

Black: referee's comments green: authors' answers

First of all, we want to thank the referee 1 for the detailed analysis of our paper.

For the details, please look into the paper with keeping track of changes.

The manuscript “Tropospheric and stratospheric NO retrieved from ground-based FTIR measurements” by Zhou et al presents findings in the retrieval of NO using ground-based solar absorption FTIR at two sites, Xianghe (polluted) and Mado (background/pristine), contrasting the retrieval sensitivity. The work presented fits well within the scope of this journal. Below I have a short list of comments/suggestions that the authors may want to consider for the final version.

Major comments

1. I find that the manuscript lacks sufficiently novel findings in the retrieval strategy. As authors mentioned in the introduction, until now, there are few studies focusing on FTIR NO retrieval and past studies have shown little sensitivity in the troposphere. However, in this work authors show results of a single retrieval strategy, i.e, a single micro-window of NO₂ has been adapted from past studies, e.g., Notholt et al. (1995). Since the manuscript tries to show the retrieval of NO in the troposphere I was expecting to see a thorough description of optimized windows and retrieval parameters, instead authors only mentioned what was included but do not show an optimization. Are there more micro-windows appropriate for NO?. If there are no other suitable windows for NO I highly suggest mentioning it. In general, a description of the optimization is missing.

Thanks for the suggestion. Before finalizing the retrieval window, we have looked at all the NO absorption lines (Figure A1). The NO lines at 1900 cm⁻¹ is selected because of the strongest line intensity and they are less affected by H₂O. The observed FTIR spectra (Figure 2 in the AMTD paper) show that the line intensity on the left side of 1900 cm⁻¹ (1850 - 1900) is less than that on the right side of 1900 cm⁻¹ (1900 - 1950), because of the H₂O absorption and the optical filter (NDACC Filter 0). As a result, we focus on the windows in the spectral range between 1900 and 1950 cm⁻¹. In fact, only the spectra around 1900 and 1930 cm⁻¹ are less affected by H₂O. We tested several windows around 1930 cm⁻¹, and compared the retrievals with that from 1900 cm⁻¹ window. It is found that the uncertainties of the retrievals from 1930 cm⁻¹ region are much larger than that of the retrieval from 1900 cm⁻¹, because the line intensities around 1930 cm⁻¹ are 5-10 times less than at 1900 cm⁻¹. Therefore, in the end, we choose the 2 strongest NO lines around 1900 cm⁻¹ as the retrieval window, which are the same as the previous studies (Notholt et al., 1995 and Wiacek et al. 2006).

We have added more information in the revised version.

“The strong NO absorption lines are between 1800 and 1950 cm⁻¹. In order to select strong NO lines and to reduce the interference from H₂O, several windows have been tested. We find that the NO absorption lines at 1900 cm⁻¹ are the optimal choice for ground-based FTIR NO retrieval at Xianghe and Mado, which have been used in the previous studies (Notholt et al., 1995 and Wiacek et al. 2006).”

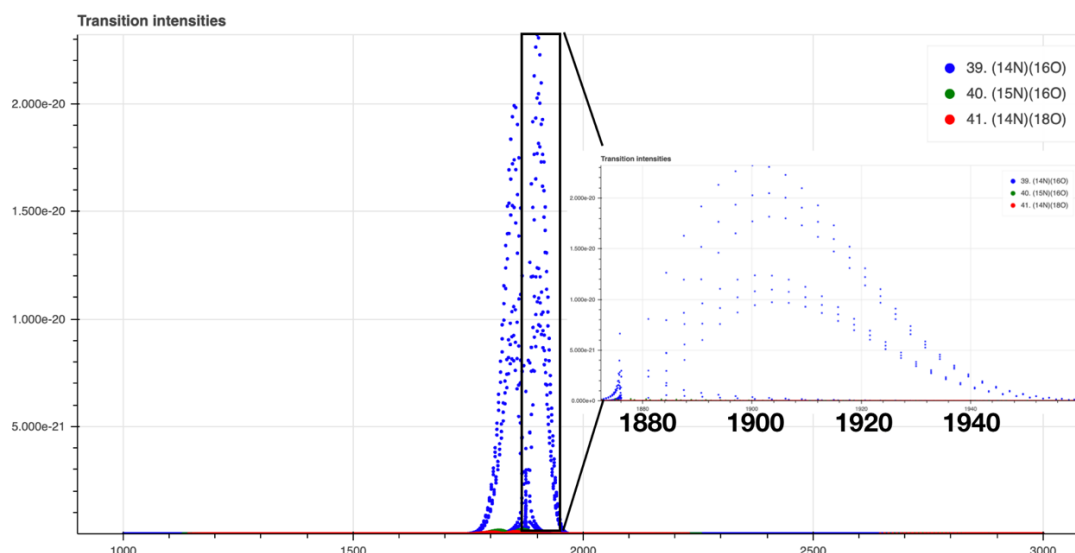


Figure A1. The intensities of the NO absorption lines from the HITRAN2016 linelist.

2. It is concluded that tropospheric NO is not well retrieved during the summer because of high water vapor abundance. My understanding from the manuscript is that high water vapor reduces the signal to noise ratio. From my previous comment, is there a region where water vapor has less influence?.

Unfortunately, the answer is No.

Also, I highly recommend checking the zenith angle dependency in the summer vs winter. In my opinion, it may have an effect, for example when the zenith angle is high the optical path may be more sensitive to lower tropospheric air mass, hence NO may be retrievable during high zenith angles. Do measurements in winter vs summer cover the same zenith angle ranges?

Agree that the SZA is also important for FTIR NO retrieval. But the dominate factor caused the significant difference in summer and winter is the water vapor abundance.

With similar SNR of spectra, the DOF of the NO profile increases with SZA. The reason for the increased DOF is that the optical path becomes large with a high SZA, so that more information of NO is retrieved. However, in summer, the SNR of the spectrum is very low due to a high H₂O column. Figure A2 shows that only a few successful NO retrievals are available in JJA (summer) at Xianghe. The converged retrievals in summer are generally with a small SZA (<50°) and a low H₂O column. Non-converged retrievals (failed) are generally with a large SZA in summer, because the slant column of H₂O increases with the air mass factor ($\sim 1/\cos(\text{SZA})$). In winter, the H₂O column is much lower, and we can get the converged NO retrieval even with a large SZA (>50°). In summary, the dominant difference between two spectra in summer and winter with a similar SZA, such as 60°, is the SNR, which is affected by the H₂O column. Therefore, we highlight that the dominant factor affecting the FTIR NO retrieval is the H₂O column difference between summer and winter at Xianghe. Figure 2 in the AMTD paper shows that the spectra at 1900 cm⁻¹ are almost saturated with a high H₂O column. As a result, in a wet condition, we are not able to retrieve NO for both tropospheric and stratospheric parts.

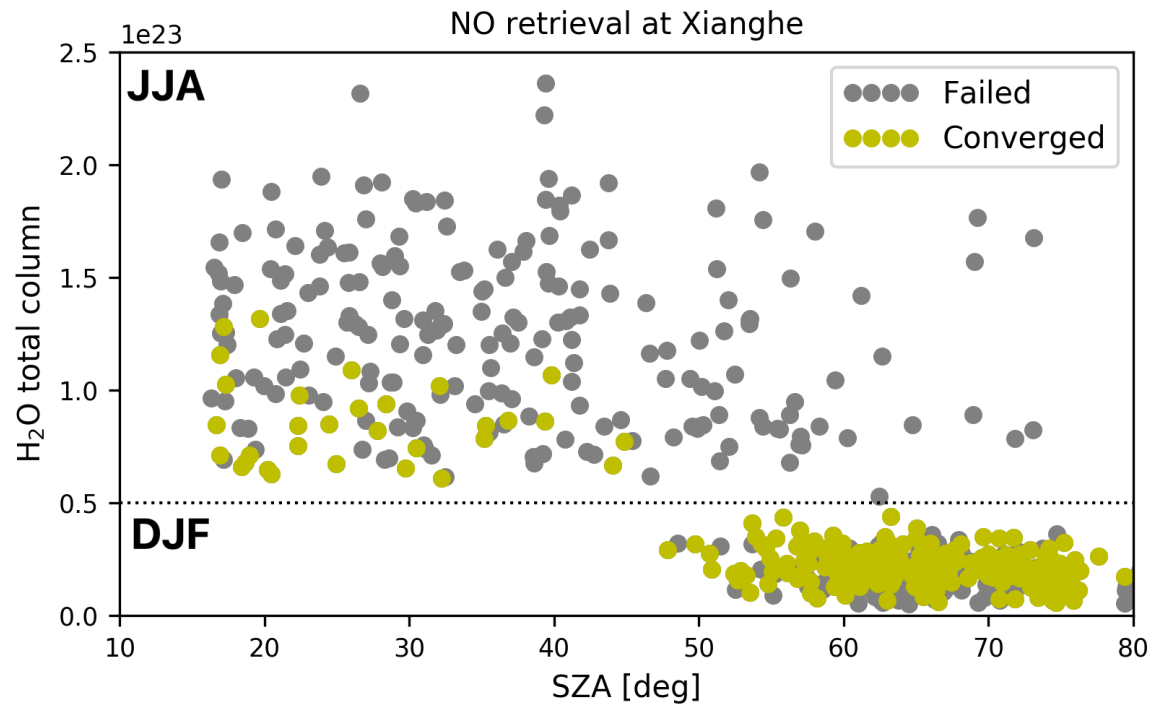


Figure A2. The FTIR NO retrievals from all the spectra in JJA (above the dashed line) and DJF (below the dashed line) at Xianghe, with the converged retrievals colored with yellow and the failed retrievals colored with grey. The H₂O total columns in summer are much larger than those in winter. The spectra are recorded with a wider range of SZA in summer as compared to winter.

3. There is a contrast between Xianghe (polluted) and Maïdo (background), however it is not mentioned what would be the detection limit of the NO using these observations. Please include an assessment in the detection limit.

Thanks for the suggestion. We agree that it is very useful to give detection limits for tropospheric NO retrievals. However the situation is not so straightforward. This study shows that the NO retrieval depends on the SNR of the spectra and the NO concentration. Assuming that all the spectra are recorded under clear-sky condition, the SNRs are then strongly affected by H₂O column and SZA. We cannot give an absolute value of NO concentration as the detection limit. Instead, we focus on the retrievals at Xianghe and Maïdo, and add the discussion about the NO variations at the two sites.

“In summary, we cannot retrieve NO in the troposphere at Maïdo, because the NO mole fraction near the surface (NO_{surf}) is low, with a typical value of less than 0.1 ppb. At Xianghe, the spectra recorded under a wet condition (mainly occur in summer) do not allow us to retrieve the tropospheric NO either. In winter, all the retrievals at Xianghe provide both tropospheric and stratospheric NO partial columns (Figures 4 and 5). The retrieved NO_{surf} in winter varies from 1.3 to 47.2 ppb, with a mean of 11.4 ppb and an std of 10.7 ppb. For all the 240 retrievals in winter, the mean of the H₂O total column is 2.3×10^{22} molecules/cm², and the mean of the SZA is 65.3°. A relatively lower NO_{surf} at Xianghe can be detected under the condition of a low H₂O total column and a large SZA. For example, if we select the retrievals with the NO_{surf} less than 3 ppb (26 out of 240), the mean of the H₂O total column becomes 1.7×10^{22} molecules/cm², and the mean of the SZA is 68.1°.

4. Authors show correlation between NO and CO measured by the same instruments. While NO and CO may have the same common emission sources there are very different species, e.g., CO lifetime is significantly larger and can be transported from other regions, etc. Are there any co-located or close-by in-situ measurements of NO that can be used to see tropospheric columns and enhancements?. I would expect some correlation between in-situ and retrieved lower tropospheric NO since the averaging kernels show high sensitivity in the boundary layer.

Thanks for the suggestion, unfortunately, there is no NO in situ measurement available at Xianghe. Instead, we add the comparison between the FTIR NO and MAX-DOAS NO₂ measurements. An BIRA-IASB/IAP MAX-DOAS instrument is operated at the same building of the FTIR instrument at Xianghe, which observes several air pollutants, including NO₂. Figure A3 shows that the co-located FTIR NO and MAXDOAS NO₂ partial columns in the lower troposphere (0-4 km) show a good correlation, with the R of 0.86.

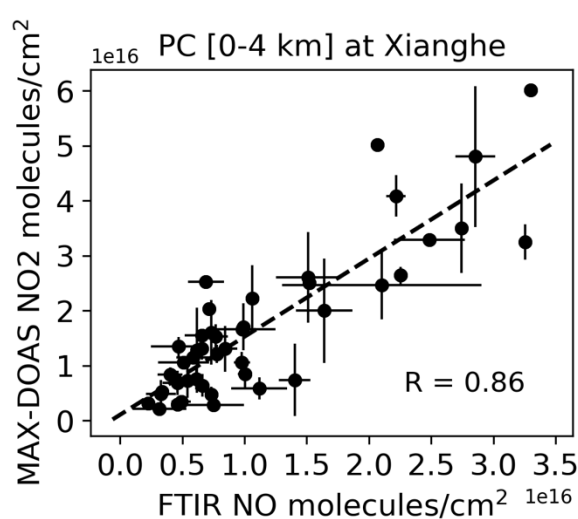


Figure A3. The correlation between the daily means of the FTIR retrieved NO tropospheric partial columns and the MAX-DOAS retrieved NO₂ tropospheric partial columns. The error bar is the daily std, and the black dashed line is the linear fit.

Specific comments

In the abstract: Nitric oxide (NO) is a key active trace gas in the atmosphere, which contributes to form “bad” ozone (O₃) in the troposphere and to the destruction of “good” O₃ in the stratosphere. I highly recommend avoiding good/bad ozone. Instead, something like this:

“Nitric oxide (NO) is a key active trace gas in the atmosphere, which contributes to form harmful ozone (O₃) in the troposphere and to the destruction of O₃ in the stratosphere”

Done

Sometimes ozone is spelled other times O₃ is used, be consistent in the manuscript and I highly recommend using “ozone”.

Done.

P2,l26. It is mentioned that at Xianghe the NO is high, please include values.

Added.

P2, I31. Is there a reason for only using MIPAS? Why not compare it to ACE-FTS?

Because of the occultation geometry, the overpass time of ACE-FTS is about 06:00 and 18:00 at local time. There are no FTIR measurements at these two overpass windows. In order to reduce the large diurnal variation of the stratospheric NO partial column (Figure 4), we compare FTIR and MIPAS measurements. The overpass time of MIPAS is about 10:30 and 22:30, and we use the daytime measurements to compare with the co-located FTIR measurements.

P3. In the description of FTIR sites, please add additional information such as resolution of FTIR measurements, time resolution, i.e., how often do you measure in the region of interest?. Are there additional in-situ measurements of NO around Xianghe & Maïdo?. It is mentioned that NO_x annual emission at Xianghe is one of the largest around the world, could you include typical concentrations comparing Xianghe and Maïdo?

More information is added now.

P4, Figure 1. The obs-cal is shown in the upper plot but in the bottom plot they are not shown, maybe adding the obs and calc in the bottom plot would be more clear.

We prefer to keep it unchanged. Adding the obs and calc spectra makes the plot very busy.

P4. I have several comments/suggestions regarding the NO a priori profile:

- CAM-Chem is used at Xianghe because WACCM underestimates surface NO concentration. However, CAM-Chem is used up to 50 km, which potentially makes the stratospheric a priori different from WACCM. I wonder why CAM-Chem was not used only in the lower troposphere then WACCM to use similar a priori for Maïdo and Xianghe?. Did you assess the impact of different a priori profiles in the stratosphere?

The difference between the CAM-Chem and WACCM is mainly in the troposphere. In the stratosphere, the difference between CAM-Chem and WACCM is relatively small (within 10%). We have tested both CAM-Chem and WACCM as the a priori profile in the stratosphere at Xianghe, the relative difference of NO total column is less than 0.5%.

- Likely NO shows a strong seasonal cycle, did you assess monthly prior profiles?

We prefer to use the fixed a priori. Figure 3 shows that the FTIR retrieval can well capture the NO changes even with a low a priori profile in the stratosphere. In addition, the NO is not only changing with the season, but also with the local hour. The fixed a priori profile can help us to reduce the impact of the a priori information when looking at the seasonal and diurnal variations of NO.

P5, L2-L8. How is the SNR defined?. Are the spectra compared in the summer/winter taken at a similar zenith angle?, maybe I miss it but how does the SNR affect the DOFs?

“The SNR is defined as the ratio of the maximum intensity of the spectra in the NO retrieval window to the root mean square error of the spectra in the noise window between 1650 and 1700 cm⁻¹”. – added.

The discussion about the SZA see above (the responds to the major comment 2).

“The covariance matrix of the measurement is calculated as $1/\text{SNR}^2$ for the diagonal values and 0 for the off-diagonal values. As a result, the retrieval information is strongly affected by the SNR.” – added.

P6, 110. It is mentioned that summer retrievals are limited. It is concluded that the decrease of DOFs in the summer is due to low SNR because of greater water vapor columns. One more thing to assess, in my opinion, is the dependency in the sza, could you please indicate if measurements over summer & winter cover similar zenith angles?. Maybe the optical path using high zenith angles has more sensitivity over the lower troposphere, hence greater DOFs?. In general, the sza dependency is missing and may also contribute to low DOFs in the summer.

See the reply to the major comment 2.

P9, 112-15. First it is described that NO decreases after 14:00 for some months, e.g. January but different for other months, e.g., February. Please add a reason for this. Furthermore, if the fittings are not robust I suggest removing them.

The fittings at Xianghe are not robust due to the lack of measurements, especially before 9:00 and after 16:00. Following the suggestion, and the fittings at Xianghe are removed now.

P13, 14. I suggest adding, maybe next to Figure 9, the monthly mean seasonal variation of MIPAS and FTIR (since there are no coincident dates). This would allow the reader to see the difference in amplitudes mentioned in the text.

Done

P15. L2-9. In the context of Figure 10, the manuscript indicates that when the DOF is larger than 0.5 in the troposphere there is no linear relationship between the retrieved tropospheric and stratospheric partial column. However, I do see it as enhancements of NO₂ in the troposphere are not correlated with stratospheric NO₂, how do you disentangle the atmospheric chemistry and the retrieval DOFs?

We suppose that the referee is talking about NO instead of NO₂.

Due to different physical and chemical progresses, there is no direct link between the tropospheric and stratospheric NO. Therefore, if the FTIR retrieval can separate the NO in the troposphere and stratosphere, it is expected to observe a weak correlation between the tropospheric and stratospheric partial columns (this is the case for the retrievals with DOF larger than 0.5 in the troposphere). Otherwise, if the FTIR retrieval is not able to separate the NO in the troposphere and stratosphere, the retrieved NO in the troposphere is then affected by the NO signal in the stratosphere so that there is a relative large correlation between the tropospheric and stratospheric partial columns (this is the case for the retrievals with DOF less than 0.5 in the troposphere).

Have you explored Figure 10 but color coded by SZA?

As discussed above, the SZA is not the dominate parameter here.