

Dear Referee#2,

We would like to thank your suggestions in order to improve our manuscript, which are fully addressed below. Your comments appear in bold.

Best regards,
Omaira García et al.

A) Specific comments:

Section 1: What do you mean exactly by ozone "Programme"?

There was a mistake with this term throughout the manuscript. We meant the different divisions or departments related to ozone activities at the Izaña Observatory: "Ozone Program", "FTIR Program" and "ECC and in-situ surface Program". These terms have been changed in the revised manuscript.

Section 2.1 (p 3435 line 3): Are there any references about the comparison between the two FTIR measurements?

There is no a specific paper addressing the comparison between the IFS 120M and IFS 120/5 HR at the Izaña station. Nonetheless, this intercomparison for some atmospheric gases has been performed in previous works. For example, Sepúlveda et al. [2012] found that for the methane total column at Izaña the relative differences between the two spectrometers are less than 0.5% ($\pm 1\sigma$), while for the water vapour amounts are less than 1% (Matthias Schneider, personal communication). In our work, we document differences less than 2.5% for the ozone partial columns.

In the literature there are some studies comparing FTIR spectrometers at other sites, showing differences typically of 1% or less for different atmospheric gases (e.g., ozone, methane, carbon dioxide, nitrous oxide, water vapour...) [Meier et al., 2005; Sussmann et al., 2009; Messerschmidt et al., 2010].

Section 2.1 (p 3435 line 9): Since this paper is for technical journal, you may want to add some more instrumental details about the instrument (FOV, ILS, filters, numbers of scans, detectors, etc...) or add a reference about those details.

Following the referee's suggestions, some technical details about the FTIR instrument have been included in section 2.1 of the revised manuscript (see text below).

"For NDACC, the solar absorption spectra are measured in the mid-infrared spectral region ($740\text{--}4250\text{ cm}^{-1}$, corresponding to $13.5\text{--}2.4\text{ }\mu\text{m}$), which is covered by six individual measurements applying different filters in order to achieve an optimal signal to noise ratio. In this spectral region the FTIR spectra are recorded using a potassium bromide (KBr) beamsplitter, whereby two liquid nitrogen-cooled detectors are applied: a mercury cadmium telluride (MCT) for wavenumbers below 1850 cm^{-1} and an indium antimonide photodiode (InSb) for higher wavenumbers. For operational ozone measurements the FTIR spectra covering the 1000 cm^{-1} region were measured with an aperture of 1.5 mm, which corresponds to field of view of only 0.2° . Therefore, it only analyses sunlight coming from the center of the solar disc (diameter of 0.5°).

In order to increase the signal to noise ratio several scans, with a high spectral resolution of 0.005 cm^{-1} (maximum optical path difference, OPD_{max} , of 180 cm), are co-added (8 for the ozone measurements). Thereby, the measurement of one spectrum takes about 10 minutes. At Izaña the FTIR spectra are measured on two or three days per week. "

Section 3.1 (p 3436 line 12): Why do you perform retrievals on a logarithmic scale? What are the advantages compared to a linear one?

The ozone amounts around the tropopause are highly variable. Under these conditions a logarithmic scale inversion is superior to a linear scale inversion [Schneider et al., 2008, and references herein]. In the troposphere and middle stratosphere, where the variabilities are smaller, normal and log-normal distributions are very similar and the application of a linear or a logarithmic scale does not significantly affect the result. Furthermore, only the inversion on a logarithmic scale allows for a constraint against ratio profiles, i.e., an optimal estimation of isotopologue ratio profiles of $^{50}\text{O}_3/^{48}\text{O}_3$ [Schneider et al., 2006]. The isotopologue ratio R , such as $R=[^{50}\text{O}_3]/[^{48}\text{O}_3]$ where $[X]$ signifies the volume mixing ratio of X , are typically reported relative to a standard ratio R_0 (please refer to Johnson et al., 2000 for more details):

$$\delta[\text{‰}] = 1000\text{‰} \times (R/R_0 - 1)$$

Section 3.1 (p 3437 line 7): Why do you make the assumption of heavy ozone enrichment of 100%? Can you explain?

As mentioned in section 3.1, the ozone retrieval strategy used in this work retrieves the different ozone isotopologues on a logarithmic scale, which allows for making a constraint on isotopologue ratio profiles. As a priori for the typical ozone isotopologue ratio profiles and their covariances we use the typical values reported in the literature [Johnson et al., 2000; Mauersberger et al., 2001]. They found average total enrichments of about 100‰ for $^{50}\text{O}_3$ and $^{49}\text{O}_3$. This value is used in this work. Note that there was a mistake in the manuscript in the percentage of ozone enrichment assumed. We considered 100‰, i.e., 10% of mean variation as a priori for the ozone isotopologue ratios throughout the atmosphere, and not 100% as appears in the manuscript.

Section 3.2 (p 3438 line 2): In figure 2, Avk (8-18 km) in setup C seems negative compared to setup A and B. What is the effect of this on retrieved ozone concentrations?

The ozone concentrations are retrieved on a logarithmic scale, thereby figure 2 of manuscript shows the columns of averaging kernels (avks) expressed as $\ln[\text{ozone}]$ avks. The columns of avks give the response of the retrieval to a perturbation in the state vector. Therefore, the negative values at a certain level indicate an anti-correlation between the response of the FTIR system at the level where is caused the perturbation and the levels where the avks values are negative. Please note that logarithm scale admits negative values of volume mixing ratio profiles.

Section 3.2 (p 3438 line 10): You observe some annual cycle in the dof time series, why does dof vary throughout the year?

The degree of freedom for signal (dof) mainly depends on the ozone absorption signature (ozone slant column). We simulated two spectra with the same settings for the ozone inversion and the same ozone amount in the slant path (i.e., same absorption signature), but different observing geometry (i.e., different solar zenith angle). This means that for the two situations the ozone total column amounts are different. The retrieval of both spectra reproduces these different ozone column amounts, but yields the same total dofs. The dofs is strongly anti-correlated with the ozone slant column amounts (see Figure 1).

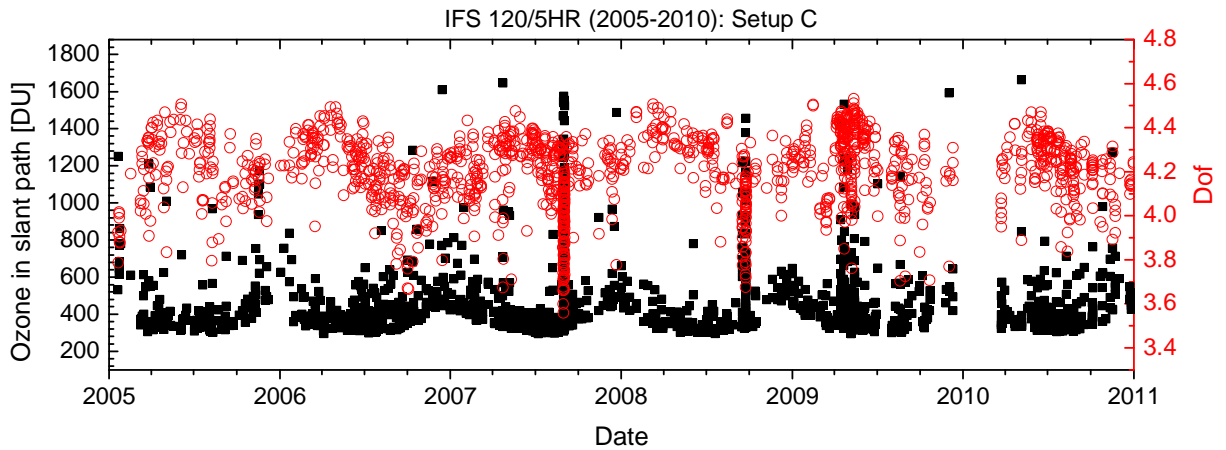


Figure 1. Time series of the ozone amount in the slant path [DU] (black squares) and of total dof (red circles) for the setup C between 2005 and 2010 (IFS 120/5 HR).

Section 3.3, Table 2: You say that Av_k (A) is almost equal to Av_k (B), which is the reason to exclude Av_k (A) from Figure 1. But considering the difference in the value of the dof in Table 2, you should probably add a comment about these differences in this section.

The shape of av_k s (setup A) is quite similar to av_k s (setup B) as we can observe in Figure 2, but not the absolute values. Hence the dofs for setup B are larger than setup A. The Figure 2 of the manuscript has been changed by the following one, including the av_k s for setup A in order to get a better comparison among setups.

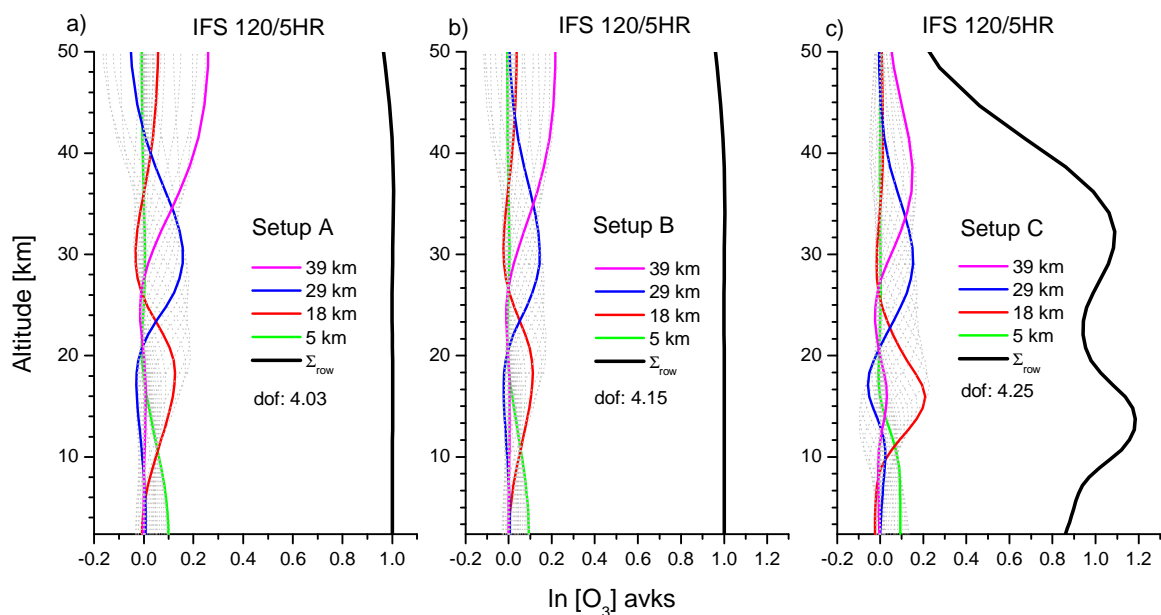


Figure 2. FTIR averaging kernels, av_k s, for retrieved ozone values using the setup A (a), setup B (b) and setup C (c), expressed as $\ln[O_3]$, for the Izaña spectrometer 120/5HR. Σ_{row} (black line) is the total sensitivity of FTIR system and dof is the degrees of freedom for signal.

Section 3.3 Figure 4: Baseline error profiles do not have the same pattern for A, B and C. Can you explain why?

The vertical sensitivity of the FTIR system varies depending on setup applied for retrieving the ozone partial columns, as observed in Figure 2. Therefore, the response to any perturbation or error does not show the same

vertical pattern for all setups. Different vertical profiles are also observed for other error sources, such as temperature and ILS (instrumental line shape).

Section 3.3 (p 3440 line 2): Temperature retrievals are important for accuracy of ozone data. This has already been demonstrated in Schneider, M and Hase, F (2008), you could add this reference here.

The reference of Schneider and Hase [2008] has been included in section 3.3 of the manuscript.

Section 3.4: What affects modulation efficiency and phase error over time?

There are several issues affecting the instrumental line shape (ILS) of a FTIR instrument over time. For example at Izaña, we detected a drift in the modulation efficiency time series due to the wear off of mechanical parts of the scanner pads at the end of 2007. These parts were replaced by new ones and the IFS 120/5HR was re-aligned, showing a jump in the modulation efficiency time series at June 2008 (see Figure 5 of manuscript).

Section 4: The introduction of this section is almost a repetition of the general introduction. You may make it more concise.

The introduction of section 4 has been slightly modified in the revised manuscript (see text below):

“Before assessing annual cycles and trends it is very important to check the consistency of the ozone time series. In this section, we use the coincident measurements of total ozone column from Brewer spectrometers and surface ozone from in-situ analysers for empirically documenting the quality and long-term stability of the ECC sonde dataset.”

Conclusion: You might add some perspectives and future works of this study.

Analysing time series of coincident measurements provides more insights into accurate instrumental drift than that obtained from the individual ozone trends. The error sources and how they can affect the estimated ozone trends can be examined in detail. For example, a regular ILS monitoring, applying low pressure gas cell measurements, is very important for FTIR trend studies, because it avoids artificial trends due to drifts in the ILS. Furthermore, we think that a simultaneous temperature retrieval is important, since it can significantly reduce the risk of artificial trends caused by possible drifts in the temperature uncertainty, thereby theoretically increases the reliability of the FTIR trends. In our study we observe that the temperature retrieval modifies the estimated trends but that the respective modifications remain with the trends' uncertainties. Using a realistic constraint instead of an ad-hoc constraint does not significantly affect the observed trends. The realistic constraint is important for reproducing the large day-to-day variability (see comparisons in Sect. 5), but it does not significantly affect the estimated trends. Therefore, the continuous intercomparison of measurement techniques over time is important to provide more confidence to the FTIR results.

B) Technical comments:

- p 3433 line 11: add a coma after "2100".

- p 3433 line 26: "since 1999" may be placed at the end of the sentence.

- p 3434 line 1: Izaña Observatory and Its Ozone Programme is capitalized so it should also be in the title of section 2 and the same at line 11 and 22 for the word Programme (as well as p 3441 line 22).

- p 3434 line 20: the "p" of programme should be capitalized.
- p 3434 line 25: add a coma after "January 2005".
- p 3435 line 4: delete the word "network" after NDACC as it is repetitive.
- p 3435 line 9: "maximum Optical Path Difference".
- p 3438 line 28: "Line Of Sight".
- p 3445 line 22: repetition of the word "small".
- p 3449 line 15: "19990-2010" should be 1999-2010.
- Table 1: define the word "Tfe".
- Figure 6: add in the caption that it is about setup C.
- Figure 12: define "/10a" in the caption.

All technical comments have been corrected in the manuscript according to Referee's suggestions.

References:

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