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 Maido (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 H_2O. 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 H_2O 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 H_2O. 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 that 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 H_2O, 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 Maido, which have been used in the previous studies (Notholt et al., 1995 and Wiacek et al. 2006)."
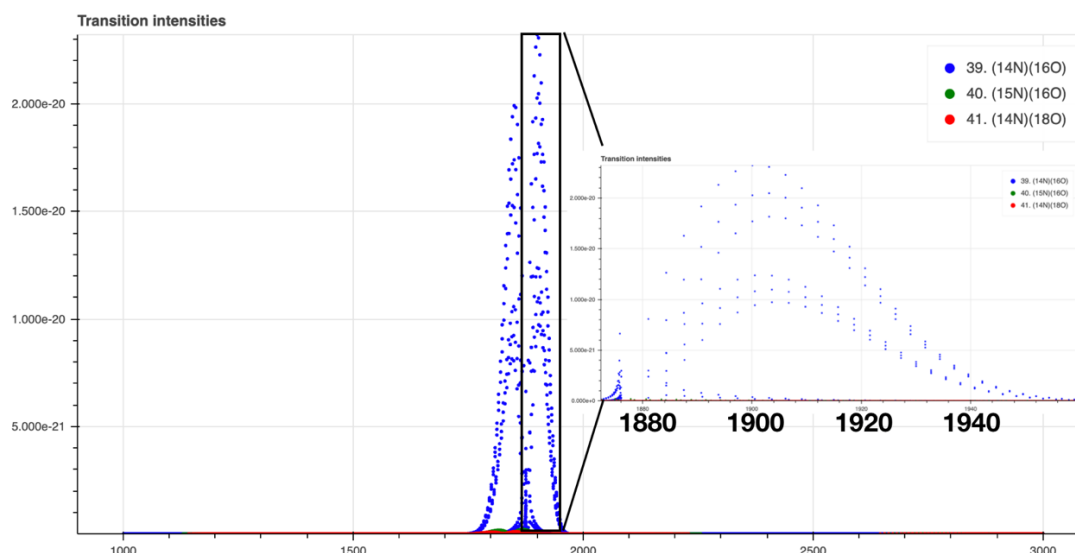
Figure A1. The intensities of the NO absorption lines from the HITRAN2016 linelist.

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 H_2O 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 H_2O column. Non-converged retrievals (failed) are generally with a large SZA in summer, because the slant column of H_2O increases with the air mass factor ($\sim 1/\cos(SZA)$). In winter, the H_2O 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 H_2O column. Therefore, we highlight that the dominant factor affecting the FTIR NO retrieval is the H_2O 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 H_2O column. As a result, in a wet condition, we are not able to retrieve NO for both tropospheric and stratospheric parts.
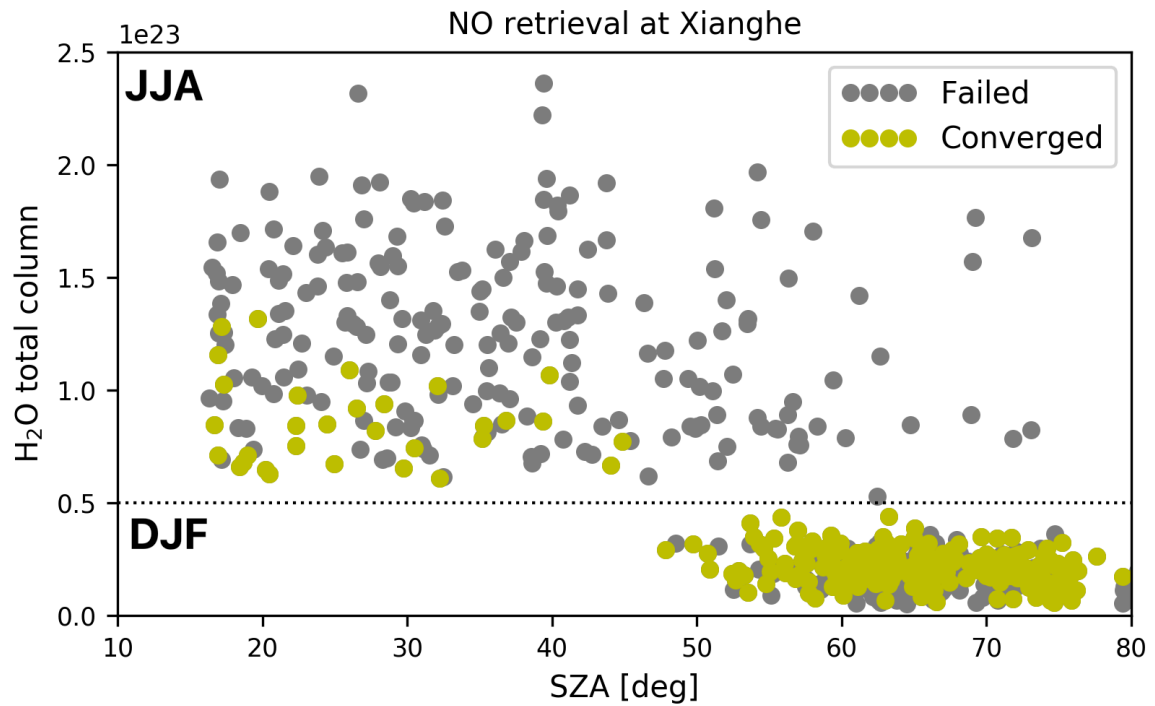
Figure A2. The FTIR NO retrievals from all the spectra in JJA (above the dashed line) and DJF (below the dashed line) at Xianghe, with the converged retrievals colored with yellow and the failed retrievals colored with grey. The H$_2$O total columns in summer are much larger than those in winter. The spectra are recorded with a wider range of SZA in summer as compared to winter.

3. There is a contrast between Xianghe (polluted) and Maido (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 H$_2$O 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 Maido, 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 H$_2$O total column is 2.3 $\times 10^{22}$ molecules/cm^2, 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 H$_2$O 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 H$_2$O total column becomes 1.7 $\times 10^{22}$ molecules/ cm^2, 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 ther 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 NO_2 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 NO_2. Figure A3 shows that the co-located FTIR NO and MAXDOAS NO_2 partial columns in the lower troposphere (0-4 km) show a good correlation, with the R of 0.86.
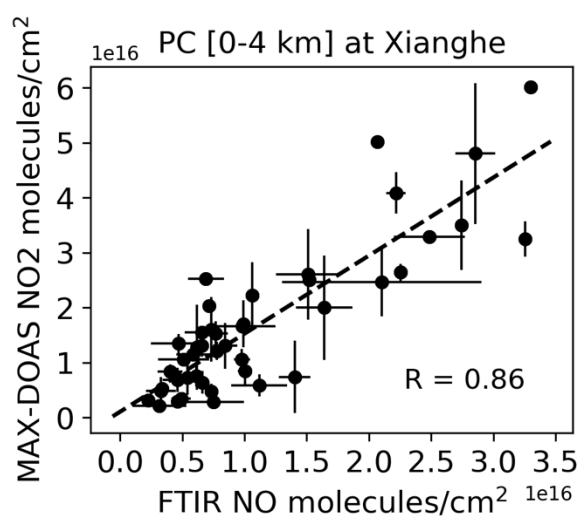

Figure A3. The correlation between the daily means of the FTIR retrieved NO tropospheric partial columns and the MAX-DOAS retrieved NO_2 tropospheric partial columns. The error bar is the daily std, and the black dashed line is the linear fit.

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, l31. 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 & Maido?. It is mentioned that NOx annual emission at Xianghe is one of the largest around the world, could you include typical concentrations comparing Xianghe and Maido?

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 CAMChem was not used only in the lower troposphere then WACCM to use similar a priori for Maido and Xainghe?. 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 prior 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 $1/SNR^2$ 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, l10. 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, l12-15. 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, l4. 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 NO_2.

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.

First of all, we want to thank the referee 2 for the detailed analysis of our paper.
For the details, please look into the paper with keeping track of changes.

General Comment:

The paper by Zhou et al is a report of column measurements of NO from two sites, one in a polluted area of the Northern Hemisphere (Xianghe, China), and the other in a remote part of the Southern Hemisphere (Maido, ReUnion Island). These data also represent a polluted urban area (in the troposphere) and non-polluted site. This would appear to be the first report of a successful analysis of NO in the troposphere from a ground based FTIR, a nuiance that the authors do not explicitly state. Ground-based NO columns has been reported before in the literature, and invariably from NDACC sites that do not in general, see the sort of heightened levels of NO that is reported at Xianghe. So while the stratospheric columns and comparison with satellite data is not new, the tropospheric partial columns of NO are unique, at least as a first report in the literature. Similar data at other Chinese sites may exist and indeed, other potential NDACC sites near large cities that may or may not have enhanced levels of NO near the ground, but the potential is there to explore.

Thanks for the suggestion. We address the importance of this study in the revised version by adding the following sentence:

"We present the first study of a successful analysis of NO in the troposphere from a ground-based FTIR site. The tropospheric and stratospheric NO retrieval might be possible at other potential FTIR sites inside/near large cities with enhanced levels of NO near the surface."

The methods used follow reasonably standard software procedures that have been developed over many years within the NDACC, but NO is not one of the normal target molecules reported by this network. The authors here represent an experienced team who have a very good track record in this area of atmospheric spectroscopy. The paper is not claiming to provide an extensive description of their method, but refer to a few papers in the literature where this is done. A few more details on how they derived some of the parameters used in the analysis, should be fleshed out a bit, as is mentioned below in the comments sections.

Given that NO2 is an integral part of the NOx family along with NO, it would have been an obvious addition to add NO2 to this analysis. This added molecule is readily available in the FTIR spectra, as the authors know, so this would have been an obvious choice to make alongside CO. Or alternatively, in a city like Xianghe, are there air quality monitors like a NOx box that measures NO/NO2?

FTIR NO_2 retrievals at Maido and Xianghe are still under investigation within the EU-ACTRIS framework. Therefore, we did not discuss the FTIR NO_2 retrieval here. We are still working on the FTIR NO_2 harmonization within the NDACC-IRWG network, including Maido and Xianghe, and will present the result in a separate study.

There are no such air quality monitors measuring NO and NO_2 simultaneously. But, there is a nearby BIRA-IASB/IAP MAX-DOAS at Xianghe, providing NO_2 columns. The MAX-DOAS tropospheric NO_2 measurements at Xianghe have been used for satellite validation and atmospheric pollution studies (Hendrick et al., 2014;Verhoelst et al., 2021). In the revised

version, the co-located MAX-DOAS NO_2 measurements are compared with FTIR NO measurements in the lower troposphere at Xianghe. A good agreement between the FTIR NO and MAX-DOAS NO_2 partial columns in the vertical range between 0 and 4 km, with the R value of 0.86. The high correlation with NO_2 is encouraging.

There is also the question of why there is not a modelling component to this paper? So really the question is: is this paper about a new measurement capability (tropospheric NO), or a comparison between a polluted and non-polluted site, or a satellite comparison, or what? So before this paper is published, the purpose of this paper and the new novel aspects need to be clearly pointed out.

Thanks for the suggestion. To make the target of the study clear, the following state has been added in the introduction.

"The aims of this study are 1) to investigate whether it is possible to retrieve NO partial columns in the troposphere and stratosphere from the ground-based FTIR measurements, especially at the polluted site Xianghe; 2) to better understand the diurnal, synoptic and/or seasonal variations of NO partial columns in the stratosphere (and troposphere if possible) observed by the ground-based FTIR measurements at Xianghe and Maido, together with other measurements, such as co-located satellite measurements."

The level of written English in general ok, but there are a few grammatical issues which are listed in the comments.

Thanks a lot for correcting the grammatical issues.

Specific comments:

1. P1, L7: " ...almost not able to be retrieved ..." => "...is very difficult to retrieve..."

Done

2. P1, L20: "basically" => "mainly"

Done

3. P2, L2: "The stratospheric..." => "Stratospheric..."

Done

4. P2, L4: "...(Park et al,. 2012), the stratosphere..." => "...(Park et al,. 2012), stratosphere..."

Done

5. P2, L23: "...even so for ..." => "... even for..."

Done

6. P3, L4: "…to Beijing." => "…of Beijing"

Done

7. P3, L6: "…recording the near …" => "… recording near …"

Done

8. P4, L11: define WACCM with a reference.

Done

9. P4, L16: place this definition and reference to WACCM in line 11.

This is the definition of CAM-Chem not WACCM.

10. P4, L18: "…above that is still taken…" = > "…above 50 km is taken …"

Done

11. P4, L19: expand a bit on the Tikhonov equation. It is entered here without explaining any of the terms. Explain how a value of 50 was obtained.

Done

12. P5, L7: "The HBR cell …" => "HBr cell …"

Done

13. P5, L15: …"several less…" => "…several orders of magnitude less…"

Done.

14. P5, L16: this sentence would read better as; "Therefore, in the stratosphere the FTIR retrievals during the daytime are much larger than the a priori profile."

Done.

15. P5, L19: "…have the sensitivity…" => "…have sensitivity…

Done

16. P5, L20: This is a little misleading the way this is written. Not all layers are sensitive to the stratosphere, since there is no information in the troposphere. A more correct way to put this is that there is sensitivity to NO in the layers in the stratosphere. Note also some sensitivity in the upper troposphere between 10 and 16km, particularly at Maido.

Agree, the sentence is reworded now.

17. P6, L2: Presume this is the average dofs over the entire datasets?

Yes, "over the entire datasets" is added now.

18. P7, L9: "...to the HITRAN2016..." => "...to the HITRAN2016 linelist..."

Done

19. P8, fig 4 caption: "...DOF equalling.." => "...DOF's equal ..."

Change to "DOF of 0.5"

20. P8, L4: "...estimated 13.5%..." => "...estimated to be 3.5%..."

Done

21. P8, L8: "...less than that of NO..." => " ...less than the NO..."

Change to "The random uncertainty of NO stratospheric partial column is less than the random uncertainty of NO total column"

22. P8, L9: " ...less ..." => "smaller"

Done

23. P9, L5: suggest this sentence reads "Due to photochemical reactions (Kondo et 5 al., 1990), a large diurnal variation of the stratospheric NO is expected."

Accepted.

24. P9, L7: "...SZA of measurements." => "...SZA of the measurements."

Done

25. P9, L7: "...2 order..." => "... 2nd." There are a few other locations where this appears.

Done

26. P9, L8: "...t is in a fraction of local hour)." => "...t is a fraction of the local hour)."

Done

27. P9, L12: "...with the time." => "...with time."

Done

28. P9, L18: "...formed NO..." => "... NO formed..."

Done

29. P9, L20: "...stratosphere, then ..." => "....stratosphere, so..."

Done

30. P9, L23: "...and of 0.74..." => "...and 0.74..."

Done

31. P10, error budget: what about inferring species? A solar model is used (but not mentioned as part of the retrieval strategy, for example table 1) so presumably this is part of the retrieved parameters. But does this solar model include both solar line strength and shift?

Added now.

32. P11, fig 7 caption: "The R is the ..." => "R is the ..."

Done

33. P12, L1: "...t is in fraction of year..." => "...t is fraction of the year..."

Done

34. P12, L2: "...which is relative..." => "...is relative..."

Done

35. P12, L10: "...on one hand..." => "...on the one hand..."

Done

36. P12, L29: "...both start measuring..." => "...both started measuring..."

Done

37. P12, L34: "...smoothed with FTIR..." => "...smoothed with the FTIR..."

Done

38. P13, L5: "...are similar observed..." => "...are similar as observed..."

Changed to "The seasonal variations of the stratospheric NO partial columns observed by MIPAS and FTIR measurements are similar, with a high value in summer and a low value in winter"

39. P13, L9: "...The possible reason is that..." => "...The possible reason for this difference is that..."

Done

40. P14, figure 9: The key needs to be reasonably self-explanatory. The numbers and trends in the key should be in the figure caption. For example the black dot entry should read MIPAS daily means, and the number of points can go into the figure caption. Same comment for all the other entries. The colour coding is also not consistent between what is described in the caption and what appears on the graph. For example, the blue shadow for MIPAS is actually purple, the blue solid line for MIPAS is green, while the purple shadow for the FTIR is pink. This could be related to the way colours are displayed in the pdf reader.

Done. Color is corrected, and More information is added in the figure caption.

41. P14, L2: "...which is corresponding..." => "...which corresponds..."

Done

42. P15, figure 10 caption: "Scatter plots between..." => "Scatter plots at Xianghe between..."

Done

43. P15, figure 10 caption: a comment about the way this plot is presented and captioned. The explicit way of knowing that this figure represents Xianghe is the caption title, which is fine But the caption explanation should be more explicit about what the data is and where is from since there is more than one site.

Thanks for the comments. More information is added in the caption.

44. P15, L8: "...slightly large..." => "...slightly larger..."

Done

45. P15, L8: "It is because that the..." => "The reason for this increased correlation is ..."

Done

46. P15, L7-9: The underlying reason is the increased cross-relation between the tropospheric and stratosphere layers, due to the individual averaging kernels being broader.

Right, it is also added now.

47. P15, L11: why are there no tropospheric NO measurements in summer? This maybe explained later (high water?), but a reference could be placed here that this will be explained later in the paper.

Done.

48. P15, L12: would this normally be expressed as mean (std) is 1.4 (1.0) x 10^16, as it is in the abstract.

Done

49. P16, figure 11 caption, last sentence: this colour is not yellow, more light green. Maybe this is a function of the pdf viewer?

The colors are fine on my PC.

50. P16, figure 12 caption: "...CO tropospheric partial columns." => "CO tropospheric partial columns at Xianghe."

Done

51. P16, L2: "...combustion for..." => "...combustion from ..."

Done

52. P16, L4: individual => independent

Done

53. P17, L25: depend => dependent

Done

References

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Verhoelst, T., Compernolle, S., Pinardi, G., Lambert, J.-C., Eskes, H. J., Eichmann, K.-U., Fjæraa, A. M., Granville, J., Niemeijer, S., Cede, A., Tiefengraber, M., Hendrick, F., Pazmiño, A., Bais, A., Bazureau, A., Boersma, K. F., Bognar, K., Dehn, A., Donner, S., Elokhov, A., Gebetsberger, M., Goutail, F., Grutter de la Mora, M., Gruzdev, A., Gratsea, M., Hansen, G. H., Irie, H., Jepsen, N., Kanaya, Y., Karagkiozidis, D., Kivi, R., Kreher, K., Levelt, P. F., Liu, C., Müller, M., Navarro Comas, M., Piters, A. J. M., Pommereau, J.-P., Portafaix, T., Prados-Roman, C., Puentedura, O., Querel, R., Remmers, J., Richter, A., Rimmer, J., Rivera Cárdenas, C., Saavedra de Miguel, L., Sinyakov, V. P., Stremme, W., Strong, K., Van Roozendael, M., Veefkind, J. P., Wagner, T., Wittrock, F., Yela González, M., and Zehner, C.: Ground-based validation of the Copernicus Sentinel-5P TROPOMI NO2 measurements with the NDACC ZSL-DOAS, MAX-DOAS and Pandonia global networks, Atmos. Meas. Tech., 14, 481–510, https://doi.org/10.5194/amt-14-481-2021, 2021.

Tropospheric and stratospheric NO retrieved from ground-based FTIR measurements

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Abstract. Nitric oxide (NO) is a key active trace gas in the atmosphere, which contributes to form ~~"bad" ozone (O_3)~~ harmful ozone in the troposphere and to the destruction of ~~"good" O_3~~ ozone in the stratosphere. In this study, we present the NO retrieval from ground-based Fourier-transform infrared (FTIR) solar absorption spectrometry measurements at a polluted site (Xianghe, China) and a background site (Maïdo, Reunion Island). The Degree Of Freedom (DOF) of the NO retrieval is 2.3±0.4 (1σ) at
5 Xianghe and 1.3±0.1 at Maïdo.

~~The high NO mole fraction near the surface at Xianghe allows us to derive tropospheric and stratospheric NO partial columns separately, albeit the tropospheric column is almost not able to be retrieved in summer (June-August) because of the high water vapor abundance. At~~ By looking at the FTIR NO retrievals at Xianghe and Maïdo, ~~the NO retrieval is only sensitive to the stratosphere. The FTIR measurements at Maïdo show~~ we find that the stratospheric NO partial column ~~increases from the early
10 morning to about 14:00 local time and starts decreasing thereafter. The stratospheric NO partial column~~ is large in summer as compared to winter at both sites, and the seasonal variation of the FTIR stratospheric NO partial columns is consistent with that observed by the co-located Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) satellite measurements. ~~We observe a good correlation between the carbon monoxide (CO) and NO daily partial columns in the troposphere~~ A large diurnal variation in the stratospheric NO partial column is observed by the FTIR measurements at Maïdo, with an increase
15 from the early morning to about 14:00 local time and a decrease thereafter.

Due to the low NO concentration near the surface, the FTIR NO retrieval is only sensitive to the stratosphere at Maïdo. The high NO mole fraction near the surface at Xianghe allows us to derive tropospheric and stratospheric NO partial columns separately, albeit the tropospheric column is very difficult to retrieve in summer (June-August) because of the high water vapor abundance. A good correlation is found between the NO observed by the FTIR measurements ~~at Xianghe with a correlation
20 coefficient of 0.70, because both species have similar anthropogenic sources.~~ and other air pollutants (NO_2 and CO) in the troposphere at Xianghe. It is the first study of a successful analysis of NO in the troposphere from a ground-based FTIR site.

1

The tropospheric and stratospheric NO retrieval might be possible at other potential FTIR sites inside/near large cities with enhanced levels of NO near the surface.

1 Introduction

Nitric oxide (NO) is a major component of the nitrogen oxides family ($NO_x = NO + NO_2$), which plays key roles in atmospheric chemistry. In the troposphere, NO is an air pollutant, related to the formation of ground-level ozone (O_3), peroxyacetyl nitrate (PAN), nitric acid (HNO_3) and aerosols (Crutzen, 1979; Ng et al., 2007; Monks et al., 2015). NO sources near the surface are mainly of anthropogenic origin. Delmas et al. (1997) pointed out that about 50% of the NO emissions are caused by the combustion of fossil fuel, and about 20% are from the biomass burning. The remaining 30% are ~~basically~~ mainly from natural lightning and microbial activity in soils. In the stratosphere, NO participates in an important set of catalytic reactions which deplete ozone (Crutzen, 1970). ~~The stratospheric~~ Stratospheric NO is mainly coming from the oxidation of nitrous oxide (N_2O), which is a stable trace gas that can be transported upward to the stratosphere in the tropical region. As atmospheric N_2O has been increasing since the 1970s mainly due to increasing use of fertilizers (Park et al., 2012), ~~the stratospheric O_3~~ stratospheric ozone depletion caused by NO_x will play a more important role in the future, especially as the stratospheric chlorine burden is declining (Portmann et al., 2012). In the mesosphere and thermosphere, NO is formed by energetic particle precipitation (Randall et al., 2007), which can be transported downward to the stratosphere affecting the ozone chemistry, especially in the winter polar region (Meraner and Schmidt, 2016).

Space-borne sensors, e.g. the Atmospheric Chemistry Experiment - Fourier Transform Spectrometer (ACE-FTS) making solar occultation measurements (Bernath et al., 2005) and the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) looking at thermal emission at the limb (Fischer et al., 2008), can provide global NO distributions. However, these satellite measurements provide almost no information in the troposphere. Moreover, it is difficult to derive the diurnal variation of NO from these satellite measurements. Because of the weak intensities of the NO absorption lines (Gordon et al., 2017), as far as we know, there is no nadir-looking satellite to measure the NO near the surface. Ground-based Fourier-transform infrared (FTIR) spectrometers affiliated with the Network for Detection of Atmospheric Composition Change (NDACC) (De Mazière et al., 2018) record direct solar absorption spectra in the infrared region with a high spectral resolution (0.0035 - 0.005 cm^{-1}) under clear sky conditions. More than 20 atmospheric species can be retrieved from the FTIR observed spectra, and the data have been widely used to investigate the change of atmospheric composition, to support satellite validation and model verification (De Mazière et al., 2018). However, until now, there are few studies focusing on FTIR NO retrieval. Notholt et al. (1995) showed that the NO total columns can be retrieved from the FTIR spectra with a high spectral resolution of 0.0035 cm^{-1} at Ny-Alesund. Wiacek et al. (2006) succeeded in retrieving NO in the stratosphere, mesosphere and in the lower thermosphere from the ground-based FTIR measurements at Toronto and Eureka, but they found that there is almost no information in the troposphere for the FTIR NO retrievals at Eureka, and even ~~so~~ for measurements taken in the Toronto mega-city.

In this study, we investigate NO retrievals from ground-based FTIR measurements with a focus on the retrieved profile in the troposphere and stratosphere at two different sites: Xianghe, a polluted site in China and the Maïdo observatory on

Reunion Island, a background site. ~~As the NO mole fraction near the surface at Xianghe is quite high, we show that~~ The aims of this study are 1) to investigate whether it is possible to retrieve ~~the~~ NO partial columns in the troposphere and stratosphere ~~separately from the FTIR measurements~~ from the ground-based FTIR measurements, especially at the polluted site Xianghe; 2) to understand the diurnal, synoptic and/or seasonal variations of NO partial columns observed by the ground-based FTIR measurements in the stratosphere (and troposphere if possible) at Xianghe and Maïdo, together with other measurements, such as co-located satellite measurements. In Section 2, we give a brief introduction to the sites and the FTIR measurement technique, and discuss the FTIR NO retrieval strategy and retrieval uncertainties. In Section 3, we discuss the time series of the FTIR NO retrievals at Xianghe and Maïdo, including the diurnal and seasonal variations of the FTIR retrieved partial columns of NO in the stratosphere. In addition, the FTIR NO retrieved stratospheric partial columns are compared with the co-located MIPAS satellite measurements. Moreover, the FTIR retrieved tropospheric partial columns of NO at Xianghe are discussed in Section 4. Finally, conclusions are summarized in Section 5.

2 Measurement sites and retrieval strategy

2.1 FTIR sites

- Xianghe (39.75 °N, 116.96 °E; 50 m a.s.l.) is located in a polluted urban region in North China. It is about 70 km ~~east to~~ southeast of Beijing. A Bruker IFS 125HR spectrometer was installed at Xianghe and started measuring infrared solar absorption spectra in June 2018 (Zhou et al., 2020). The Xianghe site is operated in the Total Column Carbon Observing Network (TCCON) mode by recording ~~the~~ near infrared spectra from 4000 to 12000 cm^{-1} using an InGaAs detector (Yang et al., 2020), but infrared spectra with a spectral range from 1800 to 5200 cm^{-1} are also recorded with a liquid N_2 InSb cooled detector. The spectra at Xianghe used for the NO retrieval are operated with the NDACC IRWG optical filter no.5 (Blumenstock et al., 2021). The maximum optical path difference (MOPD) is 257 cm, which corresponds to a spectral resolution of 0.0035 cm^{-1}. There are normally 1-5 observed spectra on each measurement day. According to the Emissions Database for Global Atmospheric Research (EDGAR v4.3.2) (Crippa et al., 2018), the NO_x annual emission at Xianghe in 2012 is larger than 1000 tonnes/yr/(0.1 deg)^2, which is one of the largest NO_x emission rates around the world. ~~As a result, the~~ The NO concentration near the surface in this region ~~is much larger than at background sites, which~~ was reported of about 5-20 ppb (Tang et al., 2009). The high NO concentration provides an opportunity to ~~see~~ study whether it is possible to retrieve tropospheric NO columns from the ground-based FTIR spectra.

- The Maïdo (21.08 °S, 55.38 °E; 2155 m a.s.l.) observatory, located on a mountain at Reunion Island, is about 700 km east of Madagascar in the southern hemisphere tropical region. The Bruker IFS 125HR spectrometer at Maïdo is affiliated with the NDACC-InfraRed Working Group (IRWG) (De Mazière et al., 2018), and has been measuring solar absorption spectra quasi continuously since March 2013 (Zhou et al., 2016). The infrared spectra in the spectral range from 800 to 2000 cm^{-1} are recorded with a liquid N_2 cooled MCT detector and the infrared spectra in the spectral range from 2000 to 5200 cm^{-1} are recorded with a liquid N_2 cooled InSb detector. The spectra at Maïdo used for the NO retrieval

are also operated with the NDACC IRWG optical filter no.5. Different from Xianghe, the spectra at Maïdo used for the NO retrieval are operated with 2 MOPD of 120 cm and 257 cm, corresponding to spectral resolutions of 0.0072 cm^{-1} and 0.0035 cm^{-1}, respectively. The short MOPD is operated with a large SZA (>60°) to reduce the uncertainty of the light path change. The long MOPD is operated with a small SZA. There are normally 1-10 spectra on each measurement day. Since NO is not among the baseline species in the NDACC-IRWG network, it is the first time that we study the NO retrieval at the Maïdo site. As the NO_x surface concentration is low at Maïdo, with a typical value of 0.1-0.5 ppb (Rocco et al., 2020), it can be considered as a background site as compared to Xianghe.

2.2 FTIR retrieval strategy

The SFIT4 v0.9.4.4 retrieval code, updated from SFIT2 (Pougatchev et al., 1995), based on the optimal estimation method (Rodgers, 2000) is applied to retrieve the NO profile from the infrared spectra observed at Xianghe and Maïdo. A line-by-line model has been implemented in the forward model of the SFIT4 code to calculate the transmittance at a given wavenumber range:

$$\boldsymbol{Y} = \boldsymbol{F}(\boldsymbol{x}, \boldsymbol{b}) + \boldsymbol{\varepsilon}, \tag{1}$$

where $\boldsymbol{Y}$ is the observed spectrum, $\boldsymbol{F}(\boldsymbol{x}, \boldsymbol{b})$ is the forward model, with the inputs from the retrieved parameters ($\boldsymbol{x}$) and ~~not retrieved~~ non-retrieved model parameters ($\boldsymbol{b}$) and $\boldsymbol{\varepsilon}$ is the uncertainty. The pressure and temperature dependences of the line shape allow us to retrieve some pieces of vertical information of the target gas. The HITRAN2016 spectroscopy (Gordon et al., 2017) is used here, and the strongest NO absorption lines are distributed in the range between 1820 and 1930 cm^{-1}. ~~The NO absorption lines at 1900.07 and 1900.08 cm^{-1} have been used in Notholt et al. (1995) and Wiacek et al. (2006), as they have the strongest line intensities and are less affected by~~ In order to select the strong NO lines and to reduce the interference from other species, ~~such as water vapor. In this study, we choose the window of 1899.90-1900.10~~ especially H_2O, several windows have been tested. We find that the NO absorption lines at 1900 cm^{-1} ~~for the~~ are the best choice for ground-based FTIR NO retrieval at Xianghe and Maïdo, which have also been used in the previous studies (Notholt et al., 1995; Wiacek et al., 2006). Figure 1 shows an example of the spectral fitting in the retrieval window at Xianghe. In order to reduce the influence of the interfering species, the column of CO_2 is retrieved simultaneously together with the profile retrieval of NO.
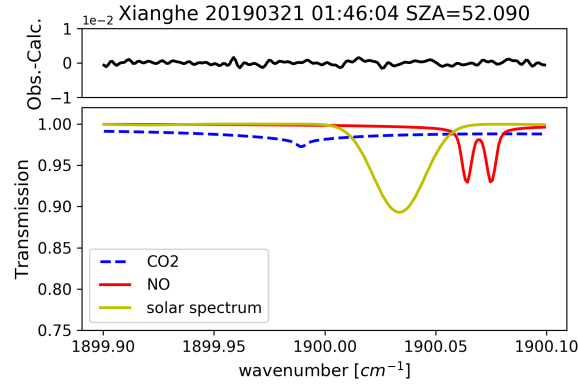
~~The SFIT4~~ A cost function ($J(x)$) is created and the STIT4 algorithm uses an iterative Levenberg-Marquardt ~~fit method for solving the optimal estimation problem, and~~ method to look for the ~~retrieved parameters~~ optimal $\boldsymbol{x}$ to minimize the $J(\boldsymbol{x})$.

$$J(\boldsymbol{x}) = [\boldsymbol{y} - \boldsymbol{F}(\boldsymbol{x})]^T \mathbf{S}_\epsilon^{-1}[\boldsymbol{y} - \boldsymbol{F}(\boldsymbol{x})] + [\boldsymbol{x} - \boldsymbol{x_a}]^T \mathbf{S}_a^{-1}[\boldsymbol{x} - \boldsymbol{x_a}], \tag{2}$$

where $\mathbf{S}_a$ is the a priori covariance matrix, and $\mathbf{S}_\epsilon$ is the measurement covariance matrix. The retrieved state vector ($\boldsymbol{x_r}$) can be written as

$$\boldsymbol{x}_r = \boldsymbol{x}_a + \mathbf{A}(\boldsymbol{x}_t - \boldsymbol{x}_a) + \boldsymbol{\varepsilon}, \tag{3}$$

$$\mathbf{A} = (\mathbf{K}^T \mathbf{S}_\epsilon^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1} \mathbf{K}^T \mathbf{S}_\epsilon^{-1} \mathbf{K}, \tag{4}$$

4

Figure 1. An example of the transmittances from NO, carbon dioxide (CO_2) and solar lines (lower) and the difference between the observed and calculated spectra (upper) in the NO retrieval window (1899.9-1900.1 cm^{-1}) at Xianghe. The measurement time (UTC) together with the solar zenith angle is shown in the title.

where x_a ~~, x_r~~ and x_t are the a priori ~~, retrieved~~ and true state ~~vector~~ vectors (retrieved parameters), respectively, ϵ is the total error on the retrieved profile minus the smoothing error, K is the Jacobian matrix and A is the averaging kernel (AVK), indicating the sensitivity of the retrieved parameters to the true parameters~~, and ϵ is the total error on the retrieved profile minus the smoothing error~~. A fixed a priori NO profile is used for all the retrievals at one site. The a priori profile of NO at Maïdo is

5   derived from the average of the ~~WACCM~~ Whole Atmosphere Community Climate Model (WACCM) monthly means within 1980-2020 (Marsh et al., 2013), which is often used to create the a priori profile within the NDACC-IRWG community. Note that the daytime and night-time model data are both used in this case. There is an underestimation of NO near the surface from the WACCM model at Xianghe. The NO mole fraction is about 0.2 ppb in the WACCM model while the surface observations in Beijing indicate that NO mole fraction in this region is about 5-20 ppb near the surface during daytime (Tang et al., 2009).

10   Therefore, we use the annual mean in 2018 from the Community Atmosphere Model with Chemistry (CAM-Chem) model (Lamarque et al., 2012) monthly means as the a priori NO profile at Xianghe, with the NO mole fraction of 9.2 ppb at the surface. Since the top pressure level in the CAM-Chem model is about 1.8 hPa ($\sim$ 50km), the a priori profile of NO at Xianghe above ~~that is still~~ 50 km is taken from the WACCM model.

The regularization matrix for the NO retrieval is created with ~~a~~ the Tikhonov L_1 method (Tikhonov, 1963). ~~$R = \alpha L_1^T L_1$~~

15   ~~with $\alpha = 50$.~~ $R = S_a^{-1} = \alpha L_1^T L_1$. To determine the value of α, we use the DOF method as the described in Steck (2002). First, we create the a priori covariance matrix (S_a) using the WACCM model monthly means. Second, the retrieval is operated using the optimal estimation method (OEM), and the DOF from the OEM is about 1.3 at Maïdo. Finally, we tune the α value to get a similar DOF using the Tikhonov method, implying $\alpha = 50$. In this study, we use the same α at both sites. The covariance matrix of the measurement (S_ϵ) is calculated as $1/SNR^2$ for the diagonal values and 0 for the off-diagonal values. As a result,

20   the AVK is affected by the signal-to-noise ratio (SNR) of the spectrum. Although there are only CO_2 and solar lines in our retrieval window, there are many strong water vapor lines adjacent to the window. Therefore, the ~~signal-to-noise ratio (SNR)~~

5

~~of the spectrum~~ SNR in this region is strongly affected by the water vapor abundance. 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}. Figure 2 shows several typical spectra observed in summer and winter at Xianghe and Maïdo. According to the National Centers for Atmospheric Prediction (NCEP) reanalysis data (Kalnay et al., 1996), the mean total

5   columns of H_2O are 3.8 $\times 10^{22}$ $molecules/cm^2$ (7.5 $\times 10^{22}$ $molecules/cm^2$ in summer and 1.6 $\times 10^{22}$ $molecules/cm^2$ in winter) at Xianghe and 2.6 $\times 10^{22}$ $molecules/cm^2$ (3.8 $\times 10^{22}$ $molecules/cm^2$ in summer and 1.0 $\times 10^{22}$ $molecules/cm^2$ in winter) at Maïdo. The H_2O interference is more important at Xianghe as compared to Maïdo. As a result, the SNR of the spectrum is less than 50 in summer and about 500 in winter at Xianghe, and it is about 200 in summer and about 700 in winter at Maïdo. ~~The~~ HBr cell measurements are operated at both sites. The instrument line shape (ILS) parameters are retrieved from

10   the cell measurements by the LINEFIT14.5 algorithm (Hase et al., 1999), and the LINEFIT outputs are used as the ILS inputs in the SFIT4 algorithm. The solar line list is included in the SFIT4 code, named 120621_solar, provided by Frank Hase (KIT), and the solar line intensity and shift are retrieved simultaneously in the NO retrieval. Table 1 summarizes the NO retrieval strategy ~~adopted~~ used in this study.

Table 1. The retrieval strategy of FTIR NO retrieval in this study.

Parameter	Setting
Retrieval window	1899.90-1900.10 cm^{-1}
Profile retrieval	NO
Column retrieval	CO_2
A priori profile	WACCM (+ CAM-Chem at Xianghe)
Spectroscopy	HITRAN2016
Regularization	Tikhonov (alpha = 50)
SNR	Calculated from the spectra
ILS	LINEFIT retrievals
Solar lines	The intensity and shift are retrieved

    Figure 3 shows the a priori and retrieved NO profiles in the vertical range between the surface and 70 km, together with

15   typical AVKs at Xianghe and Maïdo, respectively. At both sites, the maximum value of the NO mole fraction occurs at about 45 km in the stratosphere. The retrieved NO mole fraction is much larger than the a priori in the stratosphere at both sites. The a priori NO profile is created as the average of the model monthly means including both daytime and night-time data, while the NO mole fraction in the stratosphere at night is several orders of magnitude less than that during the daytime (Kondo et al., 1990; Dubé et al., 2020). Therefore, ~~the~~ in the stratosphere the FTIR retrievals during the daytime are much larger than

20   the a priori profile~~in the stratosphere~~. The retrieved NO mole fraction near the surface is about 10 ppb at Xianghe, which is comparable to the observations in Beijing of 5-20 ppb during daytime (Tang et al., 2009). The NO mole fraction near the surface is about 0.01 ppb at Maïdo. The AVK at Xianghe shows that only the layers below 2 km have ~~the~~ sensitivity near the surface, while other layers are mainly sensitive to the stratosphere. The AVK at Maïdo ~~indicates that all the layers are sensitive~~
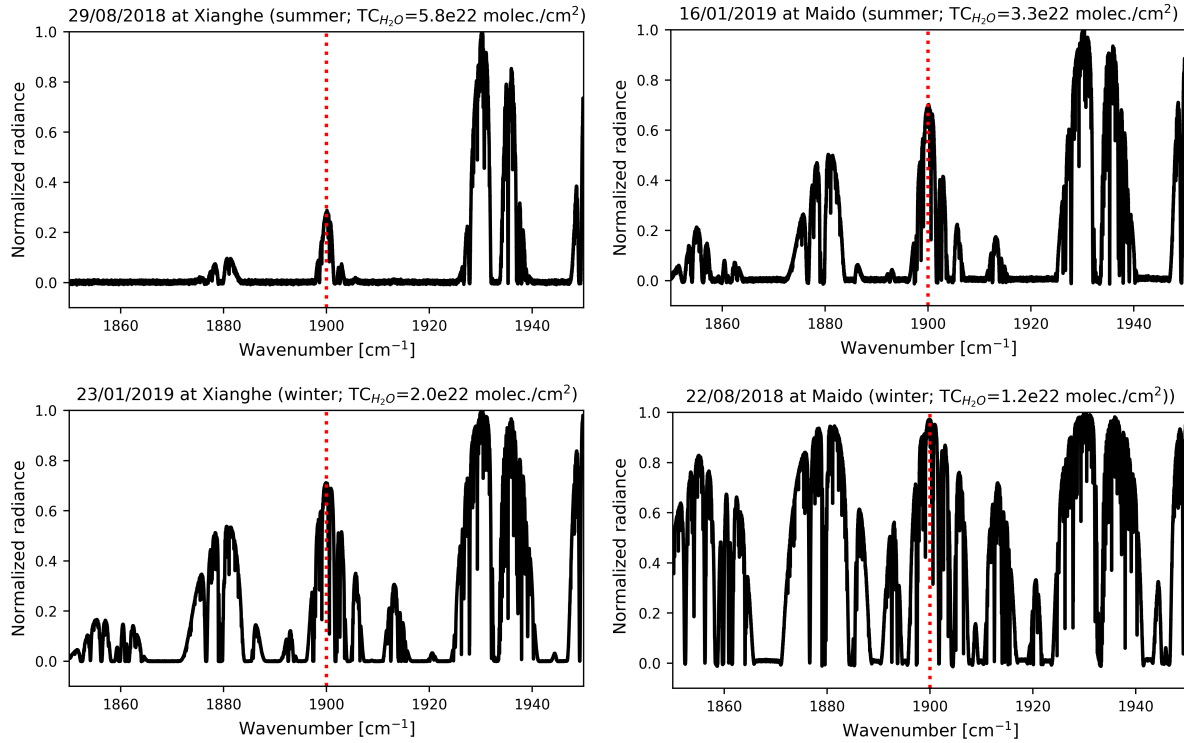
Figure 2. The normalized spectra in summer and winter at Xianghe and Maïdo, together with the total column of water vapor on these days. The red dashed line indicates the retrieval window for NO.

~~to the stratosphere, and~~ shows that the kernels of the troposphere and stratosphere both peak at the stratosphere (∼35 km), indicating that there is almost no information in the lower troposphere. According to the NCEP data, the mean tropopause heights at Xianghe and Maïdo are about 12 km and 16 km, respectively. In this study, we take the vertical range between the surface and the tropopause height (12 km at Xianghe and 16 km at Maïdo) as the troposphere and the vertical range between

5   the tropopause height and 60 km as the stratosphere.

    The trace of the AVK matrix is the degree of freedom (DOF) for signal, indicating the number of individual pieces of information. The mean DOFs of the retrieved NO ~~profile~~ profiles over the entire datasets are 2.3±0.4 (1σ) at Xianghe and 1.3±0.1 at Maïdo, respectively. Figure 4 shows the time series of the DOF in the troposphere, stratosphere, and above 60 km between July 2018 and June 2020 at Xianghe, and between March 2013 and December 2019 at Maïdo. The DOF in the vertical

10   range above 60 km is 0.20±0.06 at Xianghe and 0.10±0.02 at Maïdo. The DOF in the stratosphere is generally between 1.0 and 1.8 at both sites. The DOF in the troposphere is 0.78±0.18 with 90% of DOF from the layers below 2 km at Xianghe, reflecting that the tropospheric NO partial column is actually dominated by the NO partial column in the boundary layer. At Maïdo, the DOF in the troposphere is only 0.03±0.02. In the remainder of this study, we consider only the measurements with a tropospheric DOF larger than 0.5 (black dashed line in Figure 4) as the information on the tropospheric NO partial column

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will in this case comes mostly from the retrieval, and not from the a priori. In total, 472 out of 539 retrievals are selected, with almost none in summer (June to August). As seen in Figure 4, there is a large seasonal variation in the DOF. The DOF is determined by the SNR of the spectrum, which is highly related to the H_2O total column (Figure 5). A large H_2O abundance makes the signal in the selected spectral region weak, leading to a low DOF. The correlation coefficient (R) between DOF and H_2O total column is -0.88. Based on the linear fit, the FTIR NO retrievals at Xianghe with DOF in the troposphere larger than 0.5 are generally occurring when the H_2O total column is less than 5.7×10^{22} $molecules/cm^2$. 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 ranges 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 H_2O total column is 2.3×10^{22} $molecules/cm^2$, 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 H_2O total column and a large SZA. For example, if we only select the retrievals with the NO_{surf} less than 3 ppb (26 out of 240), the mean of the H_2O total column becomes 1.7×10^{22} $molecules/cm^2$, and the mean of the SZA is 68.1°.

Table 2 lists the systematic and random retrieval uncertainties of the NO total column at Xianghe and Maïdo, including the contributions from the major uncertainty sources, which are estimated based on the optimal estimation method (Rodgers, 2000). It is assumed that the systematic uncertainty of a priori profile is 10%, and the random uncertainty of a priori profile is calculated from the covariance matrix of the monthly a priori profiles in 2018. The measurement error matrix is created by the SNR of the spectra, so that each individual spectrum has a different measurement uncertainty matrix. The temperature systematic and random uncertainties are derived from the mean and standard deviation (std) of the differences between the NCEP and ECMWF reanalysis data. We set the systematic uncertainty of the NO spectroscopy to 10% according to the HITRAN2016 linelist (Gordon et al., 2017), and assume that there is no random uncertainty for the spectroscopy. The systematic and random uncertainties of solar zenith angles (SZA) are set to 0.1% and 0.5%, respectively. The retrieved parameter contains the interfering species (CO_2), the solar line intensity and shift, and the slope. The systematic and random uncertainties of CO_2 are set to 5 and 10%, respectively. We set 0.1%, 1.0% and 0.5% to both the random and systematic uncertainties of the slope, the solar line intensity and the solar line shift, respectively. In total, the systematic uncertainties of the FTIR NO retrieved total columns are similar at Xianghe and Maïdo (∼10.3%), and dominated by the uncertainty of the spectroscopy. The random uncertainty of retrieved NO total column is estimated to be 13.5% at Xianghe, which is larger than that of 4.2% at Maïdo. The random uncertainty is mainly coming from the smoothing error and the measurement uncertainty, where the large smoothing error at Xianghe is large due to the strong NO variation near the surface, and the large measurement uncertainty at Xianghe is coming from the low SNR of the spectra. At Maïdo, the systematic uncertainties of NO stratospheric partial column and total column are similar. The random uncertainty of NO stratospheric partial column is less than ~~that~~ the random uncertainty of NO total column, mainly due to a ~~less~~ smaller smoothing error. At Xianghe, the systematic and random uncertainties of the NO partial columns in the troposphere and stratosphere are also shown in Table 2. The systematic and random uncertainties of the stratospheric NO partial column are 10.2% and 4.4%, respectively. The systematic and random uncertainties of the
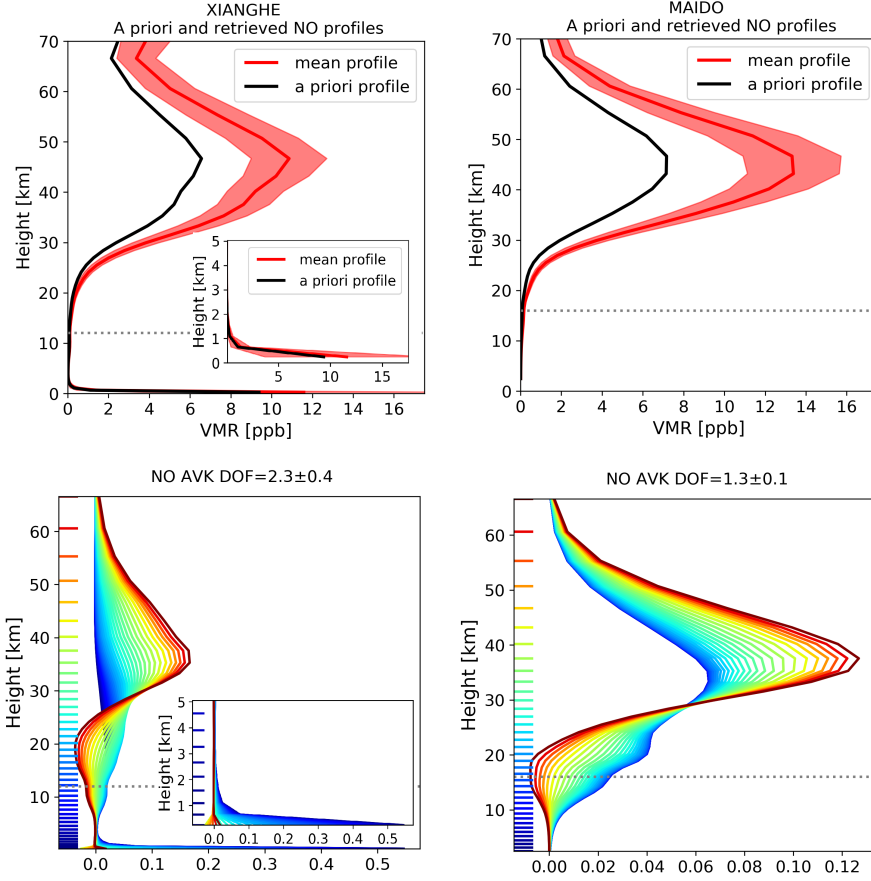
Figure 3. The a priori and retrieved NO profiles at Xianghe and Maïdo (upper panels), together with a typical averaging kernel (AVK) at each site (bottom panels). To better visualize the change near the surface, a zoom on the vertical range between 0 and 5 km is also shown for Xianghe. The red shadow in the upper panels is the standard deviation of the retrieved profiles. The dashed line indicates the tropopause height.
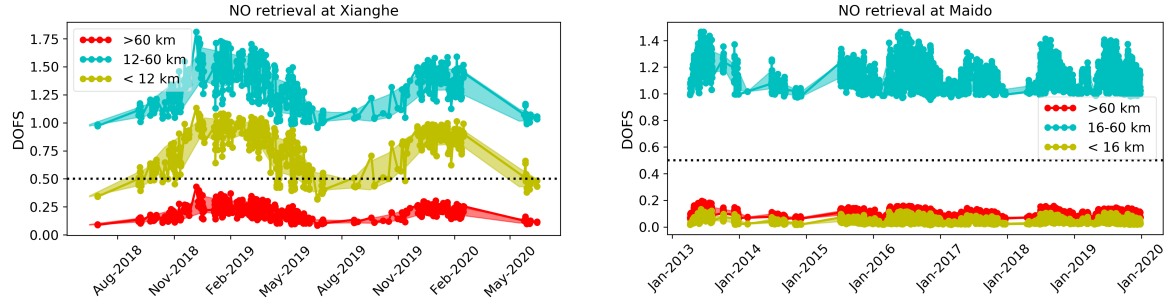
Figure 4. The series of the DOF daily mean (dots) and the std (shadow) in the troposphere, stratosphere and above at Xianghe (left) and Maïdo (right). The black dashed line is at DOF ~~equalling to~~ of 0.5.
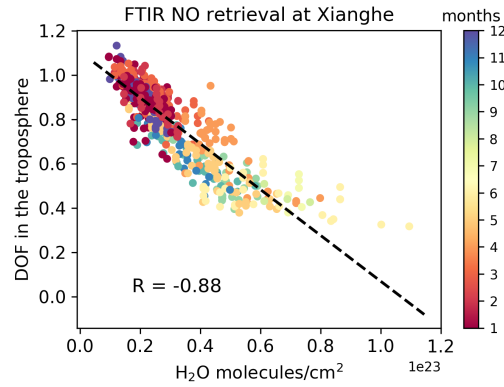
Figure 5. The scatter plots between the DOF in the troposphere and the H_2O total columns from the NCEP data, coloured with the measurement month. The black dashed line is the linear fit, and R is the correlation coefficient.

tropospheric NO partial column are 10.5% and 18.0%, respectively. The random uncertainty of the tropospheric NO partial column is larger as compared to the stratospheric partial column, and it is mainly coming from the smoothing error and the measurement uncertainty.
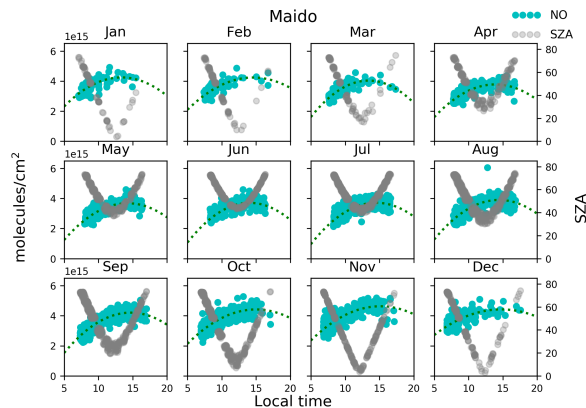
3 Stratospheric NO partial column

3.1 Diurnal variation

Due to photochemical reactions (Kondo et al., 1990), ~~it is expected to observe~~ a large diurnal variation of the stratospheric NO concentration is excepted. Figure 6 shows that the diurnal variations of stratospheric NO partial columns in all months at Maïdo, together with the SZA of the measurements. The stratospheric NO partial columns are fitted with a ~~2-order~~ second

10

Table 2. The retrieval uncertainties of the NO total and partial columns at Xianghe and Maïdo. All uncertainties are in the unit of percentage unites (%).

Site	Xianghe						Maïdo			
	Total column		Troposphere (0-12 km)		Stratosphere (12-60 km)		Total column		Stratosphere (16-60 km)	
	Systematic	Random	Systematic	Random	Systematic	Random	Systematic	Random	Systematic	Random
Smoothing	1.5	12.0	1.7	16.2	1.5	2.4	0.2	3.6	0.1	1.5
Measurement	-	6.0	-	7.5	-	2.5	-	1.7	-	1.4
Retrieved parameters	1.2	1.2	1.1	1.1	1.5	1.5	0.4	0.4	0.5	0.5
Temperature	1.4	0.6	1.5	1.2	2.8	1.5	2.5	0.5	2.6	0.6
Spectroscopy	10.1	-	10.2	-	9.8	-	10.0	-	9.9	-
Solar zenith angle	0.3	1.5	0.4	1.8	0.3	1.6	0.2	1.0	0.2	1.0
Total	10.3	13.5	10.5	18.0	10.2	4.4	10.3	4.2	10.2	2.4

Figure 6. The diurnal variation of stratospheric NO partial column at ~~Xianghe (left) and~~ Maïdo~~(right)~~, together with the solar zenith angle (grey dots). The stratospheric NO partial columns are fitted with a ~~2-order~~ second order polynomial fitting (cyan dotted line).

order polynomial fitting ($y(t) = a + bt + ct^2$; t is ~~in~~ a fraction of local hour). No fitting is applied ~~in August~~ at Xianghe due to the ~~limited successful retrievals.~~ lack of measurements, especially before 9:00 and after 16:00. Note that the fitted line is also plotted at hours with no measurements, but it does not represent the physical reality due to the absence of data.

At ~~Xianghe, the instrument starts measuring normally at 9:00 (local time; same as below) and stops at 16:00. The NO~~
5 ~~stratospheric partial column generally increases with the time. It is found that the NO stratospheric partial column starts decreasing after 14:00 in January, March, April, May, July, October and November. However, the fittings are variable, and have positive curves in February, June, September and December. The fittings at Xianghe are not robust due to the lack of measurements, especially before 9:00 and after 16:00. At~~ Maïdo, the measurement often starts at 7:00 and stops at 17:30. The FTIR measurements show that the stratospheric NO partial column increases with time until about 14:00, and it starts
10 decreasing afterwards. The decrease in NO after 14:00 indicates that more NO is converted to nitrogen dioxide (NO$_2$) than the ~~formed NO~~ NO formed from NO$_2$ at that time. This type of diurnal variation is consistent throughout the whole year at Maïdo. Based on the ~~2-order~~ second order polynomial fittings, it is found that the maximum stratospheric NO partial column occurs at 14.3$\pm$0.4 hours, which is 1.9$\pm$0.6 hours after the time of the minimum of the SZA (about 12:20). There is almost no cloud in the stratosphere, ~~then~~ so the solar radiation intensity is directly proportional to $cos(SZA)$. The stratospheric NO partial
15 columns increase with time in the morning, and we find that there is a good linear relationship between the stratospheric NO partial column and the solar radiation intensity ($cos(SZA)$) between 6:00 and 12:20 (Figure 7), with the R of 0.80 at Xianghe and ~~of~~ 0.74 at Maïdo. The fitted slope at Xianghe is 2.01$\pm$0.16$\times$10^{15}, which is close to the slope of 1.87$\pm$0.12$\times$10^{15} at Maïdo. The FTIR measurements show that the speed on the formation of stratospheric NO in the morning at Maïdo is similar to that at Xianghe.
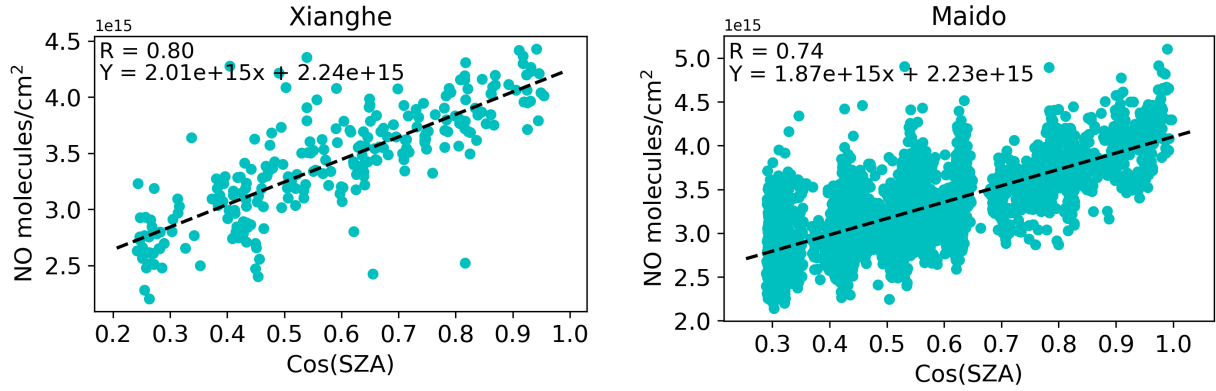
Figure 7. The correlation between the stratospheric NO partial column and the solar radiation ($cos(SZA)$) before 12:20 local time at Xianghe (left) and Maïdo (right), respectively. ~~The~~ R is the correlation coefficient, N is the measurement number, and the black dashed line is the linear fitting.

3.2 Time series and seasonal variation

Figure 8 shows the time series of the FTIR NO retrieved partial columns in the stratosphere at Xianghe and Maïdo. In order to derive the seasonal variation, the daily means $y(t)$ are fitted by a periodic function

$$y(t) = A_0 + A_1 t + \sum_{k=1}^{3} (A_{2k} \cos(2k\pi t) + A_{2k+1} \sin(2k\pi t)), \tag{5}$$

5   where t is ~~in~~ a fraction of year, A_0 is the offset, A_1 is the long-term trend, and A_2 to A_7 are the periodic amplitudes, representing the seasonal variation. The annual relative change in unit of % y^{-1} ~~, which~~ is relative to the mean of data used in the trend analysis. The daily means are calculated from only the measurements between 13:30 and 14:30 local time. The one hour time window around the maximum of the tropospheric NO partial column is used to reduce the impact of the large diurnal variation of the stratospheric NO partial column as we found in Section 3.1. Since the time coverage is relatively short at Xianghe, we

10   assume that there is no long-term trend ($A_1 = 0$).

The mean and std of the stratospheric NO partial columns between 13:30 and 14:30 are $3.6 \pm 0.5 \times 10^{13}$ $molecules/cm^2$ at Xianghe, and $4.0 \pm 0.4 \times 10^{13}$ $molecules/cm^2$ at Maïdo, respectively. The mean of the stratospheric partial columns at Maïdo is larger than that at Xianghe. The seasonal variation of NO is determined by the equilibrium between NO and NO_2 (NO_x) on the one hand and the reservoir substances, such as N_2O_5, HNO_3, $ClONO_2$, on the other hand (Jacob, 1999; Vaughan et al.,

15   2006). The FTIR measurements show that the stratospheric NO partial column is high in summer and low in winter, with a peak-to-peak amplitude of 1.1×10^{15} $molecules/cm^2$ at Xianghe and 0.8×10^{15} $molecules/cm^2$ at Maïdo. Keep in mind that the summer at Maïdo is December-February as it is located in the southern hemisphere.

The decrease in the stratospheric NO partial columns between 2013 and 2019 at Maïdo is observed by the FTIR measurements (-0.42 ± 0.57 %/yr), although the decrease is insignificant as the annual change is within the uncertainty. Galytska et al.

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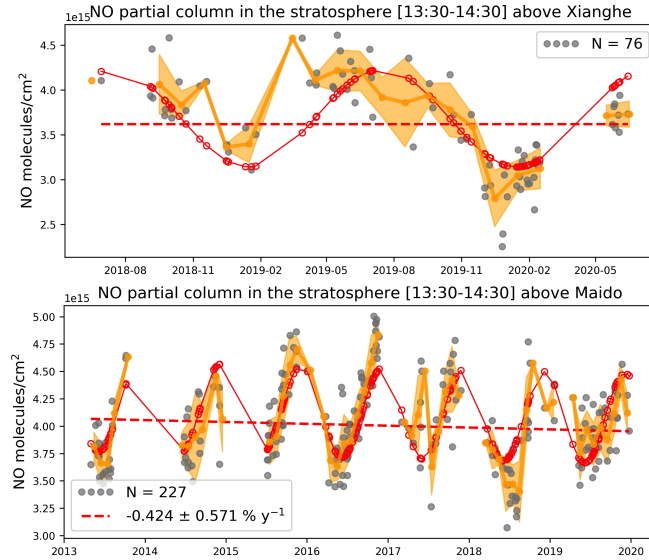
Figure 8. The time series of the FTIR NO retrieved stratospheric partial column daily means (grey dots) and monthly means and stds (yellow dots and shadow) at Xianghe (upper) and Maïdo (lower) for only the measurements between 13:30 and 14:30 local time. N is the measurement days. The red dashed line is the $A_0 + A_1 t$ in Eq. (3), the red dots and the red solid line are the fittings with the seasonal variation.

(2019) observed a significant decrease in NO_2 from the SCIAMACHY satellite measurements in the southern hemisphere between 2002 and 2012, and Dubé et al. (2020) also found a negative NO_x trend in the southern hemisphere derived from SAGE II-OSIRIS satellite measurements and the WACCM model from 2005 to 2014. Although the time coverages of the FTIR measurements at Maïdo and the two previous studies are not the same, all these studies show a consistent negative trend in NO_x in
5   the stratosphere at the latitude of Maïdo.

3.3 Comparison with MIPAS measurements

The MIPAS satellite observed the atmospheric NO concentrations globally between 2002 and 2012. There are two spectral resolutions for the MIPAS spectra: 0.05 cm^{-1} before January 2005 named full spectral resolution (FR) mode and 0.121 cm^{-1} after January 2005 named reduced resolution (RR) mode. In this study, we only use the NO MIPAS data after 2005, and the
10   versions are V5r_NO_220 and V5r_NO_221. As MIPAS has a limb view, the MIPAS only provides NO profile above ~ 10 km. The NO profile is retrieved from MIPAS spectra at 5.3 μm (Bermejo-Pantaleón et al., 2011). The vertical resolution of the NO profile is about 4-6 km, and the uncertainty of the NO profile in the altitude range of 20-60 km is 5-40 % (Sheese et al., 2016).

There are no overlap MIPAS measurements with the FTIR measurements, as Xianghe and Maïdo FTIR both ~~start~~ started
15   measuring after 2012. The MIPAS satellite has two windows overpassing one location (around 10:30 and 22:30 local time). The NO stratospheric partial column observed by MIPAS during the night (22:30) is about 1×10^5 times less than that observed

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during the day (10:30). In this section, we select all the MIPAS measurements between 2005 and 2012 within $\pm$ 2° latitude and $\pm$ 2° longitude around each FTIR site and only use the daytime-overpass measurements to compare with FTIR measurements. To take the vertical sensitivity of the FTIR retrieval into account, the MIPAS NO vertical profile is smoothed with the FTIR AVK (Rodgers and Connor, 2003). To reduce the influence from the diurnal variation in the stratospheric NO partial columns (Figure 6), the FTIR measurements used to compare with MIPAS measurement are limited to the measurements between 9:30 and 11:30.

Figure 9 shows the time series of the stratospheric NO partial columns observed by FTIR and MIPAS measurements above Xianghe and Maïdo. The seasonal variations of the stratospheric NO partial columns ~~are similar~~ observed by MIPAS and FTIR measurements are similar, with a high value in summer and a low value in winter. The amplitudes of the seasonal variations of the stratospheric NO partial columns above Xianghe and Maïdo observed by the MIAPS measurements are 1.65×10^{15} $molecules/cm^2$ and 1.19×10^{15} $molecules/cm^2$, respectively, which are larger than those observed by the FTIR measurements of 1.13×10^{15} $molecules/cm^2$ above Xianghe and 1.09×10^{15} $molecules/cm^2$ above Maïdo. The possible reason for this difference is that the retrieval uncertainty is relatively large for MIPAS measurements, as we see many large values above both sites. The uncertainties of the MIPAS stratospheric NO partial column are 20.5% and 24.7% above Xianghe and Maïdo, respectively.

The MIPAS measurements show that stratospheric NO was increasing above Xianghe and decreasing above Maïdo between 2005 and 2014, which is consistent with the negative NO_x trends in the southern hemisphere and the positive NO_x trends in the northern hemisphere observed by SAGE II-OSIRIS satellite measurements between 2005 and 2014 (Dubé et al., 2020). Above Xianghe, it is impossible to derive the long-term trend from the FTIR measurements because of the limited measurements. Above Maïdo, the annual relative change of stratospheric NO partial columns observed by MIPAS measurements between 2005 and 2012 is -0.62$\pm$0.77 %/yr, which is close to that of -0.68$\pm$0.36 %/yr observed by the FTIR measurements between 2013 and 2019. However, we observe a systematic difference of 0.35×10^{15} $molecules/cm^2$ between MIPAS and FTIR measurements, which ~~is corresponding~~ corresponds to 10.6% relative to MIPAS data and 9.6% relative to FTIR measurements. The difference is within the uncertainties of both the MIPAS and FTIR measurements.

4 Tropospheric NO partial column

In this section, we only use the tropospheric NO partial columns retrieved by the FTIR measurements with a DOF larger than 0.5 in the troposphere at Xianghe. Figure 10 shows the scatter plots between the tropospheric NO partial columns and stratospheric NO partial columns. When the DOF is larger than 0.5 in the troposphere, the R between retrieved tropospheric NO partial columns and stratospheric NO partial columns is only 0.11, indicating that there is no linear relationship between the retrieved tropospheric and stratospheric partial columns, and the retrieved tropospheric and stratospheric partial columns are almost independent. When the DOF is less than 0.5 in the troposphere, the R between retrieved tropospheric NO partial columns and stratospheric NO partial columns is slightly ~~large~~ larger (R=0.30). ~~It is because~~ The reason for this increased correlation

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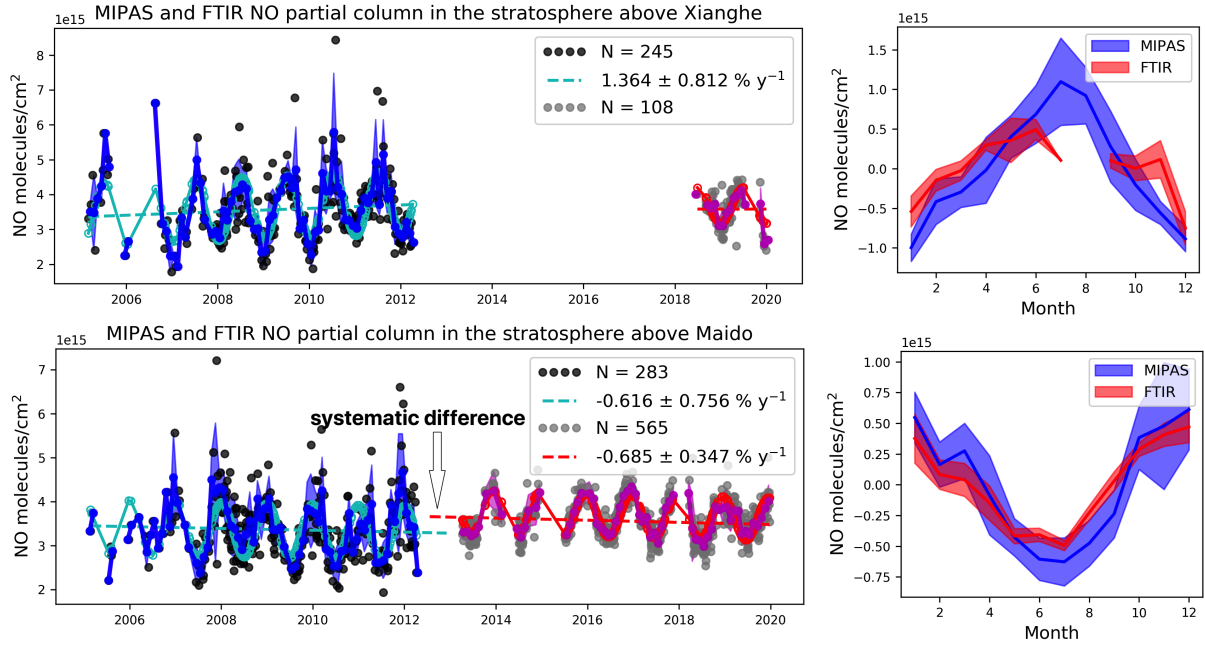
Figure 9. ~~The~~ Left panels: the time series of the stratospheric NO partial columns observed by MIPAS measurements (black dots: daily means; blue solid line: monthly mean; blue shadow: monthly std; ~~blue~~ cyan dashed line: trend fitting) and FTIR measurements (grey dots: daily means; purple solid line: monthly mean; purple shadow: monthly std; red dashed line: trend fitting) above Xianghe (upper) and Maïdo (lower). Right panels: the seasonal variations of the stratospheric NO partial columns observed by MIPAS measurements. The MIPAS measurements are selected within $\pm 2°$ latitude and $\pm 2°$ longitude around the sites. Numbers of the measurement days (N) are 245 and 283 from MIPAS at Xianghe and Maïdo, respectively. The FTIR measurements are selected with the measurement time between 9:30 and 11:~~30. N~~30, with 108 and 565 days at Xianghe and Maïdo, respectively. The annual changes of NO partial columns derived from MIPAS measurements at Xianghe and Maïdo in 2005-2012, and from the FTIR measurements at Maïdo in 2013-2019. A systematic difference is detected between the ~~measurement days~~MIPAS and FTIR NO stratospheric partial columns.
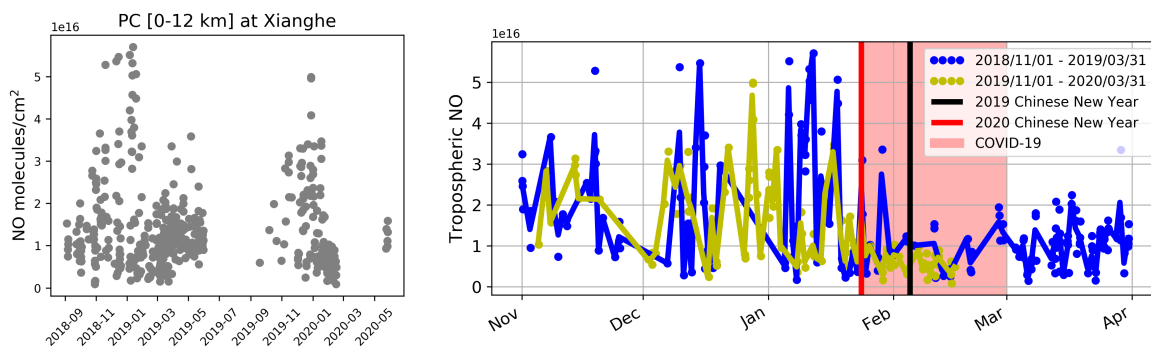
is that the retrieved tropospheric partial column is ~~actually~~ sensitive to the stratosphere, and the individual averaging kernels become broader.

Figure 11 shows the time series of the tropospheric NO partial columns at Xianghe. There is no tropospheric NO measurement in summer due to the high water vapor columns (Figure 5). In addition, due to the COVID-19 lockdown, FTIR NO measurements are not available between 17 February and 23 May 2020. The mean ~~and std~~(std) of the tropospheric NO partial columns are 1.4~~$\times 10^{16}$ molecules/cm^2 and~~ $\pm 1.0 \times 10^{16}$ molecules/cm^2 at Xianghe. The low NO partial column is close to 0, and the high value can reach up to 5.8×10^{16} molecules/cm^2. There is no clear diurnal variation of the tropospheric NO partial columns derived from the FTIR measurements, but there is a large day-to-day variation of NO tropospheric partial columns, especially in winter. The NO partial column during November 2019 - February 2020 is generally lower than that in the previous year. It is found that the FTIR tropospheric NO partial column during the COVID-19 lockdown is much less than

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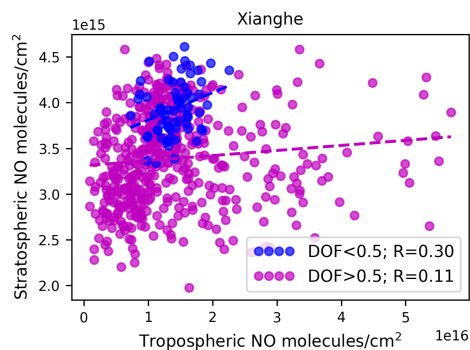
Figure 10. Scatter plots at Xianghe between the tropospheric NO partial columns and stratospheric NO partial columns with the DOF less than 0.5 (blue) and greater than 0.5 (magenta) in the troposphere. R is the correlation coefficient. Only the results at Xianghe is presented here as there is no retrieval with a DOF larger than 0.5 in the troposphere at Maïdo.

Figure 11. Left: the time series of the FTIR retrieved tropospheric NO partial columns at Xianghe. Right: the time series of FTIR retrieved tropospheric NO partial columns during November 2018 - March 2019 and November 2019 - March 2020. The blue and yellow dots are individual measurements and the solid lines are daily means.

that before the lockdown. Moreover, the mean FTIR tropospheric NO partial column between 24 January and 16 February in 2020 is $6.1 \times 10^{15} \ molecules/cm^2$, which is less than the tropospheric NO partial column of $1.1 \times 10^{16} \ molecules/cm^2$ during the same period in 2019. The decrease in tropospheric NO partial column during the COVID-19 lockdown period observed by FTIR measurements at Xianghe is generally consistent with the 25-33% decrease in NO_2 column observed by TROPOMI and OMI satellite measurements (Bauwens et al., 2020), and the 28-48% decrease in NO_2 surface concentration derived from the air pollution sites in Beijing (Wang et al., 2020).

As Xianghe is located in a polluted area, many species have the same anthropogenic sources. For example, both NO and carbon monoxide (CO) are emitted ~~from combustion for~~ by combustion from manufacturing and road transportation (Crippa et al., 2018). The FTIR observed spectra at Xianghe are used to retrieve CO following the NDACC-IRWG recommended
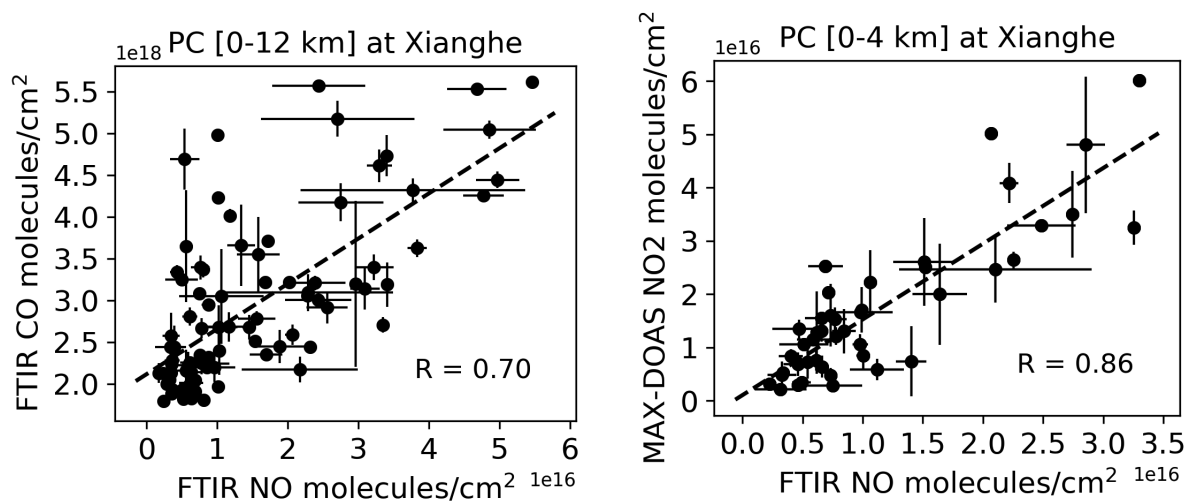
Figure 12. ~~The~~ Left: the correlation between the daily means of the FTIR retrieved NO tropospheric partial columns and the retrieved CO tropospheric partial columns in winter at Xianghe. Right: the correlation between the daily means of the FTIR retrieved NO partial columns and MAX-DOAS retrieved NO₂ partial columns between the surface and 4 km at Xianghe. The error bar is the daily std, and the black dashed line is the linear fit.

method (Zhou et al., 2019). The DOF of the retrieved CO profile is about 2.2, and there is ~~individual~~ independent information in the tropospheric CO partial column (Zhou et al., 2018). Figure 12 shows the correlation between the daily means of FTIR retrieved CO and NO partial columns in the troposphere in winter at Xianghe. The large tropospheric CO and NO partial columns are observed simultaneously. The R is 0.70, indicating that the FTIR measurements can capture the tropospheric NO

5   partial column variability on a synoptic scale.

     Although NO and CO have common emission sources, they are very different species in terms of lifetime, chemistry, and transport. Therefore, we also compare the FTIR NO measurements with the ground-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) NO₂ measurements in the troposphere at Xianghe. The MAX-DOAS instrument is operated at the same building as the FTIR instrument at Xianghe. The MAX-DOAS measurements can provide the lower

10   tropospheric NO₂ partial columns (0-4 km). For more information about the MAX-DOAS NO₂ retrieval technique, we refer to Hendrick et al. (2014) and the references therein. Due to an instrument fail, there is no data between August 2018 and September 2019 for the MAX-DOAS measurements. Nevertheless, we collect all the co-located FTIR NO and MAX-DOAS NO₂ measurements. Figure 12 shows the correlation between the daily means of FTIR retrieved NO and MAX-DOAS retrieved NO₂ partial columns in the lower troposphere (0-4 km) at Xianghe, with the R of 0.86. A good agreement between the NO and

15   NO₂ is observed, and it confirms that the FTIR retrieved tropospheric partial columns are reliable.

5 Conclusions

In this study, the ground-based FTIR solar spectra at Xianghe and Maïdo are applied to retrieve NO using the SFIT4 algorithm, with a focus on the NO partial columns in the troposphere and stratosphere. Xianghe is a polluted site with a high NO mole fraction near the surface, while Maïdo is a background site with a very low NO mole fraction near the surface. The systematic and random uncertainties of the retrieved NO total column are estimated as 10.3% and 13.5% at Xianghe, and 10.3% and 4.2% at Maïdo. The DOF of the retrieved NO profile is 2.3 ± 0.4 at Xianghe and 1.3 ± 0.1 at Maïdo. The systematic and random uncertainties of the retrieved NO partial columns at Xianghe are estimated as 10.5% and 18.0% in the troposphere, and 10.2% and 4.4% in the stratosphere.

At both sites, we can obtain the NO partial column in the stratosphere from the FTIR retrievals. The FTIR retrievals are able to derive the diurnal variation of the NO partial column in the stratosphere during the daytime, especially at Maïdo. It is found that the stratospheric NO partial column increases with time in the morning to about 12:20 and there is a linear relationship between the stratospheric NO partial column and the solar radiation intensity, with the R of 0.80 at Xianghe and 0.74 at Maïdo. The stratospheric NO partial column starts decreasing after about 14:00 at Maïdo, but at Xianghe it is hard to observe such consistent change of the stratospheric NO partial column after 14:00 due to the limited measurements. As there is a large diurnal variation in the stratospheric NO partial column, we use the measurements between 13:30 and 14:30 to derive the seasonal cycle of the stratospheric NO partial column. It is found that the phases of the seasonal variations of the stratospheric NO partial column at these two sites are similar with a high value in local summer and a low value in local winter. Moreover, the FTIR NO partial columns in the stratosphere are compared with the MIPAS satellite observations. After taking the diurnal variation of NO into account, the stratospheric NO partial columns from co-located FTIR and MIPAS measurements show similar seasonal variations at both sites. Above Maïdo, the decrease rate observed by the MIPAS measurements between 2005 and 2012 is close to that observed by the FTIR measurements between 2013 and 2019. The systematic difference between the MIPAS and FTIR measurements is about 10%, which is within their uncertainties.

The tropospheric NO partial column can be retrieved at the polluted site (Xianghe) but not at the background site (Maïdo). We select the retrieval with a DOF in the troposphere larger than 0.5 to calculate the tropospheric NO partial column. Since the SNR of the spectrum is highly ~~depend~~ dependent on the H_2O abundance, the successfully retrieved tropospheric NO is generally under a dry condition with a H_2O total column less than 5.7×10^{22} $molecules/cm^2$ at Xianghe. As a result, the tropospheric NO partial column is ~~almost not available~~ very difficult to retrieve in summer. The mean and std of the tropospheric NO partial columns at Xianghe are $1.4\pm1.0\times10^{16}$ $molecules/cm^2$. The mean FTIR tropospheric NO partial column during the COVID-19 lockdown in 2020 is lower than that before the lockdown period, and also lower than that during the same period in 2019. Large tropospheric ~~CO~~ NO_2 (or CO) and NO partial columns are observed simultaneously, indicating that the synoptic variation in the tropospheric NO partial columns can be well captured from the FTIR retrievals at Xianghe. It is the first study of a successful analysis of NO in the troposphere from a ground-based FTIR site. The tropospheric and stratospheric NO retrieval might be possible at other potential FTIR sites inside/near large cities with enhanced levels of NO near the surface.

Author contributions. MZ wrote the manuscript. MZ, MDM designed the experiment. MZ, BD and EM discussed the conceptualization. CH, NK, JMM and PW collected the FTIR measurements at Xianghe and Maïdo. BL and CV investigated about the FTIR retrieval strategy. All the authors read and commented on the manuscript.

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