR measurements. The total DOFS values overall differ by 5.5% (1000) and 5.1% (5MWs) between the
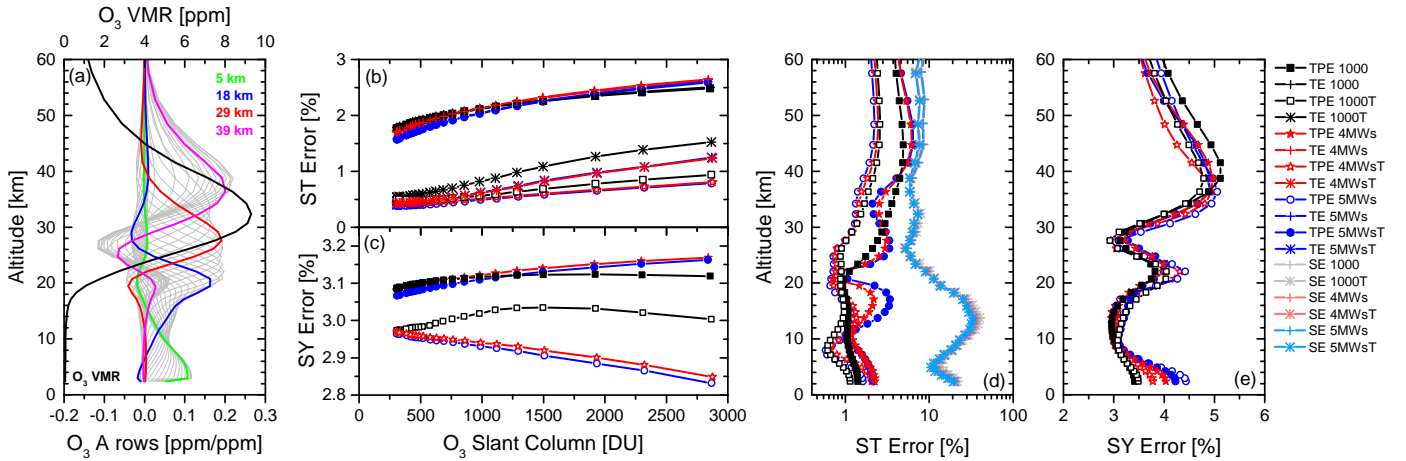
Figure 3. Summary of the theoretical quality assessment. (a) Example of averaging kernel (A) rows for the 5MWs set-up on a logarithm scale for the measured spectrum of Figure 2. Coloured lines highlight the A rows at the altitudes of 5, 18, 29 and 39 km, which are representative for the four layers detectable by the FTIR instrument (total DOFS of 4.41). The retrieved O_3 VMR profile is also shown. (b) Statistical (ST) and (c) systematic (SY) contribution of the total parameter errors (TPE, in %) and total error (TE, in %) for O_3 TCs retrieved from the set-ups 1000/1000T, 4MWs/4MWsT, and 5MWs/5MWsT as a function of O_3 slant column [DU] for measurements taken on 31st August 2007 from SZAs between 84º (∼07:00 UT) and 21º (∼13:30 UT). TPE is computed as the square root of the quadratic sum of all ST and SY error sources considered with the exception of the smoothing error (SE), while TE considers TPE and SE. Example of ST (d) and SY (e) contribution of the TPE and SE profiles [%] for all set-ups for the measured spectrum of Figure 2.

205 1999-2004 and 2008-2018 periods, respectively. When simultaneously fitting the atmospheric temperature profile, the median DOFS values slightly decrease for all strategies, because the information contained in measured spectra is then split into O_3 and temperature retrievals (the retrieved state vector space is not perfectly orthogonal). Likewise, the differences between both instruments become more accentuated (e.g. 6.6% and 5.7% between the 1999-2004 and 2008-2018 periods for 1000T and 5MWsT, respectively). As with DOFS analysis, the fitting residuals are smaller for those set-ups that use narrow micro-

210 windows and apply the temperature fit, allowing a more detailed interpretation of measured spectra to be obtained (as also summarised in Table 1). In addition, the IFS 120M retrievals are found to be considerably more variable than IFS 120/5HR data. However, it is fair to admit that the differences among retrieval strategies lie within the respective error confidence intervals, therefore no robust conclusions can be reached. Note that, in order to make a fair comparison, the fitting residuals are computed as the noise-to-signal ratio for a common spectral region contained in all set-ups (1001.47-1003.04 cm^{-1}).

3.2.2 Uncertainty Analysis

The characterisation of the different FTIR O_3 products has been completed by an uncertainty analysis, which **evaluates** how different error sources could be propagated into the retrieved products. The theoretical error **assessment** carried out in the present paper is based on Rodgers (2000), and analytically performed by PROFFIT package. The Rodgers' formalism distinguishes three types of error: (1) smoothing error (SE) associated with the limited vertical sensitivity of the remote-sensing FTIR instruments, (2) spectral measurement noise, and (3) uncertainties in the input/model parameters (instrumental characteristics, spectroscopy data, ...), which are split into statistical (ST) and systematic (SY) contributions. **Given that SE can be considered as an inherent characteristic of the remote-sensing technique, it is not included in the uncertainty assessment suggested by the NDACC IRWG (IRWG, 2014). Therefore, it has been separately considered in this work by distinguishing the total parameter error (TPE), which is calculated as the the square root of the quadratic sum of all error sources considered with the exception of SE, and the total error (TE), which considers both TPE and SE.** A detailed description of the uncertainty assessment is given in Appendix B.

In order to assess the effect of O_3 absorption signatures on the uncertainty budget, the dependence of the estimated errors on O_3 slant column (SC) amounts for each retrieval set-up has been examined. This analysis would allow possible inconsistencies between the set-ups or saturations of O_3 absorption lines at high O_3 concentrations to be detected. As shown in Figure 3, both statistical and systematic uncertainties do depend on O_3 spectroscopic signatures for all set-ups due to the increase of most of the error sources considered at larger O_3 SCs (see details in Appendix B). Figure 3 also documents that the inclusion of a simultaneous temperature retrieval significantly improves the theoretical performance for all FTIR O_3 products. Although this fit generates a negative cross-interference with the ILS, measurement noise and smoothing error (especially for the 1000T set-up, Figure B1), the temperature error contribution is in return nearly eliminated, leading to the total ST budget decreasing by ∼1%. TPE and TE range from 1.5 to 2.5% (between 250 and 3000 DU) for set-ups without a simultaneous temperature fit, while TPE varies from 0.5 to 1.0% (to 1.5% for TE due to the influence of SE) when including the temperature retrieval. The total systematic contributions also drop by 0.3% (at high O_3 SCs) with mean values of ∼3%. It is worth highlighting that an inconsistency between 4MWsT/5MWsT and 1000T set-ups has been detected in the systematic uncertainty budget, which is determined by the spectroscopy errors. For the 1000T configuration, the spectroscopic SY error exhibits a reverse smile curve with O_3 concentrations, and is considerably greater than for the narrow micro-window set-ups. This result might point to a possible saturation of the deeper O_3 lines contained in the broad window or some inconsistency in the spectroscopy parameters. For example, an erroneous parameterisation of the temperature dependence of the O_3 line width may produce systematic differences between actual and retrieved temperature profiles (Schneider and Hase, 2008), therefore affecting the absolute value of O_3 FTIR products.

Vertically, the most important contribution is SE reaching ∼40% in the UTLS region (Figure 3 (d)), where the O_3 concentrations are very variable and the profile might be highly structured. The FTIR system is not able to resolve such fine vertical structures. Excluding SE, the statistical TPE profiles are strongly linked to the atmospheric temperature

with maximal errors beyond the UTLS region (where the maximum FTIR sensitivity and the largest O_3 concentrations
250 are also located, see Figure 3 (a)). This pattern is consistently observed for both set-ups with and without fitting the
atmospheric temperature profiles. However, the error values drastically drop when considering the temperature in the
retrieval procedure. TPE values between 1.0-1.5% are expected for the 1000T, 4MWsT and 5MWsT set-ups, and as
high as 6% when the temperature fit is not taken into account. In relation to the systematic uncertainty profiles (Figure
3 (e)), they range from 3% in the UTLS and middle stratosphere (around 30 km) to 5% in the upper stratosphere. As
255 with statistical errors, temperature contribution decreases when including the atmospheric temperature profile in the
retrieval, leading to smaller systematic errors in O_3 TCs as mentioned above.

The error estimation presented here assumes the same set of uncertainty values for all set-ups, which is representative of the
IFS 120/HR instrument in the period 2005-2008 (Table B1 in Appendix B). However, some error sources do strongly depend on
instrument status (particularly the ILS function, solar pointing, and measurement noise), affecting the total uncertainty budget.
260 In order to account for the different quality periods of the IZO FTIR instruments, the uncertainty analysis for different set of
error values has been included in Appendix B.

To summarise, using several narrow micro-windows instead of a single broad region and applying a temperature profile fit
has been found to provide more precise FTIR O_3 estimations by increasing the vertical sensitivity and decreasing the expected
uncertainties. The simultaneous temperature retrieval could be a suitable approach provided the FTIR system is properly
265 characterised, with a continuous assessment of ILS function, and stable over time (e.g. IFS 120/5HR spectrometers), in order
to minimise the negative influence of the ILS uncertainties and measurement noise on O_3 retrievals. Finally, although the
narrow micro-windows set-ups provide very consistent results, the 5MWsT set-up has theoretically shown to be superior for
the typical O_3 concentrations observed at the tropical and subtropical latitudes.

4   Comparison to Reference Observations

270 ### 4.1   FTIR and Brewer Ozone Total Columns

The performance of the six FTIR O_3 retrieval strategies have been assessed by comparing them to coincident **NDACC** Brewer
O_3 TC data. In order to mitigate the influence of the O_3 intra-day variations on comparisons, only FTIR and Brewer measure-
ments within a temporal coincidence of 5 minutes have been paired, which makes a total of 2231 coincidences between 1999
and 2018.
275 Figure 4 displays the time series of the Brewer observations together with four examples of FTIR retrievals (for simplicity
only the set-ups 1000/1000T and 5MWs/5MWsT are depicted), as well as the time series of corresponding relative differences
(RD, FTIR-Brewer). The temporal O_3 TCs variations are in general reproduced well by all FTIR products. However, the
different performance of the two FTIR instruments becomes evident from this figure: while the RD values of the IFS 120/5HR
instrument are very stable over time, the IFS 120M instrument exhibits a more erratic behavior. Besides the greater variability of
280 the IFS 120M and the switch of instrument in 2005, the most remarkable feature is a discontinuity detected at the beginning of
2010 by a non-parametric change-point test (Lanzante, 1996) (at 99% confidence level). The systematic jump is of ∼1.1% for

the set-ups without fitting temperature, and is partially corrected by retrieving temperature, ∼0.7%. The change-point, already reported by García et al. (2014), is likely due to modifications on the IFS 120/5HR spectrometer (failure of the interferometer's scanner motor and its subsequent replacement). Another change-point was detected by the Lanzante's approach around the beginning of 2014, but of less intensity. It is worth highlighting that both discontinuities were also detected in the differences of **O₃ TCs retrieved from the different FTIR set-ups**, especially by those including the temperature fit. Hence, when no independent observations are available, the analysis of different FTIR products could offer additional tools for identifying inconsistencies and documenting the long-term instrumental stability.
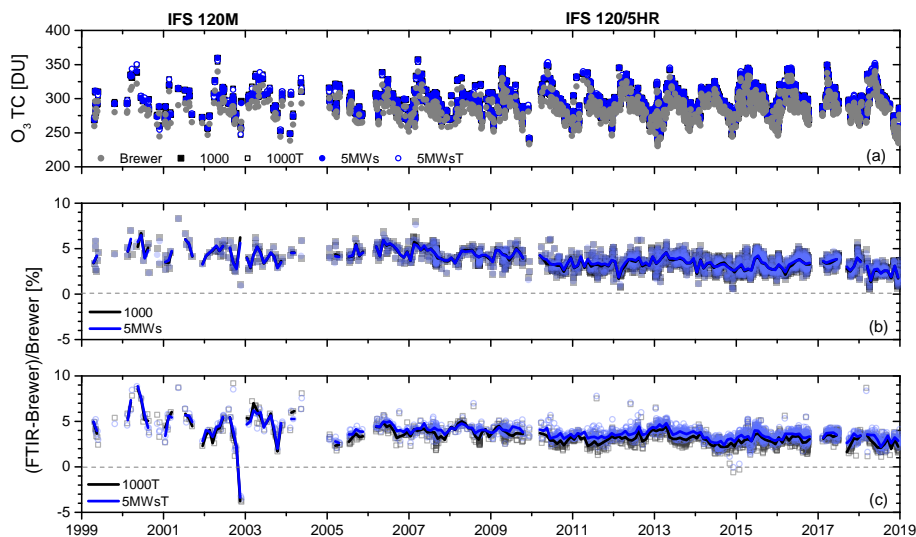
Figure 4. Summary of FTIR-Brewer comparison from 1999 to 2018. (a) Time series of O_3 TCs [DU] as observed by Brewer and FTIR 1000/1000T, and 5MWs/5MWsT set-ups. (b) Time series of the relative differences RD for the set-ups 1000 and 5MWs, which are calculated as RD[%]=100×(O_3 TC$_X$ - O_3 TC$_Y$)/O_3 TC$_Y$, where X and Y means FTIR and Brewer, respectively. (c) As for (b), but for the set-ups 1000T and 5MWsT. Solid lines in (b) and (c) correspond to monthly medians.

Figure 4 also reveals that, although the scatter of RD is significantly improved by the temperature retrieval, these strategies present in general more extreme values as compared to the Brewer data. The RD range between the percentiles 0.1^{th} and 99.9^{th} is 7.4% and 7.0% for the 1000 and 5MWs set-ups, respectively, while it is 9.3% and 8.6% for the 1000T and 5MWsT configurations, respectively. Note that, for example, the extreme RD values obtained for 1000T and 5MWsT set-ups at the beginning of 2000 and at ending of 2002 (Figure 4 (c)) are not reproduced by the 1000 and 5MWs strategies (Figure 4 (b)). This pattern is consistently observed for all set-ups and over time. The extreme RD values may indicate measurement days with an unusual temperature vertical stratification, which might be wrongly captured by the Brewer and FTIR products assuming a fixed temperature (and pressure) profile. For forward calculations of those FTIR strategies without a simultaneous temperature fit, the temperature and pressure profiles are updated daily from the NCEP database, as previously mentioned, but they are

kept constant during the O$_3$ retrieval procedure. Regarding Brewer, no temperature or pressure dependence is considered in the operational data processing (Redondas et al., 2014; Rimmer et al., 2018). Particularly, the Brewer O$_3$ TCs are computed using the so-called effective O$_3$ cross sections throughout the atmosphere (Bass and Paur, 1985), corresponding to an O$_3$ effective height of 22 km and a fixed effective temperature of the O$_3$ layer of -45ºC. **These simplifications can produce systematic (seasonal dependence) and random errors (Redondas et al., 2014; Gröbner et al., 2021). In fact, at IZO the effective temperature and O$_3$ height significantly differ from the assumed values by Brewer processing in winter months, when the extreme RD values are overall observed (Figure 4 (c)).** Nevertheless, a more dedicated study would be desirable to deeply investigate the **causes** driving these anomalous values.

When analysing in detail the intercomparison results (Table 2), it is confirmed that, **first, the more refined set-ups using narrow micro-windows offer the best performance (especially 5MWs/5MWsT) independently of the treatment of the atmospheric temperature profile, and second, the effect of the simultaneous temperature fit on the FTIR O$_3$ quality depends on the instrumental stability**. The agreement between the FTIR and Brewer observations significantly worsens for the more unstable IFS 120M spectrometer when the temperature fit is included in the retrieval procedure (largest median bias and scatter, and least correlation for the 1999-2004 period). Opposite behaviour is documented for the IFS 120/5HR periods: the temperature retrieval consistently improves the precision and accuracy of all FTIR O$_3$ products by considerably reducing the dispersion and bias of the RD distributions. Thus, the best **performance is obtained by** those set-ups using narrow micro-windows, with a RD scatter of only ∼0.6-0.7% (it increases up to ∼0.8% for the broader region set-up) for the IFS 120/5HR instrument; while it is as high as 2% for the IFS 120M when the simultaneous temperature fit is carried out. These values perfectly agree with previous studies (e.g. Schneider et al., 2008a; García et al., 2012), and lie within the expected precision of both instruments (see Sections 2.2, and 3.2.2, and Appendix B). In fact, as shown in Appendix B, total statistical errors of ∼0.5-1.5% can be expected depending on the instrument status (i.e. the instrumental degradation and solar pointing errors). **Nonetheless, Table 2 also documents that the scatter found in RD is noticeably lower than that predicted when the temperature fit is not considered, especially for the IFS 120/5HR instrument (see M$_{TE}$ values). This fact could point out that sources of uncertainty partially cancel each other out, which is not fully reproduced by the theoretical error assessment, and/or the possible overestimation of the assumed temperature uncertainty. As also shown in Appendix B, reducing the latter would contribute to reconciling the experimental and theoretical results.** Note that the scatter values of the IFS 120/5HR spectrometer could be a conservative value for the precision of FTIR O$_3$ TC estimations, since they can be interpreted as the root-squares-sum of the precision of Brewer and FTIR instruments.

Regarding the systematic differences, a median bias of ∼3-5% is obtained. **Such discrepancies are consistent with previous studies (e.g. Schneider et al., 2008a; García et al., 2012; García et al., 2016) and mainly attributed to inconsistencies between infrared and ultraviolet spectroscopic parameters (e.g. Piquet-Varrault et al., 2005; Gratien et al., 2010; Drouin and Yu, 2017; Tyuterev et al., 2019). In fact, as recently presented by Gordon et al. (2022), the most recent release of HITRAN spectroscopic database (HITRAN 2020) improves the O$_3$ line intensities in the 1000 cm^{-1} spectral band by applying a scaling factor of 3%. This correction agrees well with our theoretical uncertainty estimations and the overestimation found for the FTIR products.**

Table 2. Summary of statistics for FTIR-Brewer comparison for the set-ups 1000/1000T, 4MWs/4MWsT, and 5MWs/5MWsT: median (M, in %) and standard deviation (σ, in %) of the relative differences, and Pearson correlation coefficient (R) of the direct comparison for the periods 1999-2004, 2005-May 2008 and June 2008-2018, and for the entire time series (1999-2018). **Shown are also the median of theoretical TPE (M_{TPE}), SE (M_{SE}), and TE (M_{TE}) uncertainties.** The number of coincident FTIR-Brewer measurements is 93, 185, and 1892 for the three periods, respectively, and 2170 for the whole dataset. **The strategies showing the best performance, in terms of smallest σ and M_{TE}, are highlighted in bold for each period.**

Set-up	1999-2004 M, σ, R, M_{TPE}, M_{SE}, M_{TE} [%], [%], - , [%], [%], [%]	2005-2008 M, σ, R, M_{TPE}, M_{SE}, M_{TE} [%], [%], - , [%], [%], [%]	2008-2018 M, σ, R, M_{TPE}, M_{SE}, M_{TE} [%], [%], - , [%], [%], [%]	1999-2018 M, σ, R, M_{TPE}, M_{SE}, M_{TE} [%], [%], - , [%], [%], [%]
1000	4.29, 1.38, 0.957, 1.85, 0.23, 1.87	4.47, 0.86, 0.970, 1.85, 0.23, 1.87	3.35, 0.83, 0.982, 1.83, 0.23, 1.85	3.46, 0.95, 0.975, 1.84, 0.23, 1.85
4MWs	4.28, 1.36, 0.959, 1.79, 0.19, 1.80	4.49, 0.85, 0.971, 1.78, 0.19, 1.80	3.34, 0.82, 0.982, 1.77, 0.19, 1.78	3.45, 0.93, 0.976, 1.77, 0.19, 1.78
5MWs	4.35, **1.32**, 0.962, 1.68, 0.16, 1.68	4.53, 0.82, 0.973, 1.66, 0.17, 1.67	3.41, 0.81, 0.983, 1.65, 0.17, 1.66	3.50, 0.91, 0.977, 1.65, 0.17, 1.66
1000T	4.83, 1.97, 0.926, 0.52, 0.24, 0.57	3.79, 0.82, 0.972, 0.51, 0.15, 0.53	3.04, 0.73, 0.986, 0.51, 0.16, 0.53	3.12, 0.90, 0.977, 0.51, 0.16, 0.53
4MWsT	4.84, 1.90, 0.934, 0.44, 0.21, 0.48	3.97, 0.66, 0.981, 0.42, 0.10, 0.44	3.32, 0.68, 0.988, 0.42, 0.12, 0.44	3.40, 0.83, 0.981, 0.42, 0.12, 0.44
5MWsT	4.81, 1.82, 0.940, 0.40, 0.22, **0.44**	4.15, **0.63**, 0.983, 0.39, 0.09, **0.40**	3.44, **0.67**, 0.988, 0.39, 0.11, **0.40**	3.53, **0.81**, 0.982, 0.39, 0.11, **0.40**

Similar conclusions can be reached in general when comparison is performed as a function of O_3 signatures in the slant path (Figure 5). The temperature fit improves the performance of the stable instrument and makes it worse for the more unstable instrument, independently of O_3 SC range covered at IZO. In addition, the bias between FTIR and Brewer data overall decreases **by ~1%** as O_3 SCs increase for all set-ups (Figure 5 (a), (c) and (e)). **This dependence can in part be accounted for the Brewer systematic uncertainties in the absolute calibration process, which are amplified for low O_3 SCs (up to 0.5%, Schneider et al. (2008a)).** However, for the more stable IFS 120/5HR period (Figure 5 (e)), the bias alters this behaviour for O_3 SCs beyond ~550 DU for set-ups using narrow micro-windows when the simultaneous temperature retrieval is considered. This issue could be attributed to inconsistencies in the spectroscopic parameters at higher wavenumbers, which gain importance as O_3 concentrations increase, and is in line with the theoretical systematic inconsistency found between the 1000T and 4MWsT/5MWsT set-ups (Section 3.2.2). However, the number of FTIR-Brewer coincidences at IZO is rather small for O_3 SCs greater than 550 DU (i.e. less than ~20% of Brewer data in the 1999-2018 period), therefore a more robust dataset would be recommendable to better understand what drives this different pattern.

As pointed out by the theoretical uncertainty analysis, statistical errors are expected to increase with O_3 SCs for all set-ups. This can be seen in the scatter of RD for the IFS 120/5HR periods (Figure 5 (d) and (f)) when the temperature fit is not applied **(i.e. the scatter of RD increases by 0.2% in the 2008-2018 period at larger O_3 SCs)**. However, the intercomparison results seem not to exhibit a similar dependence when the temperature retrieval is considered, as expected. **Including o not this fit can result in differences of 0.2% at larger O_3 SCs.** This could be attributed to an underestimation of the ILS and/or baseline errors in the theoretical assessment: the ILS contribution to total uncertainty budget decreases as O_3 SCs increase and becomes more important when the temperature fit is applied **(see Figure B1)**. The same behaviour is found for baseline error (data not shown). Hence, an increment in the assumed uncertainties for these two error sources, when the temperature takes part of
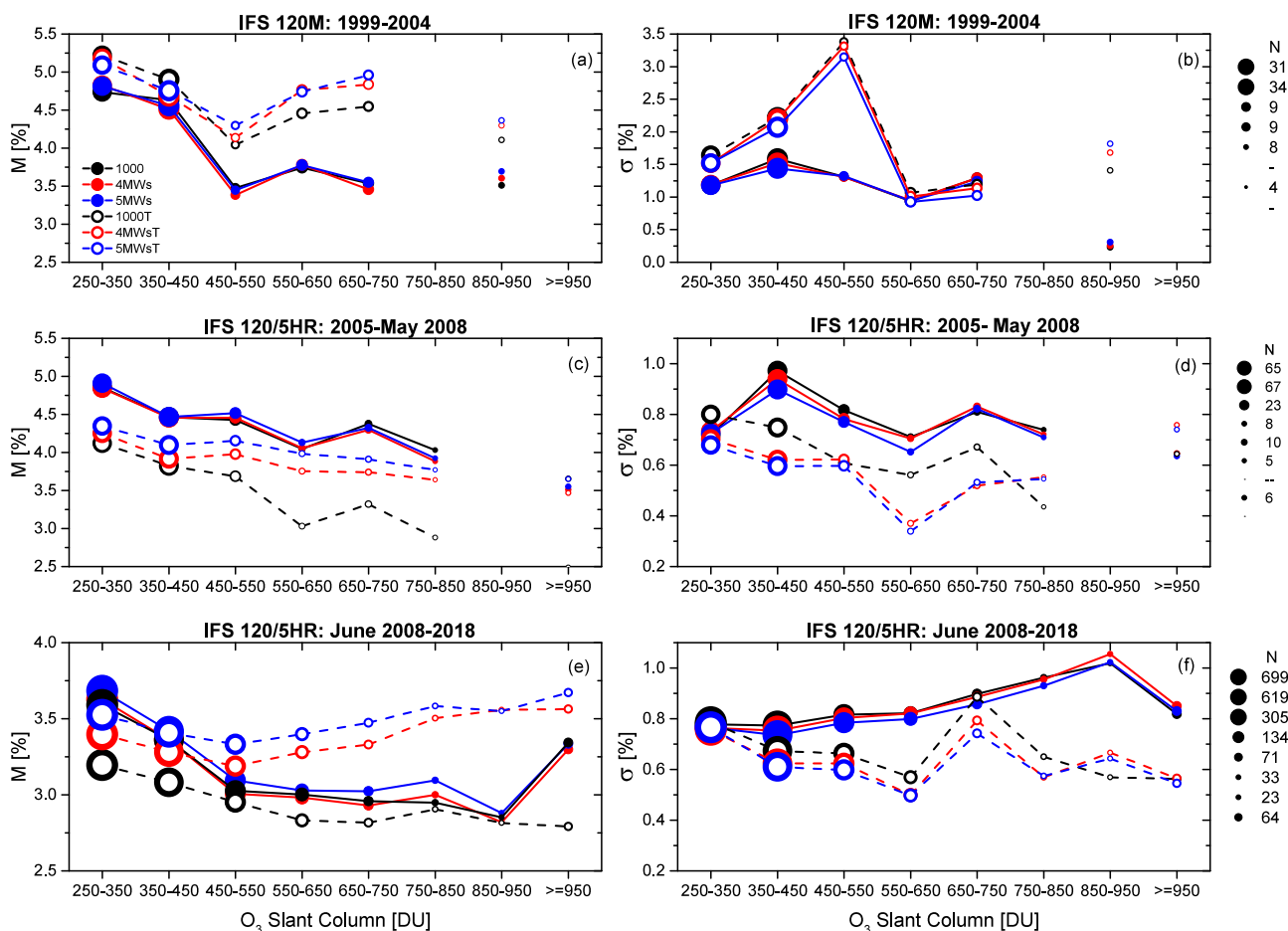
Figure 5. Median and standard deviation of relative differences RD (FTIR-Brewer) with respect to Brewer O_3 slant column [DU] for the periods 1999-2004, 2005-May 2008, and June 2008-2018. (a), (c), and (e) shows median RD (M, in %) values for the three periods, respectively, and (b), (d), and (f) the same, but for standard deviation of RD (σ, in %). Dotted area indicates the number of coincident FTIR-Brewer measurements for each O_3 SC interval (N), which are included in the legend of each subplot. For a better visualisation a scale factor of 3, 2, and 1 was applied to dotted area for the periods 1999-2004, 2005-May 2008, and June 2008-2018, respectively.

the retrieval procedure, could **reduce** partially discrepancies between the theoretical and experimental assessment. **Note that while 1000/1000T set-ups provide the most accurate O_3 TCs with respect to Brewer data for the whole O_3 SC range for**
355   **both instruments, the 5MWs/5MWsT offer the most precise O_3 TCs.** This result further corroborates that the broad region seems to be more sensitive to the negative cross-interference between the temperature retrieval and instrument status.

The long-term FTIR time series used in this study allows us to investigate the overall quality and long-term consistency of new products, but also the effects at different timescales. At a seasonal scale, the agreement between FTIR and Brewer is

excellent: the annual cycles are completely in phase with Pearson correlation coefficients greater than 0.99 for all retrieval strategies considered (Figure 6 (a) and (b)). **However, the bias between both techniques depends on O$_3$ amounts leading to a seasonal effect on RD, which is likely due to the fact that the Brewer and FTIR products exhibit different response to O$_3$ seasonal variations. On the one hand, the FTIR sensitivity is strongly anti-correlated with the O$_3$ SC annual cycle: the less the O$_3$ amounts, the less saturated the O$_3$ absorption lines. This results in minimum (maximum) DOFS in winter (spring/summer) (García et al., 2012). On the other hand, the different treatment of the atmospheric temperature and O$_3$ vertical distribution in the Brewer and FTIR data processing also generates seasonal artefacts, as stated above for the extreme RD values. In fact, including the temperature retrieval significantly modifies the RD seasonal patterns, as observed in Figure 6 (c) and (d).**
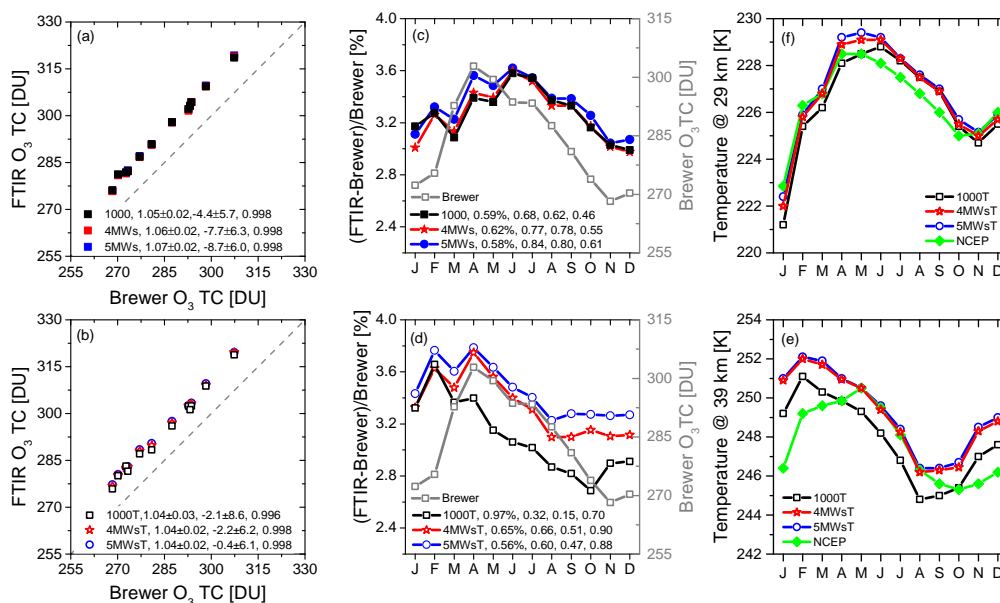
Figure 6. Summary of the FTIR-Brewer comparison at a seasonal scale for the 2009-2018 period. (a) and (b) scatter plots of the Brewer and FTIR O$_3$ TCs for the set-ups 1000/4MWs/5MWs and 1000T/4MWsT/5MWsT, respectively. (c) and (d) averaged annual cycle of Brewer O$_3$ TCs and RD for the set-ups 1000/4MWs/5MWs, and 1000T/4MWsT/5MWsT, respectively. (e) and (f) averaged annual cycle of the atmospheric temperature at 29 km and 39 km, respectively, retrieved from the set-ups 1000T, 4MWsT, and 5MWsT, as well as NCEP database. Legend in (a) and (b) displays the slope, offset and Pearson correlation coefficient of the least-square fits, and in (c) and (d) shows the amplitude of RD annual cycle (in %), and Pearson correlation coefficients between RD and Brewer O$_3$ TC annual cycles, and atmospheric temperature (at 29 km and 39 km) annual cycles, respectively.

For those approaches without a simultaneous temperature fit (Figure 6 (c)), the RD annual cycle seems to follow the typical O$_3$ TC seasonality at the subtropical latitudes: peak values in spring and minimum in autumn–winter, as a result of the joint effect of the annual shift in the height of subtropical tropopause, and annual cycle of the O$_3$ photochemical production associ-

ated to tropical insolation **(e.g. García et al., 2014; García et al., 2021)**. Hence, a significant correlation between the averaged RD and O_3 TC annual cycles for all set-ups is found, with Pearson correlation coefficients ranging from 0.68 to 0.84 for the 1000 and 5MWs strategies, respectively. This relationship drops to correlation values between 0.32 and 0.60 for the 1000T and 5MWsT set-ups, respectively. However, in return, a seasonal dependence on the upper–stratospheric temperature is detected

375 **(Figure 6 (f) displays, as an example, the averaged temperature annual cycle at 39 km from the NCEP database along with those retrieved from the FTIR set-ups)**. The correlation between the averaged annual cycles of the upper-stratospheric temperature and RD is ∼0.70 and ∼0.90 for the broad and narrow micro-window set-ups, respectively, including the temperature fit; while it is limited between 0.46 and 0.61 when the temperature retrieval is not considered. Note that a subtle relationship is found with the temperature in the middle or lower stratosphere (e.g. at 29 km in Figure 6 (e)). Additionally, it

380 has been found that the RD seasonal amplitudes are overall augmented by the temperature retrieval. The broad spectral region seems to be the most sensitive to this effect: **the RD peak-to-peak amplitude goes from 0.59% (1000) to 0.97% (1000T), while it is modified less than 0.05% for the 4MWs/5MWs set-ups.**

4.2 FTIR and ECC Ozone Vertical Profiles

In order to evaluate the influence of the six retrieval strategies on O_3 vertical distribution, Figure 7 displays the vertical profiles

385 of the relative differences between FTIR and ECC sondes for the three periods considered, while Table 3 summarises the comparison **for the O_3 layers that are sufficiently detectable well by the FTIR system, i.e., the partial column (PC) between 2.37–13 km, 12–23 km and 22–29 km (the DOFS for all these layers is typically larger than one)**. For this comparison, the approach suggested by Schneider et al. (2008b) and García et al. (2012) was followed, whereby the ECC sondes were corrected daily by comparing them to coincident Brewer data. By means of this correction, the quality and long-

390 term stability of the ECC sonde data can be significantly improved. In addition, the highly-resolved ECC profiles (x_{ECC}) were vertically-degraded ($\hat{x}_{ECC}$) applying the averaging kernels obtained in the FTIR O_3 retrieval procedure (Rodgers, 2000), as follows:

$$\hat{x}_{ECC} = \mathbf{A}(x_{ECC} - x_a) + x_a, \tag{1}$$

where x_a is the a-priori O_3 VMR profiles. **The ECC smoothing allows, on the one hand, the limited sensitivity of FTIR**

395 **data to be taken into account and, on the other hand, the effect of the different strategies on retrieved O_3 profiles to be directly assessed**. Note that, in order to homogenise the comparison, only the ECC sondes with continuous measurements up to 29 km have been considered. Beyond this altitude, the ECC data were completed using the a-priori profiles used in FTIR O_3 retrievals **for computing $\hat{x}_{ECC}$**. Finally, the temporal collocation window between FTIR and ECC sondes is extended to ± 3 hours around the sonde launch **(typically at 12 UT)** to ensure sufficient pairs for a robust comparison (N=272 in the 1999-2018

400 period).

The RD profiles show a strong vertical stratification, whereby the three independent layers detectable by the FTIR systems up to ∼30 km are clearly discernible (troposphere, UTLS, and middle stratosphere, recall Figure 3). Particularly, beyond the UTLS region, the influence of ILS uncertainties on the retrieved O_3 profiles is getting importance with altitude, since the full
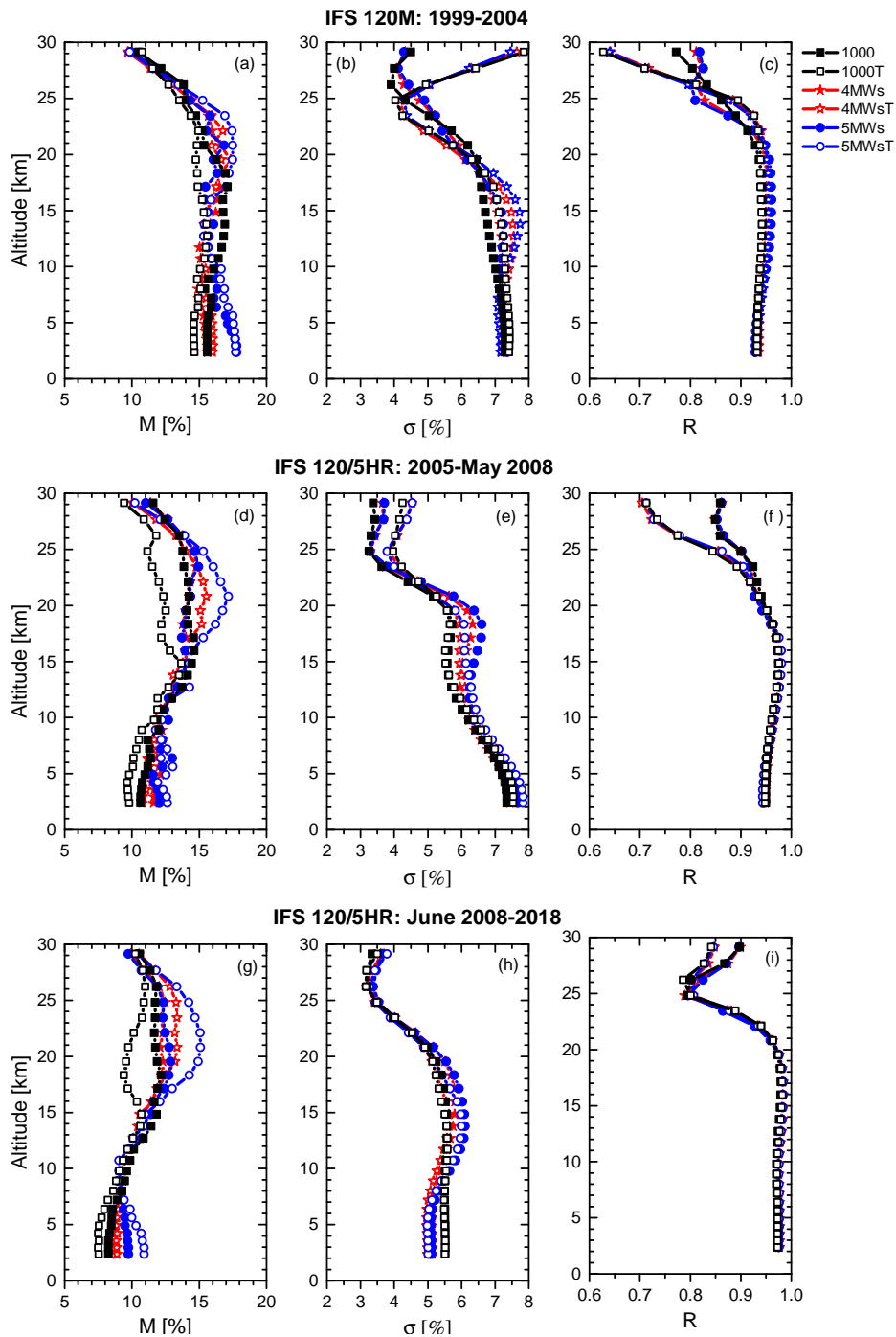
Figure 7. Summary of FTIR-smoothed ECC comparison for the periods 1999-2004, 2005-May 2008, and June 2008-2018. (a), (d), and (g) display the vertical profiles of median (M) RD (FTIR-ECC, in %) for the three periods, respectively. (b), (e), and (h) as for (a), (d), and (g), but for standard deviation of RD distributions (σ, in %). (c), (f), and (i) as for (a), (d), and (g), but for Pearson correlation coefficient. The number of coincident FTIR-ECC measurements is 56, 49, and 167 for the periods 1999-2004, 2005-May 2008, and June 2008-2018, respectively.

Table 3. Same as Table 2, but for FTIR-smoothed ECC comparison for the O_3 partial columns computed between 2.37-13 km, 12-23 km, and 22-29 km. The number of coincident FTIR-ECC measurements is 56, 49, and 167 for the three periods, respectively, and 272 for the whole dataset. **The strategies showing the best performance, in terms of smallest σ and M_{TE}, are highlighted in bold for each period.**

Set-up	1999-2004 $M, \sigma, R, M_{TPE}, M_{SE}, M_{TE}$ [%], [%], -, [%], [%], [%]	2005-2008 $M, \sigma, R, M_{TPE}, M_{SE}, M_{TE}$ [%], [%], -, [%], [%], [%]	2008-2018 $M, \sigma, R, M_{TPE}, M_{SE}, M_{TE}$ [%], [%], -, [%], [%], [%]	1999-2018 $M, \sigma, R, M_{TPE}, M_{SE}, M_{TE}$ [%], [%], -, [%], [%], [%]
FTIR-ECC at 2.37-13 km				
1000	15.86, 7.08, 0.934, 1.14, 6.34, 6.44	11.44, 6.58, 0.956, 1.09, 5.93, 6.03	9.08, 5.46, 0.970, 1.06, 5.68, 5.78	10.63, 6.61, 0.953, 1.07, 5.76, 5.86
4MWs	15.08, 7.11, 0.937, 1.26, 5.76, 5.91	12.08, **6.54**, 0.958, 1.28, 6.32, 5.48	9.38, 5.10, 0.974, 1.25, 5.17, 5.33	10.62, 6.46, 0.956, 1.25, 5.24, 5.39
5MWs	16.24, 7.09, 0.938, 1.01, 5.06, 5.16	12.30, 6.64, 0.957, 1.06, 4.75, 4.87	9.72, 5.13, 0.974, 1.02, 4.61, 4.72	10.89, 6.56, 0.956, 1.03, 4.66, 4.78
1000T	15.05, 7.30, 0.934, 0.79, 6.05, 6.10	10.39, 6.73, 0.954, 0.63, 5.64, 5.67	8.12, 5.45, 0.971, 0.62, 5.46, 5.50	10.00, 6.67, 0.953, 0.64, 5.53, 5.57
4MWsT	15.56, 7.22, 0.938, 0.91, 5.67, 5.74	11.56, 6.76, 0.957, 0.79, 5.23, 5.29	9.26, **4.94**, 0.975, 0.77, 5.10, 5.16	10.54, **6.36**, 0.958, 0.79, 5.16, 5.22
5MWsT	16.93, **7.05**, 0.940, 0.69, 4.99, **5.03**	12.76, 6.82, 0.956, 0.60, 4.68, **4.72**	10.11, 4.99, 0.976, 0.59, 4.53, **4.57**	11.20, 6.42, 0.958, 0.60, 4.59, **4.63**
FTIR-ECC at 12-23 km				
1000	17.30, 5.76, 0.914, 0.81, 2.08, 2.24	16.01, **4.54**, 0.946, 0.75, 1.75, 1.91	13.23, **4.70**, 0.959, 0.76, 1.71, 1.88	14.59, 5.23, 0.944, 0.76, 1.74, 1.91
4MWs	17.91, 5.58, 0.928, 0.50, 1.77, 1.84	15.99, 4.86, 0.943, 0.47, 1.53, 1.60	13.41, 4.82, 0.961, 0.47, 1.53, 1.61	14.79, 5.29, 0.947, 0.47, 1.55, 1.63
5MWs	17.89, **5.43**, 0.939, 0.52, 1.65, **1.73**	16.03, 4.94, 0.943, 0.59, 1.47, **1.59**	13.72, 4.81, 0.962, 0.59, 1.47, **1.59**	14.91, 5.21, 0.951, 0.58, 1.48, **1.60**
1000T	16.83, 5.64, 0.921, 0.66, 1.95, 2.06	15.19, 4.59, 0.945, 0.62, 1.63, 1.75	12.13, 4.75, 0.961, 0.62, 1.63, 1.74	13.72, 5.27, 0.946, 0.62, 1.65, 1.77
4MWsT	17.25, 5.61, 0.930, 0.48, 1.82, 1.88	16.44, 4.65, 0.947, 0.45, 1.58, 1.65	14.18, 4.73, 0.963, 0.44, 1.60, 1.66	15.30, 5.12, 0.951, 0.45, 1.62, 1.68
5MWsT	17.48, 5.72, 0.935, 0.38, 1.76, 1.81	16.91, 4.67, 0.948, 0.38, 1.56, 1.60	15.07, 4.77, 0.963, 0.37, 1.56, 1.61	16.02, **5.11**, 0.953, 0.37, 1.58, 1.62
FTIR-ECC at 22-29 km				
1000	15.92, 3.71, 0.820, 2.00, 2.87, 3.51	16.23, **2.87**, 0.888, 2.17, 2.58, 3.38	13.94, 3.17, 0.756, 2.08, 2.56, 3.30	14.76, 3.50, 0.779, 2.08, 2.59, 3.33
4MWs	16.09, 4.01, 0.793, 2.32, 2.71, 3.59	16.67, 2.88, 0.888, 2.66, 2.47, 3.63	14.16, 3.21, 0.767, 2.54, 2.53, 3.59	14.80, 3.64, 0.773, 2.53, 2.53, 3.59
5MWs	16.00, 4.10, 0.783, 2.55, 2.78, 3.79	16.43, 2.87, 0.892, 2.91, 2.55, 3.88	14.06, 3.23, 0.777, 2.80, 2.62, 3.84	14.79, 3.68, 0.776, 2.79, 2.63, 3.84
1000T	16.80, **3.54**, 0.866, 0.88, 3.10, 3.22	15.56, 3.12, 0.856, 0.78, 2.80, 2.91	13.88, 3.22, 0.735, 0.76, 2.77, 2.89	14.51, 3.55, 0.778, 0.77, 2.80, 2.90
4MWsT	16.28, 3.56, 0.864, 0.77, 3.01, 3.11	15.61, 3.36, 0.844, 0.67, 2.63, 2.71	14.45, **3.05**, 0.774, 0.67, 2.69, 2.77	14.96, **3.43**, 0.801, 0.68, 2.71, 2.79
5MWsT	16.31, 3.67, 0.856, 0.74, 2.94, **3.03**	15.28, 3.53, 0.829, 0.66, 2.59, **2.67**	14.47, 3.12, 0.775, 0.65, 2.65, **2.73**	15.06, 3.50, 0.798, 0.66, 2.67, **2.75**

width at half maximum of the narrow O_3 absorption lines and ILS function becomes to be comparable. For all set-ups and periods, the simultaneous temperature fit has turned out to worsen the agreement between FTIR and ECC sondes at higher altitudes (see standard deviation profiles in Figure 7 (b), (e), and (h)). However, as the instrument is better aligned and more stable over time, the effect of this cross-interference becomes less significant until no noticeable differences are observed for the 2008-2018 period. **For example, the scatter at 29 km for FTIR-ECC comparison only changes from 3.6% to 3.8% for the 5MWs and 5MWsT set-ups, respectively, for the 2008-2018 period, while the variation ranges between 4.3% and 7.5% for the 1999-2004 period.** In the UTLS region the best agreement is overall found for those set-ups without fitting temperature profile. This may indicate the prevalence of negative effect of the ILS uncertainties and measurement noise over the improvement attributed to the temperature fit. The same pattern is documented for the tropospheric O_3 concentrations even though the differences among retrieval strategies are not as significant as at higher altitudes. Note that these scatter values agree well with the expected uncertainty for ECC sondes ($\sim$5–15%) and with the FTIR theoretical error estimation (recall Section 3.2.2), as well as with previous works (Schneider et al., 2008b; García et al., 2012; Duflot et al., 2017, and references therein). As stated in these studies, the limited vertical sensitivity of the FTIR profiles could account for part of the dispersion observed between both datasets. Other sources of discrepancies might be the different observing geometries (i.e. the two measurement techniques sample different air masses).

The vertical stratification observed in the median RD profiles also differs between both FTIR instruments (Figure 7 (a), (d), and (g)). While all set-ups consistently show larger biases up to the UTLS region for the IFS 120M, the differences between the instruments are minimised beyond the middle stratosphere. The median bias varies from $\sim$17% to $\sim$10% at 5 km for the 5MWs/5MWsT in the 1999-2004 and 2008-2018 periods, respectively, while for the same configurations the bias is $\sim$10% at 29 km for both periods.

In summary, **considering the integrated PCs (less dependent on the FTIR vertical sensitivity) and the 2008-2018 period as reference (better instrumental alignment and more FTIR-ECC coincidences), the best performance is overall documented for the set-ups using narrow micro-windows and simultaneous temperature fit in the troposphere and stratosphere regions (Table 3). In the UTLS altitudes, where O_3 are particularly variable,** the broad micro-window strategy seems to provide the better agreement with respect to ECC data. Nevertheless, the differences among strategies lie within the respective error confidence intervals, thereby no robust conclusions can be reached. In addition, it is fair to admit that the ECC comparison only allows the FTIR vertical profiles to be analysed in detail up to $\sim$30 km. However, compensations among the ILS, temperature, measurement errors, and O_3 vertical distribution should occur at higher altitudes, which leads to the usage of narrow micro-windows (and temperature fit) clearly providing the best results in the integrated total columns, as documented by the FTIR-Brewer comparison. Unfortunately, ECC sondes do not usually reach altitudes higher than 30-34 km, thereby other measurement techniques, such as microwave or LIDAR O_3 profiles, would be of great use for further completing the quality assessment.

5   Summary and Conclusions

Accurate ozone (O_3) products are mandatory to monitor the evolution of the Earth's atmosphere system. In this context, the current paper has assessed the effect of using different retrieval strategies on the quality of O_3 products from ground-based FTIR spectrometry, with the aim of providing an improved O_3 retrieval that could be applied at any NDACC FTIR station. For this purpose, the high-quality NDACC FTIR measurements taken at the subtropical Izaña Observatory (IZO) between 1999 and 2018 has been utilised. The 20-year time series of O_3 observations has allowed us to assess, on the one hand, the quality and long-term consistency of the different FTIR O_3 products and, on the other hand, to evaluate the influence of instrumental status on the O_3 retrievals.

Quality of the FTIR O_3 products improves as the retrieval strategies become more refined by considering O_3 absorption lines in specific narrow micro-windows (between 991 and 1014 cm^{-1}) instead of using the **traditional** broad spectral region (between 1000 and 1005 cm^{-1}). Approaches using narrow micro-windows have theoretically and experimentally proven to be superior **due to the their** greater vertical sensitivity, smaller expected uncertainties, and better agreement with respect to independent data. The optimal selection of the spectral O_3 micro-windows can enhance the precision of FTIR O_3 TCs by ~0.1-0.2% with respect to the coincident **NDACC** Brewer observations taken as reference, **leading to a conservative precision of ~0.6-0.7% for the FTIR products**. But, at the same time, they have shown to be consistent with the standard NDACC set-up (i.e. no important biases were found between the different retrieval strategies).

In addition, independently of the O_3 absorption lines used, the simultaneous atmospheric temperature retrieval has been found to be a very useful tool for O_3 monitoring by ground-based NDACC FTIR systems. The scatter with respect to the Brewer data is found to be reduced up to ~0.2% when applying a temperature fit for those strategies also using narrow O_3 absorption lines. However, this improvement can only be reached provided the FTIR instrument is properly characterised and stable over time (e.g. IFS 120/5HR spectrometer). For more unstable instruments, such as the IFS 120M, the inclusion of atmospheric temperature fit in the O_3 retrieval procedure may not be recommendable, since it worsens the quality of FTIR O_3 products **due to the increase in** the cross-interference with instrumental performance. **The broad 1000 cm^{-1} region seems to be the most sensitive to this effect. Another fact that strongly distinguishes the broad and narrow set-ups is the presence of strong H_2O absorbing lines in the 1000 cm^{-1} region, which could be critical for humid FTIR sites if the H_2O cross-interference is not properly taken into account. The H_2O impact has been found to be reduced by using a two-step retrieval strategy and a simultaneous temperature fit.**

The effect of the most influential settings on FTIR O_3 retrieval procedure has been examined in this paper. Nevertheless, there is great potential **for further improvement** the precision and accuracy of FTIR O_3 products, as well as their harmonisation within the NDACC IRWG community **(comprising instruments and retrieval strategies). Additional efforts could be made with the treatment of the instrumental response, through the evaluation of the Instrumental Line Shape function in a consistent manner, given its important effects on O_3 retrievals. In addition, testing the proposed O_3 set-ups at different NDACC FTIR stations (under different humidity conditions, latitudes, altitudes, etc.) would indeed motivate the NADCC FTIR community to revise the standard O_3 retrieval strategy.** An improved O_3 monitoring could help to es-

470   timate more precisely the small expected signal of recovery or decline of O_3 concentrations, both for integrated total columns and vertical distributions, at a global scale. This is particularly challenging in those regions where O_3 concentrations are less variable, such as at the tropical and subtropical latitudes. Furthermore, new opportunities would show up to better understand the different and outstanding O_3 impacts on Earth climate system, improving their representation in the current global climate models and, thus, the knowledge of their long-term evolution.

Appendix A: Water Vapour Treatment

475

This appendix addresses the impact of the treatment of H_2O on O_3 retrievals for all O_3 set-ups comparing the one-step and two-step retrieval strategies, where:

– One-step approach refers to simultaneously retrieve the H_2O and O_3 profiles, using a Tikhonov-Philips slope constraint for both gases, so that the microwindow of 896.4–896.6 cm^{-1} is added for a better H_2O determination

480   (as done at the NDACC FTIR Lauder and Wollongong sites in Vigouroux et al. (2015)).

– Two-step approach refers to the strategy followed in the current paper and explained in detail in Section 3.1, where the H_2O a priori profiles, previously retrieved in dedicated H_2O microwindows for each spectrum, are then scaled in the O_3 retrieval.

Figure A1 illustrates the theoretical assessment of the H_2O cross-interference for both retrieval strategies (García

485   et al., 2014), where it can be seen that the H_2O interfering error is noticeable, but not critical given the especially dry conditions at IZO (less than 0.06 %) (García et al., 2021). Nevertheless, it has been found that the H_2O interference strongly depends on the micro-windows used for the O_3 retrievals (the higher impact is observed for the 1000 spectral region as expected from Figure 2), as well as on the treatment of the atmospheric temperature profile. One-step and two-step approaches provide consistent results when the simultaneous temperature fit is not included. Nonetheless,

490   provided the documented improvement of the temperature retrieval is pursued, the two-step strategy ought to be used. In this sense, the two-step strategy drastically reduces the H_2O interfering error for those set-ups using narrow micro-windows when the simultaneous temperature fit is included (4MWsT/5MWsT), leading to expected errors on the O_3 total columns smaller than 0.01 %. The H_2O interfering effect also drops for the 1000 spectral region, but to a lesser extent, given the presence of important H_2O absorption lines in that region (recall Figure 2). These results confirm that

495   using narrow O_3 absorption lines, along with a two-step inversion strategy to estimate the H_2O profile in a dedicated H_2O profile fit prior to the O_3 retrievals, results in a superior O_3 strategy. This would be especially recommendable for FTIR stations located in humid environments.

The best performance of the two-step retrieval strategy is also corroborated by comparing to Brewer observations (Figure A1 (c) and (d)). The preliminary H_2O retrievals slightly enhance the quality of the O_3 retrievals with respect to

500   the one-step strategy for all periods and set-ups. The more unstable the instrument, the greater the effect. It is worth
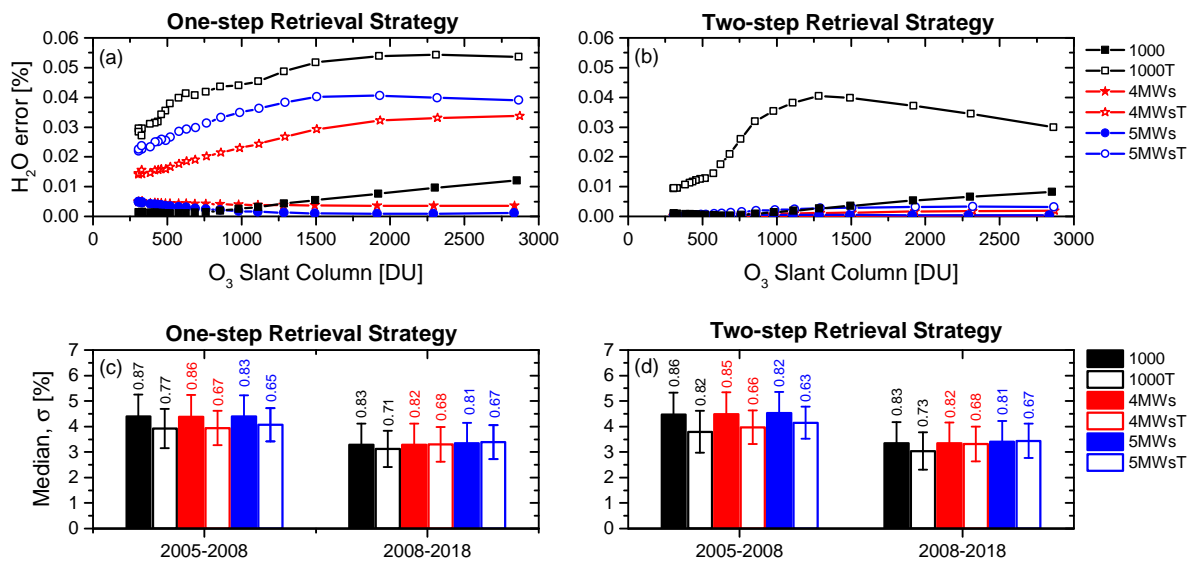
Figure A1. Summary of the impact of the treatment of H$_2$O on O$_3$ retrievals for all O$_3$ set-ups. (a) and (b) H$_2$O cross-interference error on O$_3$ total columns [%] using the one-step and two-step retrieval strategies, respectively, as a function of O$_3$ slant column [DU] for the measurements of Figure 3. (c) and (d) statistics for the FTIR-Brewer relative differences using the one-step and two-step retrieval strategies, respectively, for the periods 2005-May 2008 and June 2008-2018. Shown median (M, in %) and standard deviation values (σ, as error bars and text in %).

highlighting the fact that the differences found between the two strategies are in excellent agreement with the estimated H$_2$O interfering error values (Figure A1 (a) and (b)).

Appendix B: Uncertainty Analysis

Theoretical uncertainties of FTIR products can be estimated by following the formalism detailed by Rodgers (2000), which includes the effect of smoothing error **(SE)**, spectral measurement noise, and different model parameter sources. The difference between the retrieved state, $\hat{x}$, and real state, x, can therefore be written as a linear combination of the a-priori state, x_a, real and estimated model parameters, p and $\hat{p}$ respectively, and measurement noise ϵ:

$$(\hat{x} - x) = (\mathbf{A} - \mathbf{I})(x - x_a) + \mathbf{G}\mathbf{K}_p(p - \hat{p}) + \mathbf{G}\epsilon, \tag{B1}$$

where $\mathbf{G}$ represents the gain matrix, $\mathbf{K}_p$ the sensitivity matrix to the model parameters, $\mathbf{I}$ the identify matrix, and $\mathbf{A}$ the averaging kernel matrix.

The first term of Eq. (B1) refers to smoothing error, which has been calculated as $(\mathbf{A} - \mathbf{I})\mathbf{S}_{\mathbf{aO_3}}(\mathbf{A} - \mathbf{I})^T$. The $\mathbf{S}_{\mathbf{aO_3}}$ matrix is the O$_3$ a-priori covariance matrix, which has been computed in this work from the 1999-2018 ECC sonde climatology at IZO

according to Schneider and Hase (2008). Note that ECC sondes usually burst between 30 and 34 km, hence this climatology was completed beyond 31 km by using the WACCM-version 6 simulations for subtropical latitudes.

515   The error covariance matrix for measurement noise ($\mathbf{S_{x,\epsilon}}$) is analytically calculated by

$$\mathbf{S_{x,\epsilon}} = \mathbf{GS_{y,\epsilon}G}^T, \tag{B2}$$

where $\mathbf{S_{y,\epsilon}}$ is the covariance matrix for measurement noise in the measurement.

The error contribution of the model parameters $\boldsymbol{p}$ can be analytically estimated through the respective error covariance matrices $\mathbf{S_{x,p}}$:

520    $$\mathbf{S_{x,p}} = \mathbf{GK_p S_p K_p}^T \mathbf{G}^T, \tag{B3}$$

where $\mathbf{S_p}$ is the covariance matrix of the uncertainties $\mathbf{\Delta p}$. In the current paper, $\mathbf{S_p}$ is estimated considering error sources, values, and partitioning between random and systematic contributions listed in Table B1. **They have been identified as the typical error sources and values affecting the different FTIR products (e.g., Hase, 2007; Schneider and Hase, 2008; García et al., 2016; Gordon et al., 2022, and references therein). The statistical and systematic contributions of total**
525   **parameter errors (TPE, displayed in Figure 3) are then calculated as the square root sum of the squares of all statistical and systematic errors considered, respectively.** Note that measurement noise is considered as purely random, while spectroscopic parameters are purely systematic.

Table B1. Error sources and assumed values used in the theoretical uncertainty estimation. Last column shows the contribution of statistical (ST) and systematic (SY) sources to total error. Chann.: Channeling; MEA: Modulation Efficiency Amplitude; PE: Phase Error; Int.: Intensity; ν-scale: Spectral position; S: Intensity parameter; ν: Pressure broadening parameter.

Error Source	Error	ST/SY
Baseline (Chann. and Offset)	0.1% and 0.1%	50/50
MEA and PE (ILS)	1% and 0.01 rad	50/50
Temperature profile	2 K (<50 km)	70/30
	5 K (>50 km)	70/30
Line of Sight (LOS)	0.001 rad	90/10
Solar Lines (Int. and ν-scale)	1% and 10^{-6}	80/20
Spectroscopy	5% for S and 5% ν	0/100

As shown in Figure B1, when considering statistical error sources, the main contributors are the atmospheric temperature profile for set-ups without temperature fit (error values between 2.0-2.5%), and possible mis-alignments of the
530   **FTIR's solar tracker, given by the LOS, for all set-ups (error values up to 1.0% at larger O_3 concentrations). By contrast, O_3 TCs are almost insensitive to errors due to ILS uncertainties and measurement noise (error values smaller than 0.1-0.2%). For the set-ups with a simultaneous temperature retrieval, this fit generates a significant cross-interference**
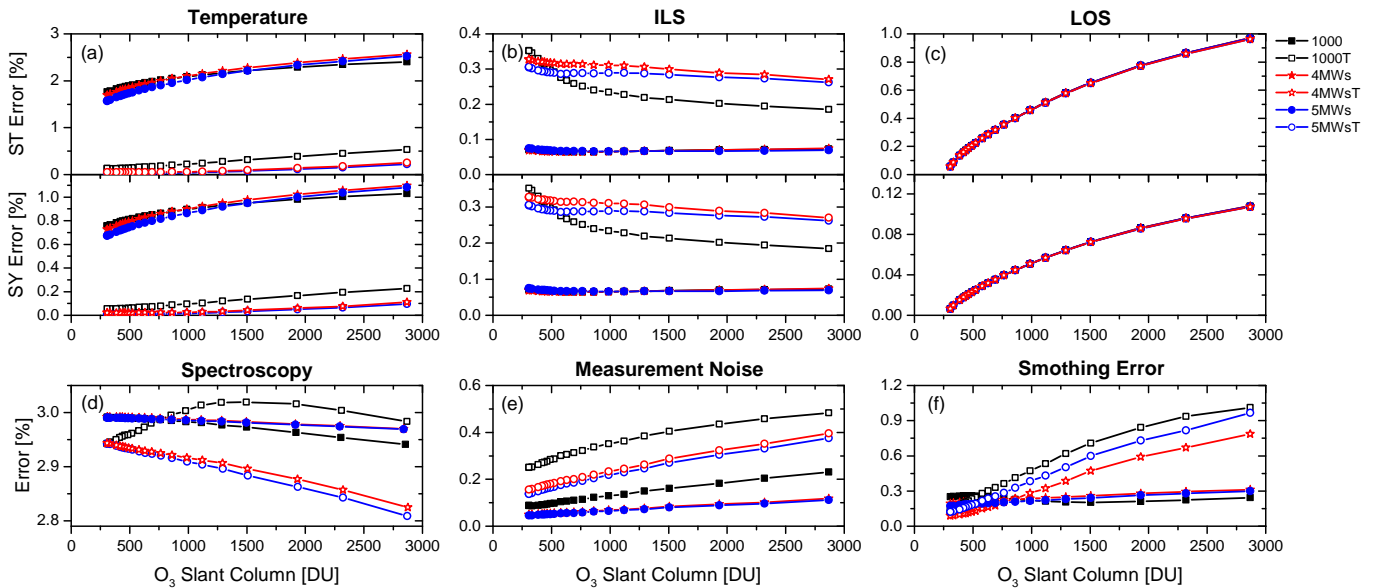
Figure B1. Estimated statistical (ST) and systematic (SY) errors [%] for O_3 TCs retrieved from all set-ups for different error sources ((a) atmospheric temperature profile, (b) ILS function, (c) LOS, (d) spectroscopic parameters, (e) measurement noise, and (f) smoothing error) as a function of O_3 slant column [DU] for the measurements of Figure 3.

with the ILS function, leading to an increment of the ILS error contribution (Schneider and Hase, 2008; García et al., 2012), but also with the measurement noise and smoothing error (especially for 1000T set-up). However, in return, the
535   temperature error contribution is nearly eliminated, leading to total ST budget considerably improves by ~1%. It is worth highlighting that the negative cross-interference between the temperature retrieval and SE is significant for O_3 SCs beyond ~500 DU due to the loss of FTIR vertical sensitivity as O_3 SCs increase (this threshold encompasses less than 20% of the O_3 observations at IZO). For the typical O_3 concentrations observed at IZO, SE is improved by temperature fit and smaller for the 4MWsT/5MWsT set-ups. This result is corroborated by the comparison to coincident
540   Brewer observations, as shown in Table 2.

     Note that in the current work the measurement noise depends on the quality of the fitted spectra Hase et al. (2004). Thereby, large values of measurement noise error are observed, where the fit residuals are slightly larger (especially in the broad spectral region, see Figure B1).

     Table B1 lists the uncertainty values representative of the IFS 120/HR instrument in the period 2005-2008. However, the error
545   sources associated to instrument status (i.e. ILS function, solar pointing, and measurement noise) can be different depending on **FTIR spectrometer's quality and stability**. In order to account for this fact, Figure B2 summarises the effect of the different sets of error values on O_3 TCs for the measurement day of Figure B1. Note that this figure only includes the error estimations for different ILS and LOS configurations (keeping the temperature profile and measurement errors fixed), and for the set-ups
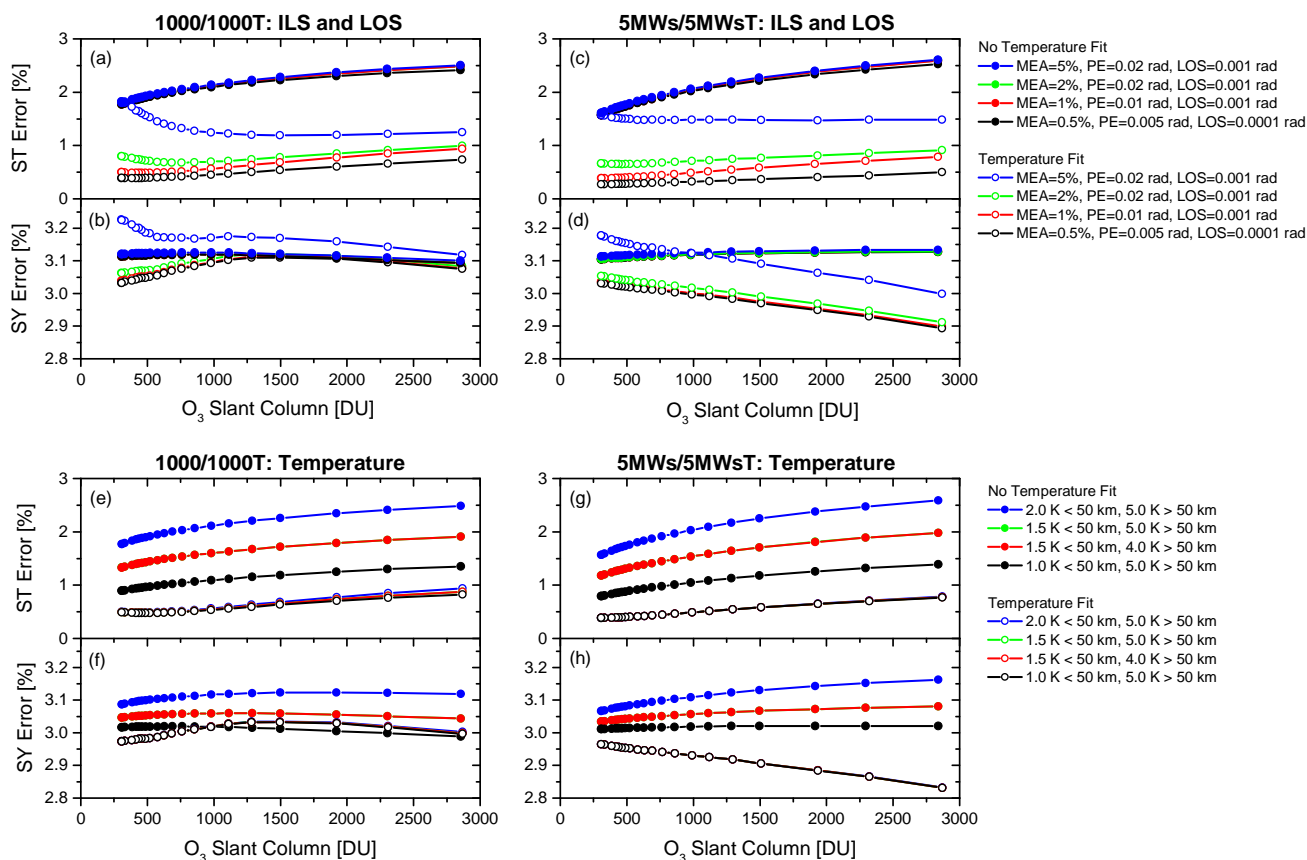
Figure B2. Estimated statistical (ST) and systematic (SY) TPE [%] for O_3 TCs retrieved from the set-ups 1000/1000T (a, b, e and f) and 5MWs/5MWsT (c, d, g and h) for different error configurations of the ILS function, LOS and atmospheric temperature profile as a function of O_3 slant column [DU] for the measurements of Figure 3.

1000/1000T and 5MWs/5MWsT set-ups (the 4MWs/4MWsT error estimations are quite similar to the 5MWs/5MWsT ones,
550 therefore they have been omitted for simplicity).

The effect of the different error sets is only noticeable when the temperature profile is simultaneously estimated with O_3 concentrations likely due to the interference between the ILS function and temperature retrieval. Under these conditions, statistical **TPE** values range from ~0.5% for uncertainties of 0.5% in the MEA and of 0.005 rad in the PE (representative of the well-aligned IFS 120/5HR instrument for the period 2008-2018) up to ~1.5% for an MEA error of 5% and PE of 0.02 rad
555 (representative of the unstable IFS 120M spectrometer). These estimated uncertainties reproduce well the changes observed in FTIR O_3 quality for the different periods when comparing to Brewer observations (**see** Table 2). The cross-interference between the temperature fit and other error sources is also evident for **systematic contributions**, especially for the worst scenario of

ILS degradation (MEA uncertainty values of 5%). Note that the inconsistency for the 1000T set-up is also observed for the different ILS set errors, corroborating the findings discussed in Section 3.2.2.

560 *Data availability.* The FTIR and Brewer data are available by request from the corresponding authors, while the ECC ozone sondes are available from the NDACC archive (www.ndaccdemo.org/).

Author contributions. O.G. and E.S. designed and wrote the structure and methodology of the current paper, and computed the calculations required. M.S., F.H., and T.B. participated in the retrieval analysis. F.H. is the author of LINEFIT and PROFFIT codes. O.G., M.S. E.S., and E.S. taken the routine FTIR measurements, and performed the maintenance and quality-control of the FTIR instruments. A.R., S.F., and 565 V.C. are responsible of maintenance and quality-control of the Brewer spectrometers, as well as of estimating the NDACC Brewer ozone observations. C.T. and N.P. are in charge of the ozone sonde programme at Izaña Observatory. Finally, all authors discussed the results and contributed to the final paper.

Competing interests. The authors declare no conflict of interest.

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