

## TABLE OF CONTENTS

<b>Table of Contents.....</b>	<b>i</b>
<b>Author responses to Reviewer #1's comments .....</b>	<b>1</b>
<b>Author responses to Reviewer #2's comments .....</b>	<b>7</b>
<b>Revised manuscript with tracked changes .....</b>	<b>16</b>

## **Responses to Reviewer #1's comments**

### **Box 1.1**

For Table Mountain, a mostly NO<sub>2</sub> free site, the diurnal variation is stratospheric, except for 1 day during the 1-week campaign. The title should say as much. “Stratospheric diurnal variability of NO<sub>2</sub> measured and modelled using direct solar and lunar spectra over Table Mountain, California (34.38°N)”.

We thank the reviewer for this interesting comment. The retrieval technique used in this manuscript does return the total column above the Table Mountain (2.25 km), no matter how small the tropospheric contribution is. The phrase in the original title, “diurnal variability of total column NO<sub>2</sub>”, has an important purpose, which is to inform the reader that our retrieval is limited to the total column NO<sub>2</sub> only and that the diurnal variability is generally a sum of the tropospheric and stratospheric diurnal variability, regardless whether the atmosphere is clean or not. Given this limitation, a diagnostic tool, like the HYSPLIT model, needs to be employed to reveal the tropospheric contribution in some cases where high total column NO<sub>2</sub> is observed, like the one we have in the manuscript on Oct 27 (see new Figure 3). In contrast, if we use the phrase “stratospheric diurnal variability”, we are afraid that the reader might have an impression that we had a retrieval technique that separate the stratospheric column from the total column.

Another suggestion made by the reviewer is to add in the title “and modelled” after “measured”. We are afraid that the suggested title may be a little inaccurate because the diurnal variability is not modelled “using direct solar and lunar spectra”. We thought of something like

“Diurnal variability of total column NO<sub>2</sub> measured using direct solar and lunar spectra over Table Mountain, California (34.38°N) and modelled in a 1-D photochemical model”

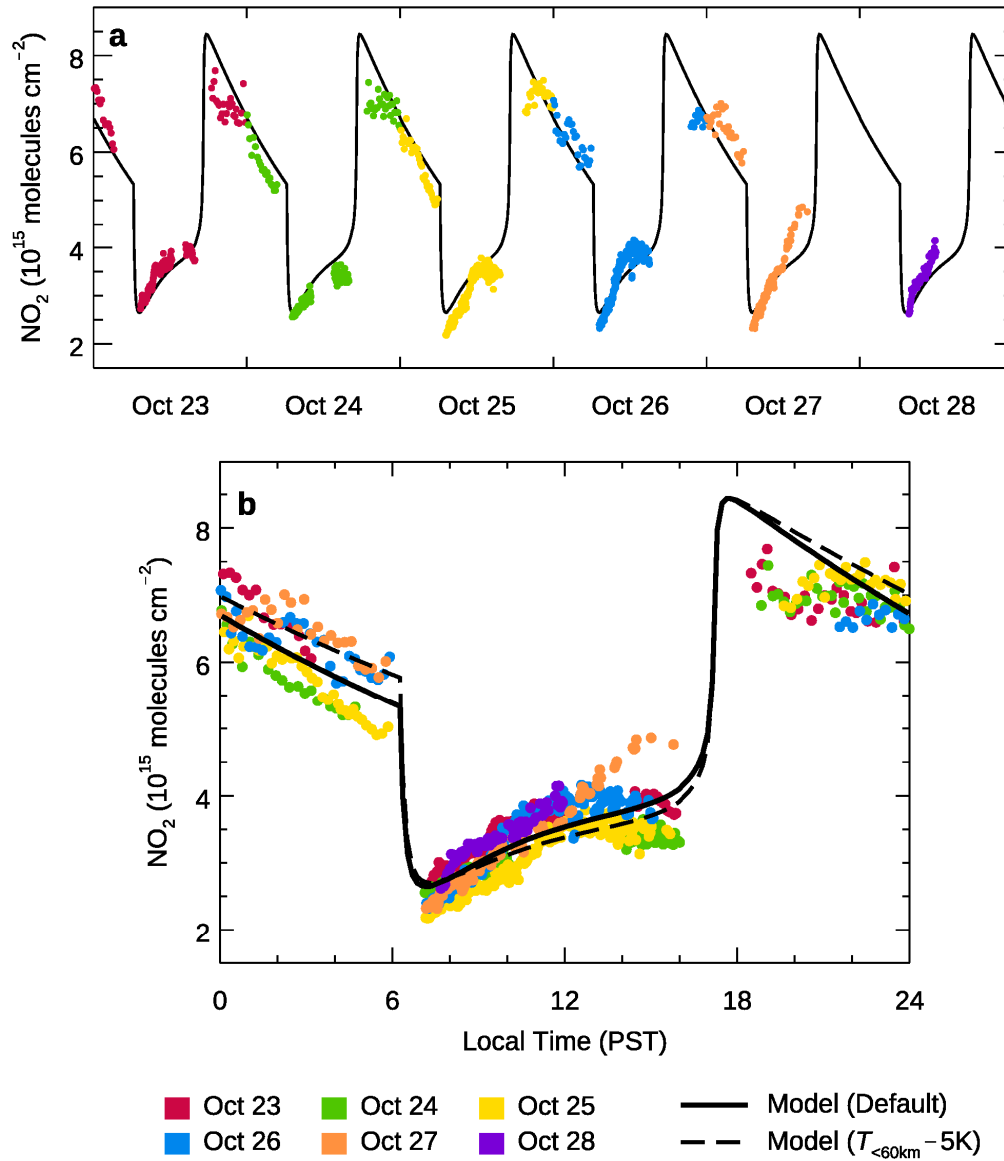
but this title looks a bit long. We think that the original title contains the most important component of the research (retrieval based on direct solar/lunar spectra) and the reader will be able to learn about our modeling work from the abstract. We believe that the original title is a balance of multiple factors. We are happy to continue to consider further suggestions should the reviewer has other concerns about the original title.

Again, we greatly appreciate all suggestions made by the reviewer. We have considered these suggestions very seriously before we made our final decisions.

Box 1.2

Since the authors have 6 days of data, it would be interesting to have an extra figure showing the daily diurnal variation in addition to Figure 3.

We have added a new panel in Figure 3 showing the daily diurnal variations as suggested:



### Box 1.3

The agreement with the model run is quite good except after sunset (Fig. 3) when the magnitude and shape are different. Is there an explanation?

We thank the reviewer for this insightful comment. Although we did not say explicitly in the manuscript, the temperature sensitivity test (Section 3.3) was intended to explore one possible cause of the difference between the model and the observation during the nighttime. The modelled rate of decrease at night with the default temperature is greater than observed (the solid line in Figure 3). Lowering the temperature by 5 K reduces the modelled rate of decrease (the dashed line). Thus, the temperature profile could be a possible reason for the different shapes at night. However, a more definitive study would be needed in future publications to investigate this problem. In response to this comment, we have added a paragraph at the beginning of Section 3.4:

“While the 1-D model simulation captures most of the observed diurnal variability, the rate of decrease in the total NO<sub>2</sub> column during nighttime is slightly overestimated in the model. Here we explore a possible uncertainty due to the prescribed temperature profile.”

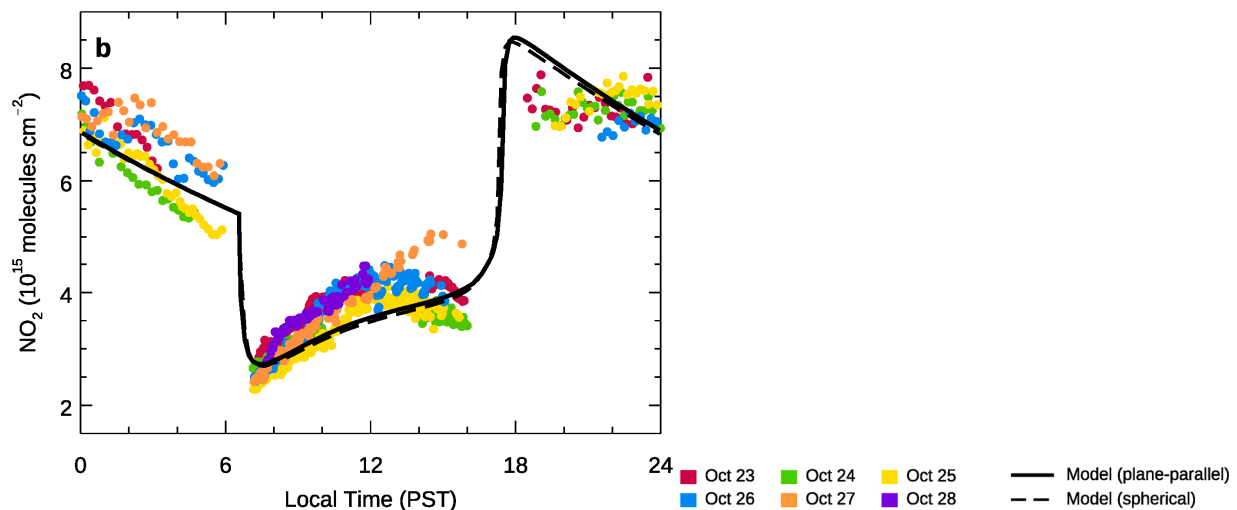
and have revised the conclusion of the same section in Line 333 of the revised manuscript

“Thus, while the equinox temperature profile used in the baseline run is sufficient for the simulation of the diurnal cycle of the NO<sub>2</sub> column, we do not exclude possible effects of temperature uncertainties on the nighttime simulation.”

### Box 1.4

I know this is not a modelling paper, but the treatment of sunrise and sunset seems incomplete. There should be a time delay as a function of altitude with the sun reaching higher altitudes first. Since the authors are not showing data during sunrise and sunset, it does not matter much.

We thank the reviewer for this insightful comment. The model results shown in Figure 4 were calculated assuming a plane-parallel atmosphere. We have conducted another calculation using the spherical geometry, where the sunrise and sunset times are dependent on altitude. We compare the resultant diurnal cycles with the one in the original manuscript below:



The above figure shows that the difference of the two diurnal cycles is much smaller than the spread of the data. Therefore, our conclusions remain unchanged when the spherical geometry is used.

In response to this comment, we added in the above figure in the new Appendix B.

#### Box 1.5

The linear fit in Figure 6 does not mean much, other than as a baseline, as there are two linear regimes, one from 07:00 to 13:00 and from 13:00 to 16:00 hours. Is there an explanation for the two regimes?

The linear fit in Figure 6 is used to compare with an independent measurement over Germany that is discussed in Section 3.3 [Fig. 3a of Sussmann et al., *Atmos. Chem. Phys.*, 5, 2657–2677, 2005, <https://doi.org/10.5194/acp-5-2657-2005>]. Sussmann et al. reported a linear increasing rate of daytime NO<sub>2</sub> for the first time. To consistently compare with their analysis, we follow their definition of a linear fit through the daytime data. Our comparison with their value corroborates the findings over two different sites in mid-latitudes.

Our simulated total column NO<sub>2</sub> also shows a regime change before and after noon, although the simulated regime change is not as strong as in the observation. Thus, based on our photochemical model, the two linear regimes are likely due to the conversion of the reservoir species N<sub>2</sub>O<sub>5</sub>. Apart from the continuous production of NO through the reaction between N<sub>2</sub>O and O(<sup>1</sup>D), the photolysis rate of N<sub>2</sub>O<sub>5</sub> peaks at local noon, causing a quadratic time dependence during the daytime and hence an apparent change in the linear regime before and after local noon. Indeed, in the original manuscript, we pointed out the important role of the N<sub>2</sub>O<sub>5</sub> conversion in Line 232:

“Figure 5 shows that the conversion between the reservoir and NO<sub>2</sub> dominates between 18 km and 34 km, consistent with the NO<sub>2</sub> diurnal cycles. Therefore, the secular NO<sub>2</sub> changes during daytime and nighttime are dominated by N<sub>2</sub>O<sub>5</sub> conversions.”

In response to this comment, we add the following in Line 308 of the revised manuscript:

“Figure 5 shows that the conversion between the reservoir and NO<sub>2</sub> dominates between 18 and 34 km, consistent with the NO<sub>2</sub> diurnal cycles. In particular, the quadratic decreasing trend of the daytime N<sub>2</sub>O<sub>5</sub> is consistent with the quadratic increasing trend of the daytime NO<sub>2</sub>. Therefore, the secular NO<sub>2</sub> changes during daytime and nighttime are dominated by N<sub>2</sub>O<sub>5</sub> conversions.”

#### Box 1.6

On the instrument: What is the stray light?

The stray light is typically of the order of 10<sup>-4</sup>–10<sup>-3</sup>, which is normally not high enough to affect the retrievals. In response to this comment, we added in Line 76:

“The stray light is typically of the order of 10<sup>-4</sup>–10<sup>-3</sup>.”

### Box 1.7

What is the SNR of each measurement?

We have estimated the SNR at full moon transit to be  $\sim 2900$  and the SNR at solar transit to be  $\sim 4900$ . The SNR is estimated by taking the standard deviation of the difference of two consecutive spectra as the noise and the signal being the average intensity. During the low Sun/Moon observations the SNR is more difficult to measure directly. However, the fitting residuals are consistent with these estimates.

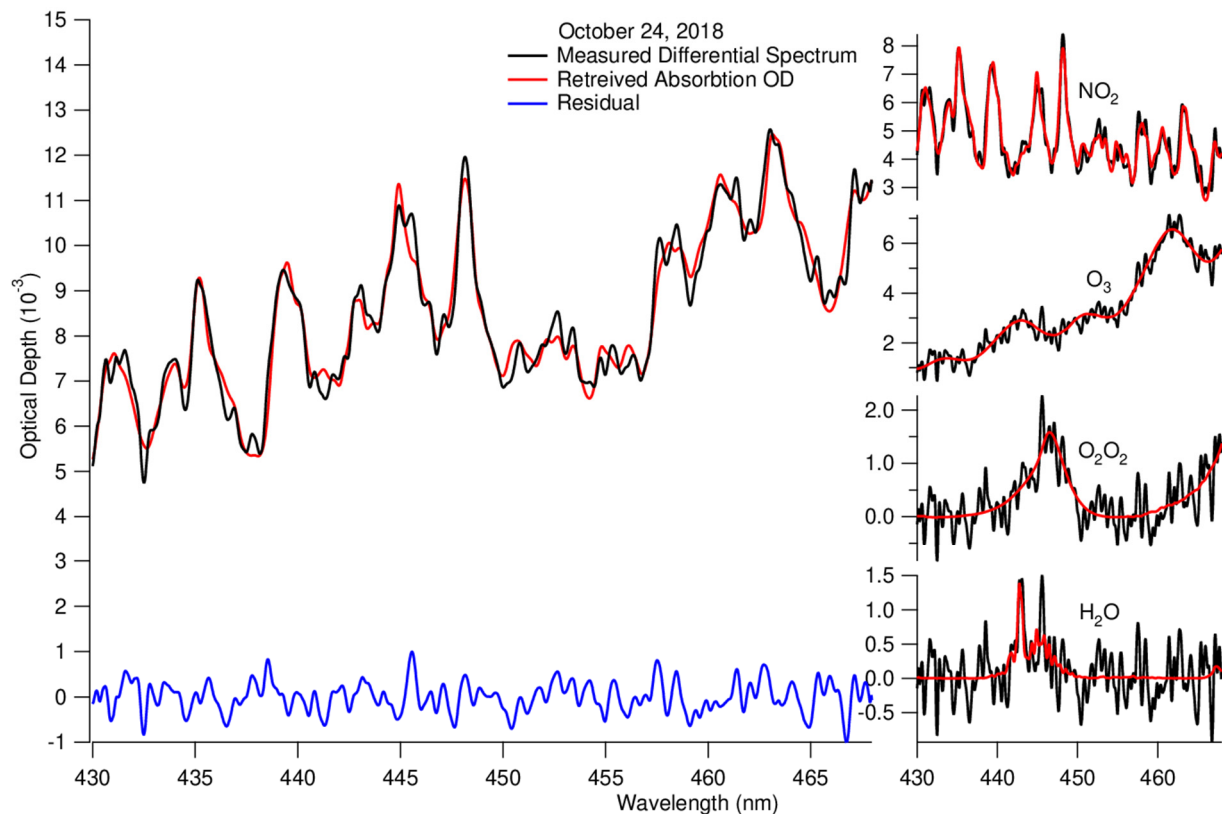
In response to this statement, we have added at the end of Section 2.1 (Line 94):

“We estimate the signal-to-noise ratio (SNR) by assuming that the standard deviation of the difference of two consecutive spectra is close to the noise and that the average intensity of the two consecutive spectra is the signal. As a result, the SNR at full moon and solar transits are  $\sim 2900$  and  $\sim 4900$ , respectively. During the low sun/moon observations the SNR is more difficult to measure directly. However, the fitting residuals are consistent with these estimates.”

### Box 1.8

I know you are working with the standard QDOAS software, but could you give examples of the DOAS fitting and residuals.

We thank the reviewer for this suggestion. We have added a new Figure 2 in the revised manuscript.



The measured spectrum is shown by the black curve on the left panel. The fitted spectrum (red) is overlaid, and the residual spectrum (blue) is shown at the bottom. Four species are considered in the spectral fit: NO<sub>2</sub>, O<sub>3</sub>, O<sub>4</sub>, and H<sub>2</sub>O. The spectral fits are performed simultaneously in QDOAS. The red lines on the right column are the fitted spectra of the corresponding species. To visualize the signal-to-noise ratios, we add the residual spectrum (blue on the left panel) to individual fitted spectra, which are shown as the black spectra in the subpanels on the right.

**Box 1.9**

The writing is clear with no significant errors. The figures are clear and easy to understand. The title should be revised. The paper should be published with only minor changes as described above.

Once again, we thank the reviewer for his/her favour in our manuscript.

## Responses to Reviewer #2's comments

### Box 2.0

King-Fai Li et al 2020 present direct sun and direct moon NO<sub>2</sub> measurements over a high altitude mostly unpolluted site, JPL-TMF near Wrightwood, CA, during 6 days (around full moon) in October 2018. They proposed to combine two Langley-like techniques to estimate amount of NO<sub>2</sub> atmospheric absorption during the reference spectrum measurement time. The proposed approach takes advantage of 1-D photochemical model to estimate diurnal variation in NO<sub>2</sub> and minimum Langley extrapolation technique to reduce the effect of NO<sub>2</sub> pollution. Modeling results are compared with the measurements. Chemical reactions for different processes are shown. Accurate measurements of diurnal NO<sub>2</sub> variation are important and the topic fits into the scope of the “Atmospheric Measurement Techniques” journal.

We thank Reviewer #2 for his/her time and useful comments that have greatly improved our manuscript.

### Box 2.1

Not sufficient measurements (only 6 days) were presented in the paper to apply minimum Langley extrapolation technique (MLE). MLE is a statistical method and requires sufficient data to “accouter” conditions with “constant” vertical columns at each solar zenith angle. This threshold was not met during this study. MLE uses as low percentile for fitting as possible (within SNR) to capture background NO<sub>2</sub>. Increasing percentile used for Langley fitting does not simply improves the statistics, as stated in the paper, but can significantly alter the result. This can be easily remediated by including more measurements, especially at this mostly clean site.

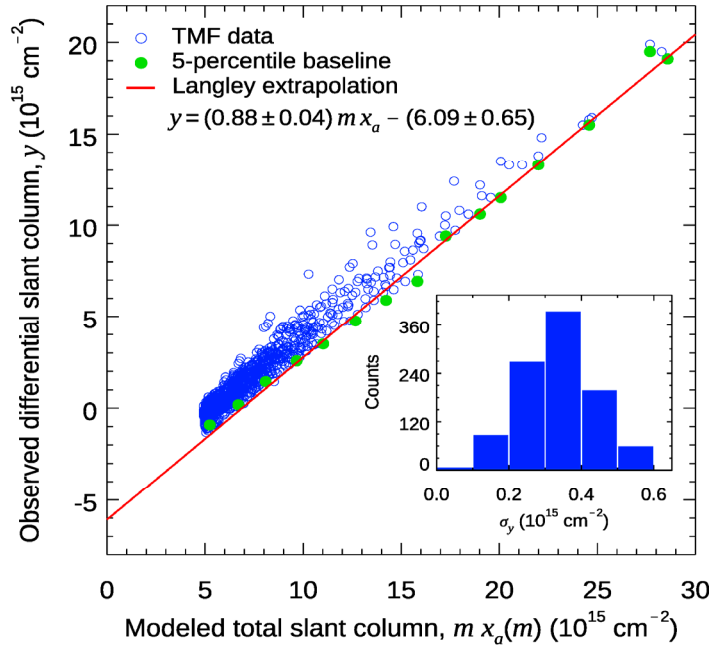
We thank the reviewer for this insightful comment. Since multiple instruments share the same dome at the TMF, the period we could run our instrument has been limited. Our preliminary measurements showed that 2 days away from the full moon would decrease the measured lunar intensity by ~20%, so we performed the measurement only when the moon was almost full to ensure a good signal-to-noise ratio (SNR). In addition to the full moon, we needed a non-cloudy atmosphere. The 6 consecutive days in October 2018 reported in this manuscript were the best period that satisfied these two conditions. It is our best interest to make more 24-hour measurements in the future.

While we agree with the reviewer that a low percentile gives a better representation of the background NO<sub>2</sub> in a polluted site, the measurement over the TMF, as a clean site, may allow a higher percentile for an adequate estimation of the background on the TMF. As our back-trajectory analysis suggests, only one day out of six showed a sign of the urban source. Most vertical spread of the Langley plot is likely due to natural daily variability in the background. We therefore argue that the 20-percentile we used in the original manuscript still lies within the background variation. Nonetheless, we follow the reviewer's suggestion and have performed another Langley extrapolation using the 5-percentile baseline. The resulting equation is



$$y = (0.88 \pm 0.08) m x_a - (6.09 \pm 0.65) \times 10^{15} \quad (5\text{-percentile}).$$

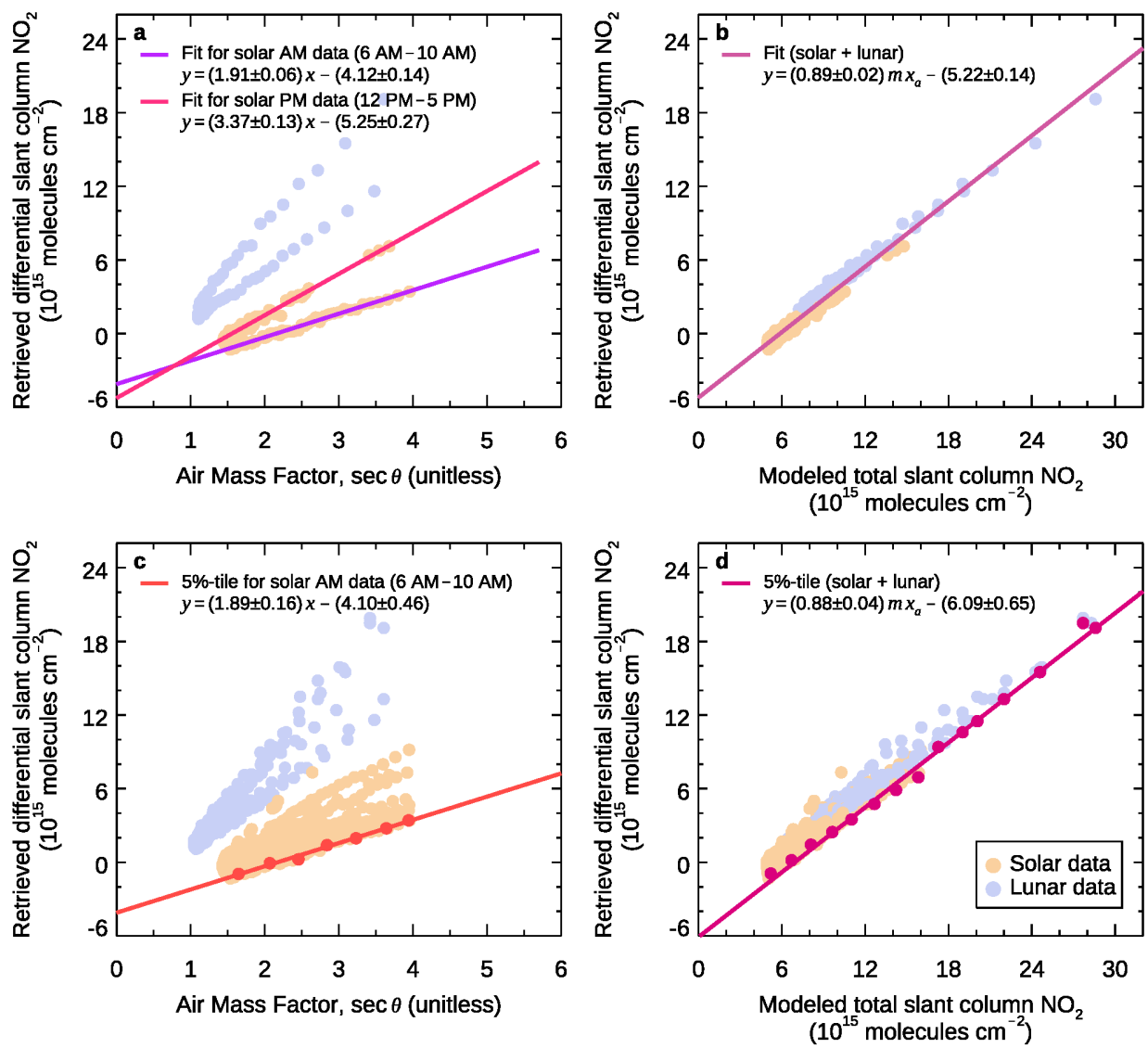
The y-intercept is now  $0.32 \times 10^{15}$  more negative than the previous value obtained using the 20-th percentile in the original manuscript (which was  $5.77 \pm 0.87 \times 10^{15}$ ) but they are well within the  $2\text{-}\sigma$  error. The new result is presented in Figure 3 of the revised manuscript:



### Box 2.2

While the idea of improving estimation of slant column density in the reference spectrum using a 1-D photochemical model is appealing, the authors have not demonstrated that it provides a better result than MLE itself. Looking at the data in Fig. 2 and 3, MLE will most likely result in lower amount in the reference spectrum, and the final vertical columns will agree significantly better with the model diurnal change than the retrieved columns (but will have an offset). Authors need to show that the results are better than the MLE by itself, and for that more measurements are required. Note, that to determine amount in the reference spectrum, full moon is not needed, since the analysis is done on the direct sun data. It is not clear from the presented results if the error in the model simulations actually is smaller than the uncertainty in MLE. This needs to be demonstrated.

We thank the reviewer for this insightful comment. The simulated diurnal cycle is used to remove the asymmetry about noon in the total column  $\text{NO}_2$ . This asymmetry is natural, and it exists even under clean conditions and cannot be dealt with by the standard MLE (as explained in Section 2.3 of the original manuscript). To further illustrate the necessity of the removal of the diurnal asymmetry, we plot the observed total column  $\text{NO}_2$  on a single day (e.g. Oct 25, 2018) against the air mass factor ( $\text{AMF} = \sec \theta$ ) as in a standard MLE.



Panel (a) plots the observations on October 25, 2018 against the air mass factor ( $AMF = \sec \theta$ ) as in a standard MLE. Based on our back-trajectory analysis, the atmosphere above TMF on October 25, 2018 should have little urban  $NO_2$  contamination. Both solar (pale orange dots) and lunar (pale blue dots) data exhibit a U shape that is due to the secular increase and decrease during the daytime and the nighttime, respectively. For the solar data, the AM data lies on the lower arm of the U shape and the PM data lies on the upper arm. For the lunar data, the reverse is true: data before sunrise lie on the upper arm of the U shape and data after sunset lie on the lower arm.

To perform a Langley extrapolation for the data shown in Panel (a), one needs to decide which of the four arms to be used for the linear regression model  $y = a AMF + b$ . The Principle of Minimum-amount suggests that we should start with the lowest arm, i.e. the daytime AM data. Note that in order to obtain the straight line passing through the 2-percentile baseline, we have ignored the points before noon (around 10 AM to 11:30 AM), i.e. points located around the bottom of the U-shape. If we use the observations between 6 AM and 10 AM, we obtain the purple line in Panel (a), which gives a  $y$ -intercept of  $(-4.12 \pm 0.14) \times 10^{15}$  molecules  $cm^{-2}$ .

The above Langley extrapolation, however, does not take any of the daytime PM and all lunar data into account. In particular, the daytime PM data should also be used to define a minimum-amount profile, given the fact that the atmosphere was mostly clean on that day. Suppose we perform another Langley extrapolation using the daytime PM data between 12 PM and 5 PM (rose line). The resultant  $y$ -intercept is  $(-5.25 \pm 0.27) \times 10^{15}$  molecules  $\text{cm}^{-2}$  ( $2-\sigma$ ), which is statistically different from the value obtained using the daytime AM data. A reasonable estimate of the  $y$ -intercept is then the average of the two values, which is  $(-4.69 \pm 0.21) \times 10^{15}$  molecules  $\text{cm}^{-2}$ .

Finally, since the wind on the TMF is mostly downhill during autumn, the lunar data also correspond to a clean atmosphere and should also be used to derive the  $y$ -intercept. If we use all four arms in Panel (a), then the average value of the  $y$ -intercept is  $(-4.36 \pm 0.25) \times 10^{15}$  molecules  $\text{cm}^{-2}$ , where the uncertainty is the root-mean-squares of the uncertainties of the four values.

In the above calculation, the ignorance of the data points near the bottom of the “U”-shape has excluded a large number of observations near local solar/lunar noon and thus the resultant  $y$ -intercept is biased by high zenith angles. It is not clear how the data near the solar/lunar noon may be kept in the standard MLE due to the assumption of the linearity in AMF. As a result, a zenith angle-dependent Langley extrapolation model needs to be developed.

The above example shows that the determination of the  $y$ -intercept of the standard MLE is not straightforward when (i) the background  $\text{NO}_2$  has secular trends in daytime and nighttime and (ii) the daytime and nighttime abundances are different before and after the terminator. In contrast, the modified MLE (MMLE) approach we have developed in this work minimizes the background diurnal asymmetry, so that the “regularized” data points almost form a straight line (Panel b) when they are plotted against the modelled diurnal cycle. The linear regression model  $y = a m x_a + b$ , where  $m x_a$  is the modelled slant column  $\text{NO}_2$ , can be applied to all data points, regardless of the time of the day or whether the data point is a solar or lunar measurement. With this MMLE, the regressed  $y$ -intercept is  $(-5.22 \pm 0.14) \times 10^{15}$  molecules  $\text{cm}^{-2}$ , which is statistically different from the average of the values derived from the four arms in the standard MLE approach.

The issue with the standard MLE is exacerbated when observations on multiple days are plotted against the AMF. The U-shape may be smeared vertically into a continuum (Panel c). The smearing, in our case, are primarily due to natural variability of the background, except for October 27 when total column  $\text{NO}_2$  appears above the continuum of the daytime data due to the urban pollution. As a result, while we are still able to define the minimum-amount profile for the daytime AM data, the determination of the minimum-amount profiles of the daytime PM and the lunar data are difficult. This leaves us the daytime AM data alone for the Langley extrapolation (red line) but, as shown above, the resultant  $y$ -intercept  $[(-4.10 \pm 0.46) \times 10^{15}$  molecules  $\text{cm}^{-2}]$  may be biased.

In contrast, the observed data points still almost form a straight line in the MMLE approach when they are plotted against the modelled diurnal cycle (Panel d). This allows the determination of the minimum-amount profile using all solar and lunar measurements (raspberry line). The resultant  $y$ -intercept,  $(-6.09 \pm 0.65) \times 10^{15}$  molecules  $\text{cm}^{-2}$ , is again statistically different from the one obtained using the standard MLE approach.

As pointed out in Box 2.1 and Box 2.8, 2 days away from the full moon would decrease the lunar signal by 20%. We thus focused on full moon to ensure a high SNR for testing our instrument.

In response to this comment, we have put the above argument in a new Appendix A of the revised manuscript.

### Box 2.3

It is unclear what benefits this approach (1D stratospheric model) will have under the “persistent” pollution levels when the total NO<sub>2</sub> abundance is dominated by anthropogenic emissions at all times.

As explained in Box 2.3 (and Appendix A of the revised manuscript), the standard MLE may have a bias in the y-intercept because the total column NO<sub>2</sub> has a natural diurnal asymmetry in the background, regardless of the pollution level. The removal of the natural diurnal asymmetry using the 1-D stratospheric model is thus necessary for NO<sub>2</sub>. The removal is also necessary to monitor the pollution level.

In addition, Table Mountain has been providing ground-based measurements for validating satellite retrievals because the site is away from the Los Angeles area and the tropospheric contribution to NO<sub>2</sub> is generally low, even during summer daytime when upslope wind from the southwest (through LA downtown) is the strongest compared to other seasons, as discussed in one of our previous publications (Wang et al., JGR 2010, 10.1029/2009JD013503, cited in the original manuscript). We thus anticipate that pollution does not pose much of a problem in our MMLE. Furthermore, the more data we have in the future, the more accurate will be the minimum-amount baseline of the Langley plot, which can be directly compared with the 1-D stratospheric model. Indeed, in the original manuscript, we wrote (Line 136):

“When a large number of measured NO<sub>2</sub> columns on clean and polluted days are plotted together against  $m x_a(m)$ , the baseline of the scattered data may be considered as the background NO<sub>2</sub> diurnal cycle in a clean atmosphere (Herman et al., 2009).”

In response to this comment, we clarify in the revised manuscript (Line 190):

“Our measurements made during October (a non-summer season) were mostly under unpolluted conditions. Thus, we applied the MMLE to derive a baseline for an estimation of the background NO<sub>2</sub> diurnal cycle, which is then used in the regression with the modelled diurnal cycle.”

### Box 2.4

Description of the DOAS fitting settings is not sufficient. What are polynomial orders (e.g. broad band, offset, wavelength shift), what sources of other gases cross sections and at what temperatures were used in the analysis? Were NO<sub>2</sub> cross sections at all five temperatures used in the retrieval? If yes, how they were fitted and combined? Why this fitting window was selected (430 and 468 nm)? How exactly air mass factor was calculated? What is the DOAS fitting quality of NO<sub>2</sub> from direct sun and direct moon (residual OD)?

We use 3<sup>rd</sup> order polynomials for broadband and offset. The NO<sub>2</sub> cross section is from Nizkorodov et al. (2004) for 215 K, 229 K, 249 K, 273 K, and 299 K, as discussed in the original manuscript. The O<sub>3</sub> cross section is from Serdyuchenko et al. (2014) for 11 temperature references ranging from 193 K to 293 K. The O<sub>4</sub> cross section is from Thalman and Volkamer 2013 at 273 K, and

H<sub>2</sub>O cross section at 296 K is from HITRAN 2016. All five cross sections were used to create a single NO<sub>2</sub> reference. The yearly average from the TMF temperature LIDAR are used to derive a reference for each altitude level by linear interpolation between each adjacent cross-section, which is also adjusted for pressure broadening using the results of Nizkorodov et al. (2004). Each level's reference is then multiplied by a weight which is proportional to the standard atmosphere and then summed to obtain a single reference used in the fitting. A similar procedure was used for the O<sub>3</sub> reference; for O<sub>4</sub> and H<sub>2</sub>O only a single reference was used.

As shown in Figure 3 of Spinei et al. (2014), the 430–468 nm window has stronger NO<sub>2</sub> absorptions relative to other wavelengths in the 411–475 nm range. In addition, this window also has less interfering absorption from other species. These two factors add up to increase the accuracy of the DOAS spectral fit.

The air mass is calculated using secant of the solar/lunar zenith angle,  $\sec(VZA)$ . Herman et al. (2009) considered an altitude correction in this equation. However, the correction is generally negligible except for  $VZA > 80^\circ$  but we do not make measurements at those VZAs.

The new Figure 2 in the revised manuscript shows an example of the spectral fit.

In response to this comment, we have added the above descriptions in the revised Section 2.2:

“The differential slant column NO<sub>2</sub> is retrieved by fitting the ratioed spectrum in a smaller window between 430 and 468 nm. This window has stronger NO<sub>2</sub> absorptions relative to other wavelengths in the instrument range (411–475 nm); see Figure 3 of Spinei et al. (2014). In addition, this window also has less interfering absorption from species other than the O<sub>3</sub>, O<sub>4</sub> (O<sub>2</sub> dimer), and H<sub>2</sub>O (see below).

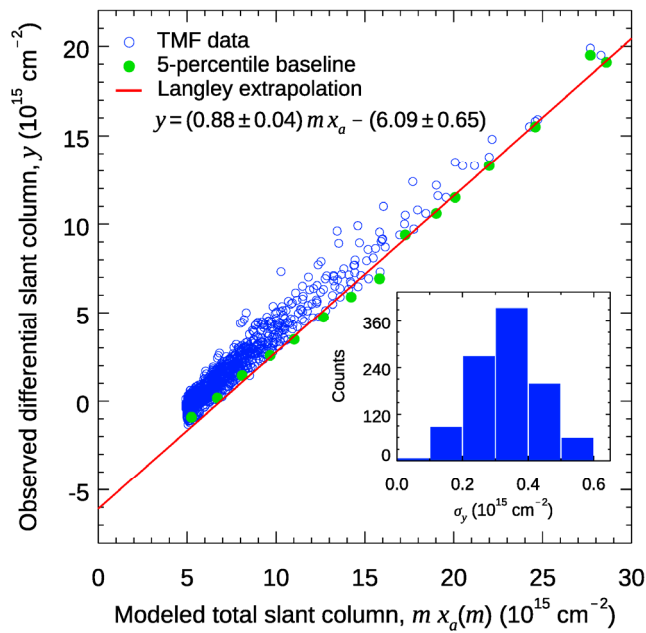
The spectral fitting is accomplished through the Marquardt-Levenberg minimization using QDOAS retrieval software (<http://uv-vis.aeronomie.be/software/QDOAS/>). The highly spectrally resolved NO<sub>2</sub> absorption cross sections at  $T = 215$  K, 229 K, 249 K, 273 K, 298 K, and 299 K based on Nizkorodov et al. (2004) are convolved to the instrument resolution using the instrument line shape function and the Voigt line shape prior to its use in QDOAS. The yearly average from the TMF temperature LIDAR measurements are used to derive a reference for each altitude level by linear interpolation between each adjacent cross-section, which is also adjusted for pressure broadening using the results of Nizkorodov et al. (2004). We use 3rd order polynomials for broadband and offset. All five cross sections were used to create a single NO<sub>2</sub> reference. Each level's reference is then multiplied by a weight which is proportional to the standard atmosphere and then summed to obtain a single reference used in the fitting. In addition to NO<sub>2</sub>, other absorptions by O<sub>3</sub>, O<sub>4</sub> (O<sub>2</sub> dimer), and H<sub>2</sub>O in the same spectral window are simultaneously retrieved. The O<sub>3</sub> cross section is from Serdyuchenko et al. (2014) for 11 temperature references ranging from 193 K to 293 K. Like NO<sub>2</sub>, all 11 cross-sections are used in the spectral fitting for O<sub>3</sub>. In contrast, for O<sub>4</sub> and H<sub>2</sub>O, only a single temperature reference is used. The O<sub>4</sub> cross section is from Thalman and Volkamer (2013) at 273 K. The H<sub>2</sub>O cross section at 296 K is from HITRAN 2016 (Gordon, 2017). Figure 2 shows an example of a fitted spectrum on October 24, 2018. The NO<sub>2</sub> abundance retrieved from QDOAS is the desired differential slant column NO<sub>2</sub> relative to our chosen reference spectrum.

The air mass factor is calculated using secant of the solar/lunar zenith angle. Herman et al. (2009) considered an altitude correction of the air mass factor. The altitude

correction is generally negligible except for zenith angles  $\geq 80^\circ$  but we do not make measurements at those zenith angles (see Section 2.1).”

**Box 2.5**  
**No error budget is presented for the measured NO<sub>2</sub> columns.**

We considered two major sources of error: the fitting residual of the DOAS spectral fit and the error of the y-intercept of the Langley extrapolation. The errors from the QDOAS fitting residual generally lies between than  $0.1 \times 10^{15} \text{ cm}^{-2}$  and  $0.6 \times 10^{15} \text{ cm}^{-2}$  ( $2\text{-}\sigma$ ) for all zenith angles, which is now shown in an inset of Figure 3 of the revised manuscript:



The error of the y-intercept of the Langley extrapolation is  $\pm 0.65 \times 10^{15} \text{ cm}^{-2}$  ( $2\text{-}\sigma$ ), which is also added in the revised Figure 3 (see the figure above). The root-mean-square of these two sources of error gives an estimate of a total error of  $\sim 0.9 \times 10^{15} \text{ cm}^{-2}$  ( $2\text{-}\sigma$ ).

In response to this comment, we added in the revised manuscript in Line 143:

The  $2\text{-}\sigma$  uncertainty due to the spectral fitting residual lies between  $0.1 \times 10^{15}$  molecules  $\text{cm}^{-2}$  and  $0.6 \times 10^{15}$  molecules  $\text{cm}^{-2}$ , with a mean of  $\sim 0.4 \times 10^{15}$  molecules  $\text{cm}^{-2}$ . The distribution of the retrieval uncertainty is shown in Figure 2 (inset).

and in Line 198:

“We estimate the total retrieval uncertainty to be the root-mean-square of the spectral fitting uncertainty and the uncertainty in  $y_0$ , which is  $0.8 \times 10^{15}$  molecules  $\text{cm}^{-2}$  ( $2\text{-}\sigma$ ).”

### Box 2.6

The paper in general reads more like a modeling paper than the measurement paper.

Thanks for this comment. Actually, Reviewer #1 has an opposite comment. The aim of this paper is to present a new instrument for measuring daytime and nighttime NO<sub>2</sub> column. Perhaps the confusion may be due to the frequent appearances of models in the retrieval strategy and the back-trajectory calculations. However, the 1-D stratospheric model is mainly used to assist, not determine, the retrieval (by minimizing the diurnal asymmetry). The retrieval per se is still observation-based, in contrast to the common Bayesian-based approach where the statistics of the *a priori* model is also used to constrain the retrieved value.

In response to this comment, in the revised manuscript, we have removed the phrase “model-based” from the name of our method. Instead, our method is now called “the modified minimum-amount Langley extrapolation” or MMLE in short.

### Box 2.7

There are routine NO<sub>2</sub> stratospheric measurements conducted by the NDACC stations (zenith sky DOAS) and total column measurements of NO<sub>2</sub> using direct sun and direct moon within Pandora Global Network. They should be mentioned in the review of NO<sub>2</sub> measurements. In general, citations tend to include mostly early works and not give current status.

We thank the reviewer for mentioning these references. We are aware of them. Indeed, we have used NDACC NO<sub>2</sub> data in our recent publication (Wang et al., Solar 11-Year Cycle Signal in Stratospheric Nitrogen Dioxide—Similarities and Discrepancies Between Model and NDACC Observations, *Solar Phys.*, doi:10.1007/s11207-020-01685-1, 2020, cited in the revised manuscript). In addition, MF-DOAS and Pandora were used in our earlier publication (Wang et al., 2010, cited in the original manuscript).

In response to this comment, we have added a number of references involved in NDACC and PGN. In particular, the statement in Line 24:

“NO<sub>2</sub> column abundance has been measured using ground-based instruments since the mid-1970s [Network for the Detection of Atmospheric Composition Change (NDACC), <http://www.ndacc.org>] ...”

has been revised as

“NO<sub>2</sub> column abundance has been measured using ground-based instruments since the mid-1970s [Network for the Detection of Atmospheric Composition Change (NDACC), <http://www.ndacc.org>] (e.g., Hofmann et al., 1995; Piters et al., 2012; Roscoe et al., 1999; Roscoe et al., 2010; Vandaele et al., 2005; Kreher et al., 2020) ...”

In addition, the statement in Line 59:

“Other techniques, such as balloon-based *in situ* measurements (May and Webster, 1990; Moreau et al., 2005), balloon-based solar occultations (Camy-Peyret, 1995) and ground-

based multi-axis DOAS (MAX-DOAS; Hönninger et al., 2004; Sanders et al., 1993) have also been employed to further characterize the vertical distributions of NO<sub>2</sub>.”

has been revised as

“Other techniques, such as balloon-based *in situ* measurements (May and Webster, 1990; Moreau et al., 2005), balloon-based solar occultations (Camy-Peyret, 1995), as well as ground-based multi-axis DOAS (MAX-DOAS; Hönninger et al., 2004; Sanders et al., 1993), multi-functional DOAS, and Pandora (Herman et al., 2009; Spinei et al., 2014) that have been actively involved in NDACC and the Pandora Global Network (Kreher et al., 2020), have also been employed to further characterize the vertical distributions of NO<sub>2</sub>.”

#### Box 2.8

It is unclear how the lunar measurement where taken. Lunar irradiance is about 10<sup>6</sup> lower than solar irradiance. In this study, integration time for sun measurements is 16 times shorter than for moon. Difference in lunar vs solar measurements (diffusers, filters, etc), and what effect it has on spectrometer illumination should be presented. Target signal-to-noise ratio stated.

We apologize for the confusion. For the sunlight measurement, we insert a diffuser plate to reduce the solar throughput by a factor of  $\sim 1.3 \times 10^{-5}$  and protect the instrument. The diffuser plate is not used during the moonlight measurement. Since the sun is  $\sim 400,000$  times the intensity of the full moon, the ratio between the light hitting our detector for solar noon (after inserting the diffuser and the filter) and lunar noon during the full moon is  $\sim 5$ . Thus, in order to maintain an approximately constant solar and lunar signal-to-noise ratio and fitting residuals, we need to vary slightly the exposure time during specific times of solar and lunar noon, typically around  $\sim 3$  s for lunar noon and  $\sim 0.6$  s for solar noon, giving a ratio of  $\sim 5$  to balance out the photon counts mentioned above. In the original manuscript, we wrote the statement (Line 77)

“The exposure time was 4 s and 0.25 s during the lunar/solar noon observations, respectively.”

The 4 s and 0.25 s are the full range of exposure times between which we varied during that week of measurement in October 2018, but the writing of this statement may be confusing. The exposure times were not constant during the measurement.

In response to this comment, the above quoted statement has been revised to (Line 86)

“When direct moonlight is measured, the diffuser plates are removed. Since the sun is  $\sim 400,000$  times the intensity of the full moon, the ratio between the light hitting our detector for solar noon (after inserting the diffuser plates) and lunar noon during the full moon is  $\sim 5$ . To maintain an approximately constant solar and lunar signal-to-noise ratio and fitting residuals, we vary the exposure time during specific times of solar and lunar noon, typically around  $\sim 3$  s for lunar noon and  $\sim 0.6$  s for solar noon, giving a ratio of  $\sim 5$  to homogenize the solar and lunar photon counts mentioned above.”



# Diurnal variability of total column NO<sub>2</sub> measured using direct solar and lunar spectra over Table Mountain, California (34.38°N)

King-Fai Li<sup>1</sup>, Ryan Khoury<sup>1</sup>, Thomas J. Pongetti<sup>2</sup>, Stanley P. Sander<sup>2</sup>, Yuk L. Yung<sup>2,3</sup>

<sup>1</sup>Department of Environmental Science, University of California, Riverside, California, USA

5 <sup>2</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA

<sup>3</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA

Correspondence to: King-Fai Li (king-fai.li@ucr.edu)

**Abstract.** A full diurnal measurement of total column NO<sub>2</sub> has been made over the Jet Propulsion Laboratory's Table Mountain Facility (TMF) located in the mountains above Los Angeles, California, USA (2.286 km above mean sea level, 34.38°N, 117.68°W). During a representative week in October 2018, a grating spectrometer measured the telluric NO<sub>2</sub> absorptions in direct solar and lunar spectra. The total column NO<sub>2</sub> is retrieved using a **modified** minimum-amount Langley extrapolation, which enables us to accurately treat the non-constant NO<sub>2</sub> diurnal cycle abundance and the effects of pollution near the measurement site. The measured 24-hour cycle of total column NO<sub>2</sub> on clean days agrees with a 1-D photochemical model calculation, including the monotonic changes during daytime and nighttime due to the exchange with the N<sub>2</sub>O<sub>5</sub> reservoir and the abrupt changes at sunrise and sunset due to the activation or deactivation of the NO<sub>2</sub> photodissociation. The observed daytime NO<sub>2</sub> increasing rate is  $(1.31 \pm 0.41) \times 10^{14} \text{ cm}^{-2} \text{ h}^{-1}$ . The total column NO<sub>2</sub> in one of the afternoons during the measurement period was much higher than the model simulation, implying the influence of urban pollution from nearby **counties**. A 24-hour back-trajectory analysis shows that the wind first came from inland in the northeast and reached the southern Los Angeles before it turned northeast and finally arrived TMF, allowing it to pick up pollutants from Riverside County, Orange County, and Downtown Los Angeles.

Deleted: model-based

Deleted: 29

Deleted: 30

Deleted: cities

## 1 Introduction

Nitrogen dioxide (NO<sub>2</sub>) plays a dominant role in the ozone (O<sub>3</sub>)-destroying catalytic cycle (Crutzen, 1970). NO<sub>2</sub> column abundance has been measured using ground-based instruments since the mid-1970s [Network for the Detection of Atmospheric Composition Change (NDACC), <http://www.ndacc.org>] (e.g., Hofmann et al., 1995; Piders et al., 2012; Roscoe et al., 1999; Roscoe et al., 2010; Vandaele et al., 2005; Kreher et al., 2020), which serve as the standards for validating satellite measurements. Noxon (1975) and Noxon et al. (1979) retrieved the stratospheric NO<sub>2</sub> column by differential optical absorption spectroscopy (DOAS) in the visible spectral range using ratios of scattered sunlight from the sky and direct sun/moonlight at low (noon/midnight) and high (twilight) air mass factors over Fritz Peak, Colorado (39.9°N). Since the optical path of sun/moonlight at dawn or dusk (solar/lunar zenith angle  $\approx 90^\circ$ ) is much longer than the optical path of the direct sunlight at noon/midnight, the NO<sub>2</sub> absorption in the noon/midnight spectrum can be assumed to be small and the NO<sub>2</sub> absorption in the

Deleted: (

Deleted: ,

twilight slant column could therefore be isolated effectively by ratioing the scattered twilight spectrum to the scattered noon spectrum. This DOAS principle also applies to ratios of direct moonlight or sunlight at low and high air mass factors. Noxon et al.'s (1979) measurements revealed sharp changes of the stratospheric NO<sub>2</sub> column before and after sunsets and sunrises at mid-latitudes. Similar DOAS measurements at high latitudes in the 1980s focused on the role of NO<sub>x</sub> in controlling O<sub>3</sub> and active halogen species in the polar stratosphere (Fiedler et al., 1993; Flaud et al., 1988; Keys and Johnston, 1986; Solomon, 1999). Johnston and McKenzie (1989) and Johnston et al. (1992) reported a reduction in the southern hemispheric NO<sub>2</sub> over Lauder, New Zealand (45.0°S), following the eruptions of El Chichón (in 1982) and Pinatubo (in 1991), respectively.

NO<sub>2</sub> column abundance has also been measured using direct solar spectra acquired by Fourier-Transform infrared (FTIR) spectrometers. Advantages of direct solar measurements are the lack of Raman scattering in the spectra, air mass factors determined geometrically rather than through a radiative transfer code, and provision of NO<sub>2</sub> column abundances at most times during the day. Sussmann et al. (2005) retrieved the stratospheric NO<sub>2</sub> column abundance over Zugspitze, Germany (47°N) using the infrared absorption in the solar spectrum near 3.43 μm. The stratospheric NO<sub>2</sub> column abundance was then subtracted from the total column estimated from satellite measurements to obtain the tropospheric column. Wang et al. (2010) demonstrated how high spectral resolution measurements using a Fourier transform spectrometer could perform absolute NO<sub>2</sub> column abundance retrievals without the need for a solar reference spectrum. Because of the solar rotation, the Fraunhofer features in the UV spectra acquired simultaneously from the east and west limbs of the solar disk are Doppler shifted while the telluric NO<sub>2</sub> absorptions are not shifted (Iwagami et al., 1995). Thus, the telluric NO<sub>2</sub> absorptions can be identified by correcting the Doppler shift without the need of an *a priori* solar spectrum. Other techniques, such as balloon-based *in situ* measurements (May and Webster, 1990; Moreau et al., 2005), balloon-based solar occultations (Camy-Peyret, 1995), as well as ground-based multi-axis DOAS (MAX-DOAS; Hönninger et al., 2004; Sanders et al., 1993), multi-functional DOAS, and Pandora (Herman et al., 2009; Spinei et al., 2014) that have been actively involved in NDACC and the Pandonia Global Network (Kreher et al., 2020), have also been employed to further characterize the vertical distributions of NO<sub>2</sub>.

Here we retrieve the total column NO<sub>2</sub> over Table Mountain Facility (TMF) in Wrightwood, California, USA (2.286 km above mean sea level, 34.38°N, 117.68°W) using Langley extrapolation to determine the reference spectrum and considering both daytime and night time chemistry. Daytime NO<sub>2</sub> concentration remains significant, albeit small relative to the night-time concentration, and varies from morning to afternoon. This daytime variation has been a source of error in determination of the DOAS reference spectrum using Langley extrapolation. Comprehensive assessment of NO<sub>2</sub> must include both daytime and nighttime values. We therefore also retrieve daytime column NO<sub>2</sub> by acquiring direct sun spectra throughout the day. We will compare the daytime and nighttime total column NO<sub>2</sub> with those simulated in a one-dimensional (1-D) photochemical model. The effect of urban pollution on the measured total column NO<sub>2</sub> can be deduced from this comparison.

Deleted: ) and

Deleted: traditionally

## 2 Data and Method

### 70 2.1 Instrumentation and measurement technique

The grating spectrometer used for the NO<sub>2</sub> spectral measurement is similar to the one used by Chen et al. (2011) and is installed in the same observatory. A heliostat and a telescope are used to direct and launch light into a fibre optic bundle placed at the focal plane of the telescope (Figure 1). The bundle consists of 19 silica fibres, 200 μm in diameter, arranged in a circular configuration (in SMA 905 connectors) on the source end and in a linear pattern on the spectrograph end. Before entering the spectrograph, light is passed through an order sorting filter (Schott GG-400 glass) and a shutter. The imaging spectrograph is a Princeton Instruments SP-2-300i with a 0.3-m focal length used with a 1200 g mm<sup>-1</sup> grating blazed at 500 nm. A CCD detector (Princeton Instruments PIXIS 400B) is placed at the focal plane of the spectrograph. The 1340 × 400 imaging array of 20 × 20 μm<sup>2</sup> pixels are vacuum sealed and thermoelectrically cooled to -80 °C.

80 ~~Our assessment showed that 2 days away from the full moon would decrease the measured lunar intensity by ~20%. Therefore, in the following analysis, we only focus on~~ acquired direct moon and direct sun spectra ~~that are within 5 to 7 days of the full moon in order to maximize the signal-to-noise ratio (SNR). In addition, to minimize the terminator effects near sunrise/sunset, we use measurements with~~ lunar/solar zenith angles less than 80°. ~~The stray light is typically of the order of 10<sup>-4</sup>-10<sup>-3</sup>.~~

85 When direct sunlight ~~is measured~~, two ground glass diffuser plates ~~are~~ inserted into the beam prior to the telescope primary to integrate over the entire solar disk and to attenuate light. Additional attenuation of light to avoid detector saturation ~~is~~ accomplished by placing a 23% open area screen in the beam just after the diffuser plates. ~~Overall, the solar throughput is reduced by a factor of ~1.3×10<sup>-5</sup>.~~ The resulting spectrum has a spectral grid spacing on the detector of 0.048 nm from 411 nm to 475 nm with a measured line shape of 0.34-nm FWHM sampled at ~7 pixels. Spectral calibration and line shape measurements ~~are~~ accomplished using a diffuse reflection of an Argon lamp near the fibre end, which gives a nearly linear result between pixel and wavelength with a small second order correction; the second order correction is considered in the calibration and the ODOAS fitting, ~~(see next section).~~

95 ~~When direct moonlight is measured, the diffuser plates are removed. Since the sun is ~400,000 times the intensity of the full moon, the ratio between the light hitting our detector for solar noon (after inserting the diffuser plates) and lunar noon during the full moon is ~5. To maintain an approximately constant solar and lunar signal-to-noise ratio and fitting residuals, we vary the~~ exposure time ~~during specific times of solar and lunar noon, typically around ~3 s for lunar noon and ~0.6 s for solar noon, giving a ratio of ~5 to homogenize the solar and lunar photon counts mentioned above.~~ At higher zenith angles, longer exposures were taken to keep the detector counts in the same range. The data were dark-corrected and averaged to obtain the desired signal levels; for the sun, this was consistently ~4 minutes; for the moon, the averaging time varied from ~8 minutes during the night of the full moon to 24 minutes on the night 3 days from full moon.

100 ~~We estimate the SNR by assuming that the standard deviation of the difference of two consecutive spectra is close to the noise and that the average intensity of the two consecutive spectra is the signal. As a result, the SNR at full moon and solar~~

Deleted: We

Deleted: for

Deleted: ° and 5 to 7 days surrounding the full moon.

Deleted: was used

Deleted: were

Deleted: was

Deleted: were

Deleted: . The

Deleted: was 4

Deleted: 25

Deleted: during the lunar/solar noon observations, respectively

Deleted:

115 transits are ~2900 and ~4900, respectively. During the low sun/moon observations the SNR is more difficult to measure directly. However, the fitting residuals are consistent with these estimates.

## 2.2 The DOAS retrieval

120 The DOAS technique is used to retrieve the NO<sub>2</sub> slant column (Noxon, 1975; Noxon et al., 1979; Platt et al., 1979; Stutz and Platt, 1996). A spectrum measured by the grating spectrometer at any time of the day is ratioed to a pre-selected reference spectrum. From the ratioed spectrum, we retrieve the differential slant column NO<sub>2</sub> relative to the column that is represented by the reference spectrum. The total slant column is then the sum of the differential slant column and the reference column.

125 Our reference spectrum is a solar spectrum measured at the TMF ground level at local noon (Chen et al., 2011). This solar reference spectrum is used to ratio all other spectra collected, including those during the solar and lunar measurement cycles. In principle, one can retrieve the reference NO<sub>2</sub> column from the reference spectrum. However, this requires precise knowledge of the solar spectrum at the top of the atmosphere in order to isolate the NO<sub>2</sub> absorption. We will use a variant of the Langley extrapolation to circumvent the need of the retrieval of the reference column (Lee et al., 1994; Herman et al., 2009); see following section for details.

130 The differential slant column NO<sub>2</sub> is retrieved by fitting the ratioed spectrum in a smaller window between 430 and 468 nm. This window has stronger NO<sub>2</sub> absorptions relative to other wavelengths in the instrument range (411–475 nm); see Figure 4 of Spinei et al. (2014). In addition, this window also has less interfering absorption from species other than the O<sub>3</sub>, O<sub>4</sub> (O<sub>2</sub> dimer), and H<sub>2</sub>O (see below).

135 The spectral fitting is accomplished through the Marquardt-Levenberg minimization using QDOAS retrieval software (<http://uv-vis.aeronomie.be/software/QDOAS/>). The high-resolution NO<sub>2</sub> absorption cross-sections at T = 215 K, 229 K, 249 K, 273 K, 298 K, and 299 K based on Nizkorodov et al. (2004) are convolved to the instrument resolution using the instrument line shape function and the Voigt line shape prior to its use in QDOAS. The yearly average from the TMF temperature LIDAR measurements are used to derive a reference for each altitude level by linear interpolation between each adjacent cross-section, which is also adjusted for pressure broadening using the results of Nizkorodov et al. (2004). We use 3rd order polynomials for broadband and offset. All five cross-sections were used to create a single NO<sub>2</sub> reference. Each level's reference is then multiplied by a weight which is proportional to the standard atmosphere and then summed to obtain a single reference used in the fitting. In addition to NO<sub>2</sub>, other absorptions by O<sub>3</sub>, O<sub>4</sub> (O<sub>2</sub> dimer), and H<sub>2</sub>O in the same spectral window are simultaneously retrieved. The O<sub>3</sub> cross section is from Serdyuchenko et al. (2014) for 11 temperature references ranging from 193 K to 293 K. Like NO<sub>2</sub>, all 11 cross-sections are used in the spectral fitting for O<sub>3</sub>. In contrast, for O<sub>4</sub> and H<sub>2</sub>O, only a single temperature reference is used. The O<sub>4</sub> cross-sections are from Thalman and Volkamer (2013) at 273 K. The H<sub>2</sub>O cross-sections at 296 K are from HITRAN 2016 (Gordon et al., 2017). Figure 2 shows an example of a fitted spectrum on October 24, 2018. The NO<sub>2</sub> abundance retrieved from QDOAS is the desired differential slant column NO<sub>2</sub> relative to our chosen reference spectrum.

**Deleted:** between 430 and 468 nm.

**Deleted:** highly spectrally resolved

**Deleted:**

**Deleted:** 215 K, 229 K, 249 K, 273 K, 298 K, and 299 K

**Deleted:** The temperature profile for the calculation of the Voigt line shape is determined by the yearly average of the TMF temperature lidar measurements.

The 2- $\sigma$  uncertainty due to the spectral fitting residual lies between  $0.1 \times 10^{15}$  molecules  $\text{cm}^{-2}$  and  $0.6 \times 10^{15}$  molecules  $\text{cm}^{-2}$ , with a mean of  $\sim 0.4 \times 10^{15}$  molecules  $\text{cm}^{-2}$ . The distribution of the retrieval uncertainty is shown in Figure 3 (inset).

Deleted: 2.3

Deleted: model-based

The air mass factor is calculated using secant of the solar/lunar zenith angle. Herman et al. (2009) considered an altitude correction of the air mass factor. The altitude correction is generally negligible except for zenith angles  $\geq 80^\circ$  but we do not make measurements at those zenith angles (see §2.1).

### 2.3 The modified minimum-amount Langley extrapolation (MMLE)

Let  $y$  be the differential slant column  $\text{NO}_2$  along the line-of-sight,  $y_0$  the reference column  $\text{NO}_2$ ,  $m$  the stratospheric airmass factor (which is proportional to the geometric secant of the solar zenith angle in the stratosphere for these direct solar and lunar observations), and  $x$  the total vertical column  $\text{NO}_2$ ;  $x$  is our target quantity. The differential slant column can be approximated as the total vertical column multiplied by the stratospheric airmass factor after the subtraction of the reference column:

$$y = m x - y_0 \quad (1)$$

If  $y_0$  were known, then  $x$  would be simply  $m^{-1}(y + y_0)$ . The Langley extrapolation technique for determination of the extra-terrestrial reference obtains  $x$  and  $-y_0$  as the slope and the intercept of the linear regression of  $y$  against  $m$ , respectively, assuming  $x$  is temporally constant (i.e. the vertical column does not change during the course of the day). In this formalism, the reference column  $y_0$  is an extrapolated value corresponding to hypothetical zero airmass ( $m = 0$ ).

The Langley extrapolation was first used to measure the solar spectrum at the top of the atmosphere (Langley, 1903) and has also been used to measure atmospheric constituents (e.g., Jeong et al., 2018; Toledano et al., 2018; Barreto et al., 2017; Huber et al., 1995; Bhartia et al., 1995). However, the assumption of a constant  $x$  is often violated due to diurnal variabilities in the atmospheric constituents driven by, e.g., the incident solar radiation, transmittance, dynamics, and human activities. In our case, the afternoon total column  $\text{NO}_2$  is greater than the morning total column  $\text{NO}_2$  (see our Figure 4). Several modifications have been proposed to relax the assumption of a constant  $x$  (e.g., Ångström, 1970; Shaw, 1976; Long and Ackerman, 2000; Cachorro et al., 2008; Kreuter et al., 2013; Marengo, 2007). In this work, we combine the modifications used in Lee et al. (1994) and Herman et al. (2009) to account for the effects due to the  $\text{NO}_2$  diurnal variability and urban pollution.

Deleted: circulation

Deleted: 3

Lee et al. (1994) replaced the constant  $x$  with an *a priori* function of  $m$ , denoted by  $x_a(m)$ :

$$y = \alpha m x_a(m) - y_0, \quad (2)$$

Eq. (2) is analogous to Eq. (1) except that now  $y$  is regressed against the product  $m x_a(m)$ ,  $\alpha$  is the slope of the regression line, and it serves as an effective scaling factor that adjusts the chemical rates in the *a priori* knowledge. Eq. (2) presents a

Deleted: ;

Deleted: target quantity that will be obtained from the

Deleted: .  $\alpha$

Deleted: model.

195 modified Langley extrapolation. The  $y$ -intercept,  $y_0$ , obtained from the modified Langley extrapolation is then used to derive the observed total vertical column through the transformation  $m^{-1}(y + y_0)$ . Note that  $\alpha$  is not used in this transformation.

Deleted: model-based

As in Lee et al. (1994), assuming the chemical processes of  $\text{NO}_2$  are much faster than the dynamical processes so that the  $\text{NO}_2$  diurnal cycle is at photochemical equilibrium, we obtain  $x_a(m)$  from a 1-D photochemical model (to be described in the next section). The  $x_a(m)$  we use corresponds to a clean atmosphere only. To perform the regression, we plot  $y$  against the product  $m x_a(m)$  (Figure 3, blue open circles). If all  $\text{NO}_2$  columns are measured on clean days, then they would ideally fall

Deleted: 2

200 on a straight line (which, apart from the natural variability in the background, holds true for Lee et al.'s (1994) measurements over Antarctica). However, if there is a pollution source near a measurement site, like the TMF, then some of the measured  $\text{NO}_2$  column may be significantly higher than  $x_a(m)$ , leading to a large vertical spread in the scattered plot. The pollution-induced deviation from  $x_a(m)$  may be highly variable, depending on the source types and the meteorology. When a large number of measured  $\text{NO}_2$  columns on clean and polluted days are plotted together against  $m x_a(m)$ , the baseline of the scattered data may be considered as the background  $\text{NO}_2$  diurnal cycle in a clean atmosphere (Herman et al., 2009). Herman et al. (2009) called their method the minimum-amount Langley extrapolation (MLE). Expanding on their terminology, we call our method, which combines the MLE with Lee et al.'s modification, the modified MLE, or MMLE. Note, however, that the MMLE differs from the optimal estimation that is commonly used in satellite retrieval, where the statistics of priori knowledge is used to constrain the retrieved value; no prior constraint is used in the MMLE.

Deleted: .

205 Our measurements made during October (a non-summer season) were mostly under unpolluted conditions (see §3.5). Thus, we applied the MMLE to derive a baseline for an estimation of the background  $\text{NO}_2$  diurnal cycle, which is then used in the regression with the modelled diurnal cycle. On the Langley plot (Figure 3), we divide the range of  $m x_a(m)$  (from  $\sim 5 \times 10^{15}$  to  $3 \times 10^{16}$  molecules  $\text{cm}^{-2}$  during our campaign) into 20 equal bins. We use the 5-percentile of the  $y$  distribution in each bin to define a baseline (Figure 3, green dots). We then fit the 5-percentile baseline to Eq. (2) and obtain the values of  $\alpha$  and  $y_0$  (Figure 3, red line). The fitted line in Figure 3 gives  $\alpha = 0.88 \pm 0.04$  and  $y_0 = (6.09 \pm 0.65) \times 10^{15}$  molecules  $\text{cm}^{-2}$  (at 2- $\sigma$  levels). This value of  $y_0$  is our reference column used for both daytime and nighttime measurements. We estimate the total retrieval uncertainty to be the root-mean-square of the spectral fitting uncertainty and the uncertainty in  $y_0$ , which is  $0.9 \times 10^{15}$  molecules  $\text{cm}^{-2}$  (2- $\sigma$ ).

Deleted: Following

Deleted: 's

Deleted: terminology, we call our

Deleted: model-based

Deleted: .

210 Our measurements made during October (a non-summer season) were mostly under unpolluted conditions (see §3.5). Thus, we applied the MMLE to derive a baseline for an estimation of the background  $\text{NO}_2$  diurnal cycle, which is then used in the regression with the modelled diurnal cycle. On the Langley plot (Figure 3), we divide the range of  $m x_a(m)$  (from

Deleted: To obtain

Deleted: .

215  $\sim 5 \times 10^{15}$  to  $3 \times 10^{16}$  molecules  $\text{cm}^{-2}$  during our campaign) into 20 equal bins. We use the 5-percentile of the  $y$  distribution in each bin to define a baseline (Figure 3, green dots). We then fit the 5-percentile baseline to Eq. (2) and obtain the values of  $\alpha$  and  $y_0$  (Figure 3, red line). The fitted line in Figure 3 gives  $\alpha = 0.88 \pm 0.04$  and  $y_0 = (6.09 \pm 0.65) \times 10^{15}$  molecules  $\text{cm}^{-2}$  (at 2- $\sigma$  levels). This value of  $y_0$  is our reference column used for both daytime and nighttime measurements. We estimate the total retrieval uncertainty to be the root-mean-square of the spectral fitting uncertainty and the uncertainty in  $y_0$ , which is  $0.9 \times 10^{15}$  molecules  $\text{cm}^{-2}$  (2- $\sigma$ ).

Deleted: Herman et al. (2009) used

Deleted: 2

Deleted: . To enhance the statistical robustness of the baseline, we use the 20-percentile instead (Figure 2)

Deleted: 20

Deleted: 2

Deleted: 2

Deleted:

Deleted: =  $5.77 \times 10^{15}$

Deleted: .

## 2.4 The photochemical model

220 Our  $x_a(m)$  is based on the Caltech/JPL 1-D photochemical model (Allen et al., 1984; Allen et al., 1981; Wang et al., 2020), shown as the black solid line in Figure 4. This photochemical model includes the stratospheric species that are important for  $\text{O}_3$ , odd-nitrogen ( $\text{NO}_x = \text{N} + \text{NO} + \text{NO}_2 + \text{NO}_3 + 2\text{N}_2\text{O}_5$ ) and odd-hydrogen ( $\text{HO}_x = \text{H} + \text{OH} + \text{HO}_2$ ) chemistry, including the reactions discussed in §3.1. Nitrous oxide ( $\text{N}_2\text{O}$ ) is the main parent molecule of  $\text{NO}_2$  in the lower stratosphere. The concentration of  $\text{N}_2\text{O}$  at the ground level of the model is fixed at 330 ppb

Deleted: 3

Deleted: Section

(<https://www.esrl.noaa.gov/gmd/hats/combined/N2O.html>). The kinetic rate constants are obtained from the 2015 JPL Evaluation (Burkholder et al., 2015).

250 The sunrise/sunset times and the solar noontime in the model are calculated using the ephemeris time. We use Newcomb parameterizations of the perturbations due to the Sun, Mercury, Venus, Mars, Jupiter, and Saturn (Newcomb, 1898). We also use Woolard parameterizations for the nutation angle and rate (Woolard, 1953). More modern calculation of the ephemeris time may be used (e.g., Folkner et al., 2014) but the difference in the resulting ephemeris time is small (less than 0.1 s) and does not significantly impact our model simulation.

255 We progress the model in time until the diurnal cycle of the stratospheric NO<sub>2</sub> becomes stationary. Throughout the progression, the pressure and temperature profiles are fixed and do not vary with time. The model latitude is set at 34.38°N and the model day is set as October 26. The total column NO<sub>2</sub> is the vertical integral of the NO<sub>2</sub> concentration. The simulation represents the NO<sub>2</sub> abundance in a clean atmosphere without tropospheric sources.

### 3 Results and Discussions

#### 3.1 Diurnal variation in total column NO<sub>2</sub>

260 Figure 4 presents our preliminary observational data (colour dots) obtained during October 23–28, 2018. During the measurements, the skies were mostly clear or only partly cloudy, so we were able to make continuous solar spectral measurements throughout the whole period. During October, the local sunrise and sunset time were around 07:00 PST and 18:00 PST, respectively. At sunrise and sunset, the ambient twilight in the background of the moonlight occultation should be accounted for in the NO<sub>2</sub> retrieval, which is beyond the scope of this work. For this work, we exclude lunar total column NO<sub>2</sub> data when the ambient scattered twilight, including those from civil sources, is significant, which typically occurs when the lunar elevation angle is less than 6° above the horizon. Figure 4a shows the daily diurnal cycles during the week of measurements and Figure 4b shows the aggregated diurnal cycle as a function of local time. The solid black line in both panels is the simulated 24-hour cycle of the total column NO<sub>2</sub> variability in the 1-D model. The dashed line in Figure 4b is a second simulation with a slightly lower temperature (see §3.4). Overall, the baseline simulation captures the observed trends during the daytime and the nighttime. The observations reveal day-to-day variability, but our back-trajectory analysis shows that the day-to-day variations during October 23–26 and 28 are likely due to natural variability of the background in the north while that on October 27 is likely due to urban sources from the Los Angeles basin in the south (see §3.5)

275 On most days, the total column NO<sub>2</sub> over TMF increased from  $\sim 2 \times 10^{15}$  molecules cm<sup>-2</sup> in the morning to  $\sim 3.5 \times 10^{15}$  molecules cm<sup>-2</sup> in the evening. There are 3 main sources of NO<sub>x</sub> contributing to the daytime increase. The ultimate source is the reaction of N<sub>2</sub>O with excited oxygen O(<sup>1</sup>D) resulting from the photolysis of O<sub>3</sub> in the stratosphere between 20–60 km, which produces nitric oxide (NO) molecules and eventually NO<sub>2</sub> through the NO<sub>x</sub> cycle aided by O<sub>3</sub>:

Deleted: 3

Deleted: The solid black line of Figure 3

Deleted: Section

Deleted: 3



285 Another major source is the photolysis of the reservoir species, nitric acid ( $\text{HNO}_3$ ) and dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ):



290 There is also a small source due to the photolysis of  $\text{NO}_3$ :



but this source is not significant due to the low  $\text{NO}_3$  abundance during daytime.  $\text{NO}_2$  is converted back into  $\text{NO}$  through the  
295 reaction with oxygen atom ( $\text{O}$ ) in the upper stratosphere (above 40 km):




or via photolysis below 40 km:

300



But since  $\text{NO}$  and  $\text{NO}_2$  are quickly interconverted within the  $\text{NO}_x$  family, Reactions R6 and R7 do not contribute to a net loss  
of  $\text{NO}_2$ . The ultimate daytime loss of  $\text{NO}_2$  is the reaction with the hydroxyl radicals ( $\text{OH}$ ) that forms  $\text{HNO}_3$ , which may be  
305 transported to the troposphere, followed by rainout:



The significant deviation of daytime  $\text{NO}_2$  from the model simulation on October 27 was likely due to urban pollution (see  
310 ).

At sunset, the photolytic destruction (Reaction R7) in the upper stratosphere terminates while the conversion of  $\text{NO}$   
(Reaction R2) continues in the lower stratosphere. Meanwhile, the production of  $\text{O}$  is significantly reduced, which also reduces  
the loss of  $\text{NO}_2$  via Reaction R6. As a result, the total column  $\text{NO}_2$  increases by a factor of  $\sim 3$  at sunset.

Deleted: section

Deleted: 4



Next, the total column NO<sub>2</sub> decreases from  $\sim 6.5 \times 10^{15}$  molecules cm<sup>-2</sup> after sunset to  $\sim 4.5 \times 10^{15}$  molecules cm<sup>-2</sup> before sunrise. During nighttime, NO<sub>2</sub> is converted to N<sub>2</sub>O<sub>5</sub> via the reaction with O<sub>3</sub> and NO<sub>3</sub>:



Most N<sub>2</sub>O<sub>5</sub> stays throughout the night, although there is a small portion that thermally dissociates back to NO<sub>2</sub> and NO<sub>3</sub>. Thus, the net effect is a secular decrease in nighttime NO<sub>2</sub>.

Finally, at sunrise, photolytic reactions resume, resulting in an abrupt decrease in the total NO<sub>2</sub> column by a factor of  $\sim 2$  due to Reactions R6 and R7.

### 3.2 Vertical profile of NO<sub>2</sub> production and loss

To better understand the contributing factors of the variability of total column NO<sub>2</sub>, we show the simulated vertical NO<sub>2</sub> profile in Figure 5. The NO<sub>2</sub> concentration is dominant between 20 km and 40 km (Figure 5a). At noontime, the model NO<sub>2</sub> profile has a peak of  $\sim 1.7 \times 10^9$  molecules cm<sup>-3</sup> at 30 km (Figure 5a, orange line). At mid-night, the NO<sub>2</sub> concentration is much higher throughout the stratosphere. The corresponding peak has a larger value of  $\sim 2.4 \times 10^9$  molecules cm<sup>-3</sup> and is shifted slightly upward to 32 km (Figure 5a, green line). Therefore, the total column NO<sub>2</sub> is dominated by the variability near 30 km.

The diurnal cycles of the NO<sub>2</sub> concentration at altitudes between 14 km and 38 km are shown in Figure 5b. These cycles show that the daytime increase and the nighttime decrease occur only in the lower stratosphere between 18 km and 34 km. At other altitudes, the daytime and nighttime NO<sub>2</sub> concentrations are relatively constant. The NO<sub>2</sub> cycles closely resemble those of N<sub>2</sub>O<sub>5</sub>. Figure 6 shows the N<sub>2</sub>O<sub>5</sub> concentrations between 14 km and 34 km. During daytime, N<sub>2</sub>O<sub>5</sub> is photolyzed into NO<sub>2</sub> and NO<sub>3</sub> through Reaction R4, leading to an increase in the daytime NO<sub>2</sub>; during nighttime, NO<sub>2</sub> is thermally converted into N<sub>2</sub>O<sub>5</sub> through Reactions R9 and R10, leading to a decrease in the nighttime NO<sub>2</sub>. Figure 6 shows that the conversion between the reservoir and NO<sub>2</sub> dominates between 18 km and 34 km, consistent with the NO<sub>2</sub> diurnal cycles. In particular, the quadratic decreasing trend of the daytime N<sub>2</sub>O<sub>5</sub> is consistent with the quadratic increasing trend of the daytime NO<sub>2</sub>. Therefore, the secular NO<sub>2</sub> changes during daytime and nighttime are dominated by N<sub>2</sub>O<sub>5</sub> conversions.

### 3.3 Daytime NO<sub>2</sub> increasing rate

Reactions (R1)–(R5) contribute the daytime increase of NO<sub>2</sub>. Sussmann et al. (2005) first obtained a daytime NO<sub>2</sub> increasing rate from ground-based measurements. They reported an annually averaged value of  $(1.02 \pm 0.06) \times 10^{14}$  cm<sup>-2</sup> h<sup>-1</sup> over Zugspitze, Germany (2.96 km, 47°N). For October alone, they obtained a value of  $(1.20 \pm 0.57) \times 10^{14}$  cm<sup>-2</sup> h<sup>-1</sup>. For comparison, we calculate the daytime increasing rate using our data between 7 AM and 4 PM. To obtain a rate corresponding to a clean atmosphere, we define a baseline of the diurnal cycle using the 20-percentile in the 15-minute bins from 7 AM to 4

Deleted: 4  
Deleted: 4a  
Deleted: 10<sup>15</sup>  
Deleted: 2  
Deleted: 4a  
Deleted: 10<sup>15</sup>  
Deleted: 2  
Deleted: 4a  
Deleted: 4b  
Deleted: 5  
Deleted: 5

PM (Figure 7). This results in a total of 37 bins, which is roughly the number of points in October shown in Figure 4a of Sussmann et al. (2005). We then apply the linear regression to the baseline and obtain an increasing rate of  $(1.31 \pm 0.41) \times 10^{14} \text{ cm}^{-2} \text{ h}^{-1}$  in October over TMF (34.4°N). Thus our value is consistent with Sussmann et al.'s (2005) value.

### 3.4 Temperature sensitivity

While the 1-D model simulation captures most of the observed diurnal variability, the rate of decrease in the total NO<sub>2</sub> column during nighttime is slightly overestimated in the model. Here we explore a possible uncertainty due to the prescribed temperature profile.

The chemical kinetic rates in the model are dependent on temperature. The temperature profile that has been used to obtain the baseline diurnal cycle corresponds to a zonal mean temperature profile at the equinox and 30° latitude (Figure 8, solid line). To test the sensitivity of the simulated 24-hour cycle of NO<sub>2</sub> column, we reduce the input temperature below 60 km by 5 K (Figure 8, dashed line). Note that the 5 K reduction is much larger than the observed tidal variation in stratospheric temperature below 50° latitude, which is ~0.1 K in the lower stratosphere and ~1 K in the middle stratosphere (Sakazaki et al., 2012). We choose this exaggerated reduction in order to clearly show the temperature effect on the NO<sub>2</sub> chemistry.

Figure 4b (dash-dotted line) shows the simulated NO<sub>2</sub> column using the reduced temperature profile. Because of the reduction in temperature, the nighttime loss due to the reactions with O<sub>3</sub> and NO<sub>3</sub> through Reactions R9 and R10 is slower. As a result, the simulated nighttime NO<sub>2</sub> column is higher than the baseline simulation but the rate of decrease agrees better with the observations. On the other hand, due to the less efficient reaction NO + O<sub>3</sub>, the simulated daytime NO<sub>2</sub> column is slightly lower than the baseline simulation but it still agrees with the daytime observation. Thus, while the equinox temperature profile used in the baseline run is sufficient for the simulation of the diurnal cycle of the NO<sub>2</sub> column, we do not exclude possible effects of temperature uncertainties on the nighttime simulation.

### 3.5 Back-trajectories

Since the TMF is located at the top of a mountain in a remote area, high values of column NO<sub>2</sub> measured on October 27, 2018, were likely due to atmospheric transport of urban pollutants from nearby cities, especially the Los Angeles megacity. While chemical processes would quantitatively alter the amount of NO<sub>2</sub> to be observed over TMF, a back-trajectory study suffices to provide evidence on how the urban pollutants may be transported to TMF.

Figure 9 shows the 24-hour back-trajectories that eventually reached TMF (2.286 km above sea level) at 3 PM during the observational period. These back-trajectories are calculated using the National Oceanic and Atmospheric Administration (NOAA)'s Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015). We use wind fields from the National Centres for Environmental Prediction (NCEP)'s North American Mesoscale (NAM) assimilation at a horizontal resolution of 12 km. To illustrate the wind speed, we plot the 6-hour intervals using the black dots on the trajectories.

The trajectories on 4 of the 6 days (October 23–26) during the observational period converged towards TMF from inland in the north and the east. These inland areas are behind the San Gabriel and San Bernardino Mountain Ranges and are

Deleted: 6

Deleted: 3a

Deleted: 29

Deleted: 30

Deleted: 7

Deleted: 7

Deleted: 3

Deleted: it still

Deleted: spread of the nighttime

Deleted: In addition

Deleted: Thus, given that the tidal temperature change in the middle atmosphere is much smaller than the change in the sensitivity test,...

Deleted: 8

405 shielded from the urbanized Los Angeles basin. Therefore, the total column NO<sub>2</sub> measured over TMF on these days closely follow the clean atmosphere simulated by the 1-D model. The trajectories on the other 2 days (October 27–28) converged towards TMF from the Los Angeles basin in the southwest. But these 2 trajectories were very different. The back-trajectory of October 27 (Figure 9, orange) started going southwestward from the Mojave Desert north of the San Bernardino Mountains at the 24-hour point and passed across the Riverside Basin between the Santa Ana Mountains and San Jacinto Mountains at 18-hour point. The Riverside Basin is one of the most polluted areas in the United States. Then the trajectory continued southwest to pass across the Orange County at the 12-hour point before it turned northwestward towards Downtown Los Angeles at the 6-hour point. Finally, the trajectory turned northeastward and reached TMF. The wind speed over the Los Angeles basin on October 27 was slower than those in other days, favouring more accumulation of pollutants over the Basin. Thus, the 24-hour back-trajectory on October 27 transported the pollutants in the Riverside Basin and the Los Angeles basin, resulting a significant surplus of NO<sub>2</sub> in the TMF observation as seen in Figure 4. In contrast, the trajectory on October 28 (Figure 9, purple) came directly from the Pacific Ocean at a relatively high speed, spending only ~4 hours in the Los Angeles basin before reaching TMF. However, our measurement on October 28 stopped at noon due to a change in instruments and we are unable to verify whether the urban source would elevate the total column NO<sub>2</sub> in that evening.

#### 4 Summary

420 We have presented the diurnal measurements of total column NO<sub>2</sub> that has been made over the TMF located in Wrightwood, California (2.286 km, 34.38°N, 117.68°W) from October 23 to October 28, 2018. The instrument measures the differential slant column NO<sub>2</sub> relative a reference spectrum at the noontime. To retrieve total column NO<sub>2</sub> in the reference spectrum, we applied a variant of the Langley extrapolation. The conventional Langley extrapolation assumes a constant column throughout the day, which does not hold for NO<sub>2</sub>. To properly consider the time-dependency of column NO<sub>2</sub>, we combine two methods independently developed by Lee et al. (1994) and Herman et al. (2009). The combined method, called the modified minimum-amount Langley extrapolation (MMLE), first obtains a baseline of the observed diurnal cycle, which is assumed to be the diurnal cycle in a clean atmosphere. Then the baseline is fitted against the modelled diurnal cycle in a 1-D photochemical model so that the column NO<sub>2</sub> in the reference spectrum is given by the y-intercept of the fitted line.

430 The measured 24-hour cycle of the TMF total column NO<sub>2</sub> on clean days agrees well with a 1-D photochemical model calculation. Our model simulation suggests that the observed monotonic increase of daytime NO<sub>2</sub> column is primarily due to the photodissociation of N<sub>2</sub>O<sub>5</sub> in the reservoir. From our measurements, we obtained a daytime NO<sub>2</sub> increasing rate of  $(1.31 \pm 0.41) \times 10^{14} \text{ cm}^{-2} \text{ h}^{-1}$ , which is consistent with the value observed by Sussmann et al. (2005), who reported a daytime NO<sub>2</sub> increasing rate of  $(1.20 \pm 0.57) \times 10^{14}$  over Zugspitze, Germany (2.96 km, 47°N). Our model also suggests that during nighttime, the monotonic decrease of NO<sub>2</sub> is primarily due to the production of N<sub>2</sub>O<sub>5</sub>. Furthermore, the abrupt NO<sub>2</sub> decrease and increase at sunrise and sunset, respectively, are due to the activation and deactivation of the NO<sub>2</sub> photodissociation.

Deleted: Basin

Deleted: Basin

Deleted: On October 28, the trajectory (Figure 8, purple) came directly from the Pacific Ocean at a relatively high speed, spending only ~4 hours in the Los Angeles Basin before reaching TMF. This fast sea breeze helped reduce the level of accumulated pollutants over the Los Angeles Basin. As a result, the NO<sub>2</sub> level measured at TMF on October 28 was also similar to a clean atmosphere. In contrast, the...

Deleted: 8

Deleted: Basin

Deleted: Basin

Deleted: 3

Deleted: model-based

Deleted: ,

Deleted: 29

Deleted: 30

The total column NO<sub>2</sub> in the afternoon on October 27, 2018 was much higher than the model simulation. We conducted a 24-hour HYSPLIT back-trajectory analysis to study how urban pollutants were transported from the Los Angeles basin. The back-trajectories in 4 of the 6 days during the measurement period went directly from inland desert areas to the TMF. The back-trajectory in another day came from the southwest coastline, spending less than 6 hours over the Los Angeles basin before reaching the TMF. Lastly, the 24-hour back-trajectory on October 27, 2018 was characterized by a unique slow wind that came from inland in the northeast and spent more than 18 hours in the Los Angeles basin, picking up pollutants from Riverside, Orange County, and finally Downtown Los Angeles before reaching TMF.

Deleted: Basin

Deleted: Basin

Deleted: Basin

#### Appendix A. Comparison of the modified MLE (MMLE) with the standard MLE

The MMLE is used to account for the diurnal asymmetry of the stratospheric NO<sub>2</sub> column before the Langley extrapolation is applied. To illustrate the necessity of the removal of the diurnal asymmetry, consider a single day of observed total column NO<sub>2</sub>. Figure A1a plots the observations on October 25, 2018 against the air mass factor (AMF = sec θ) as in a standard MLE. Based on our back-trajectory analysis, the atmosphere above TMF on October 25, 2018 should have little urban NO<sub>2</sub> contamination. Both solar (pale orange dots) and lunar (pale blue dots) data exhibit U-shapes that is due to the secular increase and decrease during the daytime and the nighttime, respectively. For the solar data, the AM data lies on the lower arm of the U-shape and the PM data lies on the upper arm. For the lunar data, the reverse is true: data before sunrise lie on the upper arm of the U shape and data after sunset lie on the lower arm.

To perform a Langley extrapolation for the data shown in Figure A1a, one needs to decide which of the four arms to be used for the linear regression model  $y = a \text{ AMF} + b$ . The Principle of Minimum-amount suggests that we should start with the lowest arm, i.e. the daytime AM data. Note that in order to obtain the straight line passing through the 2-percentile baseline, we have ignored the points before noon (around 10 AM to 11:30 AM), i.e. points located around the bottom of the U-shape. If we use the observations between 6 AM and 10 AM, we obtain the purple line in Figure A1a, which gives a  $y$ -intercept of  $(-4.12 \pm 0.14) \times 10^{15}$  molecules cm<sup>-2</sup>.

The above Langley extrapolation, however, does not take any of the daytime PM and all lunar data into account. In particular, the daytime PM data should also be used to define a minimum-amount profile, given the fact that the atmosphere was mostly clean on that day. Suppose we perform another Langley extrapolation using the daytime PM data between 12 PM and 5 PM (rose line). The resultant  $y$ -intercept is  $(-5.25 \pm 0.27) \times 10^{15}$  molecules cm<sup>-2</sup> ( $2\text{-}\sigma$ ), which is statistically different from the value obtained using the daytime AM data. A reasonable estimate of the  $y$ -intercept is then the average of the two values, which is  $(-4.69 \pm 0.21) \times 10^{15}$  molecules cm<sup>-2</sup>.

Finally, since the wind on the TMF is mostly downhill during autumn, the lunar data also correspond to a clean atmosphere and should also be used to derive the  $y$ -intercept. If we use all four arms in Figure A1a, then the average value of the  $y$ -intercept is  $(-4.36 \pm 0.25) \times 10^{15}$  molecules cm<sup>-2</sup>, where the uncertainty is the root-mean-squares of the uncertainties of the four values.

490 In the above calculation, the ignorance of the data points near the bottom of the “U”-shape has excluded a large number of observations near local solar/lunar noon and thus the resultant  $\gamma$ -intercept is biased by high zenith angles. It is not clear how the data near the solar/lunar noon may be kept in the standard MLE due to the assumption of the linearity in AMF. As a result, a zenith angle-dependent Langley extrapolation model needs to be developed.

495 The above example shows that the determination of the  $\gamma$ -intercept of the standard MLE is not straightforward when (i) the background  $\text{NO}_2$  has secular trends in daytime and nighttime and (ii) the daytime and nighttime abundances are different before and after the terminator. In contrast, the MMLE approach we have developed in this work minimizes the background diurnal asymmetry, so that the “regularized” data points almost form a straight line (Figure A1b) when they are plotted against the modelled diurnal cycle. The linear regression model  $y = a m x_a + b$ , where  $m x_a$  is the modelled slant column  $\text{NO}_2$ , can be applied to all data points, regardless of the time of the day or whether the data point is a solar or lunar measurement. With this modified MLE, the regressed  $\gamma$ -intercept is  $(-5.22 \pm 0.14) \times 10^{15}$  molecules  $\text{cm}^{-2}$ , which is statistically different from the average of the values derived from the four arms in the standard MLE approach.

500 The issue with the standard MLE is exacerbated when observations on multiple days are plotted against the AMF. The U-shape may be smeared vertically into a continuum (Figure A1c). The smearing, in our case, are primarily due to natural variability of the background, except for October 27 when total column  $\text{NO}_2$  appears above the continuum of the daytime data due to the urban pollution. As a result, while we are still able to define the minimum-amount profile (5-percentile) for the daytime AM data, the determination of the minimum-amount profiles of the daytime PM and the lunar data are difficult. This leaves us the daytime AM data alone for the Langley extrapolation (red line) but, as shown above, the resultant  $\gamma$ -intercept  $[(-4.10 \pm 0.46) \times 10^{15}$  molecules  $\text{cm}^{-2}]$  may be biased.

510 In contrast, the observed data points still almost form a straight line in the MMLE approach when they are plotted against the modelled diurnal cycle (Figure A1d). This allows the determination of the minimum-amount profile using all solar and lunar measurements (raspberry line). The resultant  $\gamma$ -intercept,  $(-6.09 \pm 0.65) \times 10^{15}$  molecules  $\text{cm}^{-2}$ , is again statistically different from the one obtained using the standard MLE approach.

#### **Appendix B. Effects of spherical geometry in the 1D model**

515 The diurnal cycle simulated in the 1D model (Figure 3) is calculated assuming a plane-parallel atmosphere, where the times of the sunrise and the sunset do not depend on altitude. For a more realistic simulation, we have conducted another calculation using the spherical geometry, so that the terminator chemistry is dependent on altitude. Figure B1 compare the simulated diurnal cycles in a plane-parallel atmosphere and in a spherical atmosphere. The difference between the two diurnal cycles is the largest in the evening but it is much smaller than the spread of the observations due to the natural variability. Therefore, the simulation with a plane-parallel atmosphere is adequate to provide a theoretical diurnal cycle for the modified Langley extrapolation.

520 **Acknowledgements.** The assistance of George Mount (Washington State University) in Langley analysis is greatly appreciated. KFL thanks Sally Newman and Tracy Xia (Bay Area Air Quality Management District) for their assistance in setting up and executing the HYSPLIT model. RK was an undergraduate research assistant under the supervision of KFL. We thank Ralf Sussmann for handling our manuscript and providing useful comments.

525 **Financial support.** Support from the NASA SAGE-III/ISS Validation, Upper Atmosphere Research and Tropospheric Composition Programs is gratefully acknowledged. YLY was supported in part by NASA grant P1847132 via UCLA. RK thanks the generous supports from the AGU Student Travel Grant Award and the Marsh Environmental Sciences Travel Award by the University of California, Riverside.

530 **Data availability.** The differential slant column NO<sub>2</sub> used in this paper can be obtained from the supplement of this article.

**Supplement.** The supplement related to this article is available online.

535 **Author contributions.** KFL and TJP prepared the manuscript, with significant conceptual input from SPS and YLY, and critical feedback from all the co-authors. SPS and TJP designed and operated the instrument at the Table Mountain. TJP retrieved the slant column NO<sub>2</sub> from the spectra and developed the Langley method. KFL and YLY performed the model simulations. RK analysed some of the observational and model data.

**Competing interests.** The authors declare that they have no conflict of interest.

540 **References**

Allen, M., Yung, Y. L., and Waters, J. W.: Vertical transport and photochemistry in the terrestrial mesosphere and lower thermosphere (50–120 km), *J. Geophys. Res.*, 86, 3617–3627, doi:10.1029/JA086iA05p03617, 1981.

Allen, M., Lunine, J. I., and Yung, Y. L.: The vertical-distribution of ozone in the mesosphere and lower thermosphere, *J. Geophys. Res.*, 89, 4841–4872, doi:10.1029/JD089iD03p04841, 1984.

545 Ångström, A.: Apparent solar constant variations and their relation to the variability of atmospheric transmission, *Tellus*, 22, 205–218, doi:10.3402/tellusa.v22i2.10215, 1970.

Barreto, A., Roman, R., Cuevas, E., Berjon, A. J., Almansa, A. F., Toledano, C., Gonzalez, R., Hernandez, Y., Blarel, L., Goloub, P., Guirado, C., and Yela, M.: Assessment of nocturnal aerosol optical depth from lunar photometry at the Izana high mountain observatory, *Atmos. Meas. Tech.*, 10, 3007–3019, doi:10.5194/amt-10-3007-2017, 2017.

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: ,

Deleted: https://

Deleted: .org/

560 Bhartia, P. K., Taylor, S., McPeters, R. D., and Wellemeyer, C.: Application of the Langley plot method to the calibration of the solar backscattered ultraviolet instrument on the Nimbus-7 satellite, *J. Geophys. Res. Atmos.*, 100, 2997–3004, doi:10.1029/94JD03072, 1995.

Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18, JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, 2015.

565 Cachorro, V. E., Toledano, C., Berjón, A., de Frutos, A. M., and Sorribas, M.: Comment on "On Langley plots in the presence of a systematic diurnal aerosol cycle centered at noon: A comment on recently proposed methodologies" by F. Marengo, *J. Geophys. Res. Atmos.*, 113, D11210, doi:10.1029/2007JD009137, 2008.

Camy-Peyret, C.: Balloon-borne infrared Fourier Transform spectroscopy for measurements of atmospheric trace species, *Spectrochim. Acta A*, 51, 1143–1152, doi:10.1016/0584-8539(94)00145-2, 1995.

570 Chen, C. M., Cageao, R. P., Lawrence, L., Stutz, J., Salawitch, R. J., Jourdain, L., Li, Q., and Sander, S. P.: Diurnal variation of midlatitudinal NO<sub>3</sub> column abundance over table mountain facility, California, *Atmos. Chem. Phys.*, 11, 963–978, doi:10.5194/acp-11-963-2011, 2011.

Crutzen, P. J.: The influence of nitrogen oxides on atmospheric ozone content, *Q. J. R. Meteorol. Soc.*, 96, 320–325, doi:10.1002/qj.49709640815, 1970.

575 Fiedler, M., Frank, H., Gomer, T., Hausmann, M., Pfeilsticker, K., and Platt, U.: Ground-based spectroscopic measurements of stratospheric NO<sub>2</sub> and OClO in Arctic winter 1989/90, *Geophys. Res. Lett.*, 20, 963–966, doi:10.1029/92GL00088, 1993.

Flaud, J. M., Camy-Peyret, C., Brault, J. W., Rinsland, C. P., and Cariolle, D.: Nighttime and daytime variation of atmospheric NO<sub>2</sub> from ground-based infrared measurements, *Geophys. Res. Lett.*, 15, 261–264, doi:10.1029/GL015i003p00261, 1988.

580 Folkner, W. M., Williams, J. G., Boggs, D. H., Park, R. S., and Kuchynka, P.: The Planetary and Lunar Ephemerides DE430 and DE431, JPL Interplanetary Network Progress Report, accessible at [http://ipnpr.jpl.nasa.gov/progress\\_report/42-196/196C.pdf](http://ipnpr.jpl.nasa.gov/progress_report/42-196/196C.pdf), 42-196, 2014.

585 Gordon, I. E., Rothman, L. S., Hill, C., Kochanov, R. V., Tan, Y., Bernath, P. F., Birk, M., Boudon, V., Campargue, A., Chance, K. V., Drouin, B. J., Flaud, J. M., Gamache, R. R., Hodges, J. T., Jacquemart, D., Perevalov, V. I., Perrin, A., Shine, K. P., Smith, M. A. H., Tennyson, J., Toon, G. C., Tran, H., Tyuterev, V. G., Barbe, A., Császár, A. G., Devi, V. M., Furtenbacher, T., Harrison, J. J., Hartmann, J. M., Jolly, A., Johnson, T. J., Karman, T., Kleiner, I., Kyuberis, A. A., Loos, J., Lyulin, O. M., Massie, S. T., Mikhailenko, S. N., Moazzen-Ahmadi, N., Müller, H. S. P., Naumenko, O. V., Nikitin, A. V., Polyansky, O. L., Rey, M., Rotger, M., Sharpe, S. W., Sung, K., Starikova, E., Tashkun, S. A., Vander Auwera, J., Wagner, G., Wilzewski, J., Weislo, P., Yu, S., and Zak, E. J.: The HITRAN2016 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer*, 203, 3–69, doi:10.1016/j.jqsrt.2017.06.038, 2017.

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

605 Herman, J., Cede, A., Spinei, E., Mount, G., Tzortziou, M., and Abuhassan, N.: NO<sub>2</sub> column amounts from ground-based Pandora and MFDOAS spectrometers using the direct-sun DOAS technique: Intercomparisons and application to OMI validation, *J. Geophys. Res. Atmos.*, 114, D13307, doi:10.1029/2009JD011848, 2009.

Hofmann, D., Bonasoni, P., Demaziere, M., Evangelisti, F., Giovanelli, G., Goldman, A., Goutail, F., Harder, J., Jakoubek, R., Johnston, P., Kerr, J., Matthews, W. A., McElroy, T., McKenzie, R., Mount, G., Platt, U., Stutz, J., Thomas, A., Vanroozendael, M., and Wu, E.: Intercomparison of UV/visible spectrometers for measurements of stratospheric NO<sub>2</sub> for the Network for the Detection of Stratospheric Change, *J. Geophys. Res. Atmos.*, 100, 16765–16791, doi:10.1029/95JD00620, 1995.

Hönninger, G., von Friedeburg, C., and Platt, U.: Multi axis differential optical absorption spectroscopy (MAX-DOAS), *Atmos. Chem. Phys.*, 4, 231–254, doi:10.5194/acp-4-231-2004, 2004.

615 Huber, M., Blumthaler, M., Ambach, W., and Stachelin, J.: Total atmospheric ozone determined from spectral measurements of direct solar UV irradiance, *Geophys. Res. Lett.*, 22, 53–56, doi:10.1029/94GL02836, 1995.

Iwagami, N., Inomata, S., Murata, I., and Ogawa, T.: Doppler detection of hydroxyl column abundance in the middle atmosphere, *J. Atmos. Chem.*, 20, 1–15, doi:10.1007/BF01099915, 1995.

Jeong, U., Tsay, S. C., Pantina, P., Butler, J. J., Loftus, A. M., Abuhassan, N., Herman, J. R., Dimov, A., Holben, B. N., and Swap, R. J.: Langley Calibration Analysis of Solar Spectroradiometric Measurements: Spectral Aerosol Optical Thickness Retrievals, *J. Geophys. Res. Atmos.*, 123, 4221–4238, doi:10.1002/2017JD028262, 2018.

Johnston, P. V., and McKenzie, R. L.: NO<sub>2</sub> observations at 45°S during the decreasing phase of Solar Cycle 21, from 1980 to 1987, *J. Geophys. Res. Atmos.*, 94, 3473–3486, doi:10.1029/JD094iD03p03473, 1989.

Johnston, P. V., McKenzie, R. L., Keys, J. G., and Matthews, W. A.: Observations of depleted stratospheric NO<sub>2</sub> following the Pinatubo volcanic eruption, *Geophys. Res. Lett.*, 19, 211–213, doi:10.1029/92GL00043, 1992.

625 Keys, J. G., and Johnston, P. V.: Stratospheric NO<sub>2</sub> and O<sub>3</sub> in Antarctica: Dynamic and chemically controlled variations, *Geophys. Res. Lett.*, 13, 1260–1263, doi:10.1029/GL013i012p01260, 1986.

Kreher, K., Van Roozendael, M., Hendrick, F., Apituley, A., Dimitropoulou, E., Frieß, U., Richter, A., Wagner, T., Lampel, J., Abuhassan, N., Ang, L., Anguas, M., Bais, A., Benavent, N., Bösch, T., Bogner, K., Borovski, A., Bruchkouski, I., Cede, A., Chan, K. L., Donner, S., Drosoglou, T., Fayt, C., Finkenzeller, H., Garcia-Nieto, D., Gielen, C., Gómez-Martín, L., Hao, N., Henzing, B., Herman, J. R., Hermans, C., Hoque, S., Irie, H., Jin, J., Johnston, P., Butt, J. K., Khokhar, F., Koenig, T. K., Kuhn, J., Kumar, V., Liu, C., Ma, J. Z., Merlaud, A., Mishra, A. K., Müller, M., Navarro-Comas, M., Ostendorf, M., Pazmino, A., Peters, E., Pinardi, G., Pinharanda, M., Piters, A., Platt, U., Postlyakov, O., Prados-Roman, C., Puentedura, O., Querel, R., Saiz-Lopez, A., Schönhardt, A., Schreier, S. F., Seyler, A., Sinha, V., Spinei, E., Strong, K., Tack, F., Tian, X., Tiefengraber, M., Tirpitz, J. L., van Gent, J., Volkamer, R., Vrekoussis, M., Wang, S., Wang, Z., Wenig, M., Wittrock, F., Xie, P. H., Xu, J., Yela, M., Zhang, C., and Zhao, X. Y.: Intercomparison of NO<sub>2</sub>, O<sub>4</sub>, O<sub>3</sub> and HCHO slant column measurements by MAX-DOAS and zenith-sky UV-visible spectrometers during CINDI-2, *Atmos. Meas. Tech.*, 13, 2169–2208, doi:10.5194/amt-13-2169-2020, 2020.

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/



655 Kreuter, A., Wuttke, S., and Blumthaler, M.: Improving Langley calibrations by reducing diurnal variations of aerosol  
 Ångström parameters, *Atmos. Meas. Tech.*, 6, 99–103, doi:10.5194/amt-6-99-2013, 2013.

Langley, S. P.: The "solar constant" and related problems, *Astrophys. J.*, 17, 89–99, doi:10.1086/140999, 1903.

Lee, A. M., Roscoe, H. K., Oldham, D. J., Squires, J. A. C., Sarkissian, A., Pommereau, J. P., and Gardiner, B. G.:  
 Improvements to the accuracy of measurements of NO<sub>2</sub> by zenith-sky visible spectrometers, *J. Quant. Spectrosc. Radiat.*  
 660 *Transfer*, 52, 649–657, doi:10.1016/0022-4073(94)90031-0, 1994.

Long, C. N., and Ackerman, T. P.: Identification of clear skies from broadband pyranometer measurements and calculation of  
 downwelling shortwave cloud effects, *J. Geophys. Res. Atmos.*, 105, 15609–15626, doi:10.1029/2000JD900077, 2000.

Marenco, F.: On Langley plots in the presence of a systematic diurnal aerosol cycle centered at noon: A comment on recently  
 proposed methodologies, *J. Geophys. Res. Atmos.*, 112, D06205, doi:10.1029/2006JD007248, 2007.

665 May, R. D., and Webster, C. R.: Balloon-borne laser spectrometer measurements of NO<sub>2</sub> with gas-absorption sensitivities  
 below 10<sup>-5</sup>, *Appl. Optics*, 29, 5042–5045, doi:10.1364/AO.29.005042, 1990.

Moreau, G., Robert, C., Catoire, V., Chartier, M., Camy-Peyret, C., Huret, N., Pirre, M., Pomathiod, L., and Chalumeau, G.:  
 SPIRALE: a multispecies in situ balloonborne instrument with six tunable diode laser spectrometers, *Appl. Optics*, 44,  
 5972–5989, doi:10.1364/AO.44.005972, 2005.

670 Newcomb, S.: Tables of the Sun, *Astron. Pap. Amer. Ephem. VI, Part I*, 7–170, 1898.

Nizkorodov, S. A., Sander, S. P., and Brown, L. R.: Temperature and pressure dependence of high-resolution air-broadened  
 absorption cross sections of NO<sub>2</sub> (415–525 nm), *J. Phys. Chem. A*, 108, 4864–4872, doi:10.1021/jp049461n, 2004.

Noxon, J. F.: Nitrogen dioxide in stratosphere and troposphere measured by ground-based absorption spectroscopy, *Science*,  
 189, 547–549, doi:10.1126/science.189.4202.547, 1975.

675 Noxon, J. F., Whipple, E. C., and Hyde, R. S.: Stratospheric NO<sub>2</sub>. Part I. Observational method and behavior at mid-latitude,  
*J. Geophys. Res. Oceans*, 84, 5047–5065, doi:10.1029/JC084iC08p05047, 1979.

Piters, A. J. M., Boersma, K. F., Kroon, M., Hains, J. C., Van Roozendaal, M., Wittrock, F., Abuhassan, N., Adams, C.,  
 Akrami, M., Allaart, M. A. F., Apituley, A., Beirle, S., Bergwerff, J. B., Berkhout, A. J. C., Brunner, D., Cede, A., Chong,  
 J., Clemer, K., Fayt, C., Frieß, U., Gast, L. F. L., Gil-Ojeda, M., Goutail, F., Graves, R., Griesfeller, A., Großmann, K.,  
 680 Hemerijckx, G., Hendrick, F., Henzing, B., Herman, J., Hermans, C., Hoexum, M., van der Hoff, G. R., Irie, H., Johnston,  
 P. V., Kanaya, Y., Kim, Y. J., Baltink, H. K., Kreher, K., de Leeuw, G., Leigh, R., Merlaud, A., Moerman, M. M., Monks,  
 P. S., Mount, G. H., Navarro-Comas, M., Oetjen, H., Pazmino, A., Perez-Camacho, M., Peters, E., du Piesanie, A., Pinardi,  
 G., Puentedura, O., Richter, A., Roscoe, H. K., Schönhardt, A., Schwarzenbach, B., Shaiganfar, R., Sluis, W., Spinei, E.,  
 Stolk, A. P., Strong, K., Swart, D. P. J., Takashima, H., Vlemmix, T., Vrekoussis, M., Wagner, T., Whyte, C., Wilson, K.,  
 685 M., Yela, M., Yilmaz, S., Zieger, P., and Zhou, Y.: The Cabauw Intercomparison campaign for Nitrogen Dioxide measuring  
 Instruments (CINDI): design, execution, and early results, *Atmos. Meas. Tech.*, 5, 457–485, doi:10.5194/amt-5-457-2012,  
 2012.

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Formatted: Superscript

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Formatted: Subscript

Deleted: https://

Deleted: .org/

Platt, U., Perner, D., and Patz, H. W.: Simultaneous measurement of atmospheric CH<sub>2</sub>O, O<sub>3</sub>, and NO<sub>2</sub> by differential optical absorption, *J. Geophys. Res. Oceans Atmos.*, 84, 6329–6335, doi:10.1029/JC084iC10p06329, 1979.

Roscoe, H. K., Johnston, P. V., Van Roozendaal, M., Richter, A., Sarkissian, A., Roscoe, J., Preston, K. E., Lambert, J. C., Hermans, C., Decuyper, W., Dzienus, S., Winterrath, T., Burrows, J., Goutail, F., Pommereau, J. P., D'Almeida, E., Hottier, J., Coureul, C., Didier, R., Pundt, I., Bartlett, L. M., McElroy, C. T., Kerr, J. E., Elokhov, A., Giovanelli, G., Ravegnani, F., Premuda, M., Kostadinov, I., Erle, F., Wagner, T., Pfeilsticker, K., Kenntner, M., Marquard, L. C., Gil, M., Puentedura, O., Yela, M., Arlander, D. W., Hoiskar, B. A. K., Tellefsen, C. W., Tornkvist, K. K., Heese, B., Jones, R. L., Aliwell, S. R., and Freshwater, R. A.: Slant column measurements of O<sub>3</sub> and NO<sub>2</sub> during the NDSC intercomparison of zenith-sky UV-visible spectrometers in June 1996, *J. Atmos. Chem.*, 32, 281–314, doi:10.1023/A:1006111216966, 1999.

Roscoe, H. K., Van Roozendaal, M., Fayt, C., du Piesanic, A., Abuhassan, N., Adams, C., Akrami, M., Cede, A., Chong, J., Clémer, K., Frieß, U., Ojeda, M. G., Goutail, F., Graves, R., Griesfeller, A., Grossmann, K., Hemerijckx, G., Hendrick, F., Herman, J., Hermans, C., Irie, H., Johnston, P. V., Kanaya, Y., Kreher, K., Leigh, R., Merlaud, A., Mount, G. H., Navarro, M., Oetjen, H., Pazmino, A., Perez-Camacho, M., Peters, E., Pinaridi, G., Puentedura, O., Richter, A., Schönhardt, A., Shaiganfar, R., Spinei, E., Strong, K., Takashima, H., Vlemmix, T., Vrekoussis, M., Wagner, T., Wittrock, F., Yela, M., Yilmaz, S., Boersma, F., Hains, J., Kroon, M., Piters, A., and Kim, Y. J.: Intercomparison of slant column measurements of NO<sub>2</sub> and O<sub>4</sub> by MAX-DOAS and zenith-sky UV and visible spectrometers, *Atmos. Meas. Tech.*, 3, 1629–1646, doi:10.5194/amt-3-1629-2010, 2010.

Sakazaki, T., Fujiwara, M., Zhang, X., Hagan, M. E., and Forbes, J. M.: Diurnal tides from the troposphere to the lower mesosphere as deduced from TIMED/SABER satellite data and six global reanalysis data sets, *J. Geophys. Res. Atmos.*, 117, D13108, doi:10.1029/2011JD017117, 2012.

Sanders, R. W., Solomon, S., Smith, J. P., Perliski, L., Miller, H. L., Mount, G. H., Keys, J. G., and Schmeltekopf, A. L.: Visible and near-ultraviolet spectroscopy at McMurdo station, Antarctica. Part 9: Observations of OCIO from April to October 1991, *J. Geophys. Res. Atmos.*, 98, 7219–7228, doi:10.1029/93JD00042, 1993.

Serdyuchenko, A., Gorshchev, V., Weber, M., Chehade, W., and Burrows, J. P.: High spectral resolution ozone absorption cross-sections — Part 2: Temperature dependence, *Atmos. Meas. Tech.*, 7, 625–636, doi:10.5194/amt-7-625-2014, 2014.

Shaw, G. E.: Error analysis of multi-wavelength sun photometry, *Pure Appl. Geophys.*, 114, 1–14, doi:10.1007/BF00875487, 1976.

Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, 37, 275–316, doi:10.1029/1999RG900008, 1999.

Spinei, E., Cede, A., Swartz, W. H., Herman, J., and Mount, G. H.: The use of NO<sub>2</sub> absorption cross section temperature sensitivity to derive NO<sub>2</sub> profile temperature and stratospheric-tropospheric column partitioning from visible direct-sun DOAS measurements, *Atmos. Meas. Tech.*, 7, 4299–4316, doi:10.5194/amt-7-4299-2014, 2014.

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

Deleted: https://

Deleted: .org/

750 Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., and Ngan, F.: [NOAA's HYSPLIT atmospheric transport and dispersion modeling system](#), *Bull. Amer. Meteorol. Soc.*, 96, 2059–2077, doi:10.1175/BAMS-D-14-00110.1, 2015.

Deleted: NOAA's

Deleted: https://

Deleted: .org/

Stutz, J., and Platt, U.: Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods, *Appl. Optics*, 35, 6041–6053, doi:10.1364/AO.35.006041, 1996.

Deleted: https://

Deleted: .org/

755 Sussmann, R., Stremme, W., Burrows, J. P., Richter, A., Seiler, W., and Rettinger, M.: Stratospheric and tropospheric NO<sub>2</sub> variability on the diurnal and annual scale: a combined retrieval from ENVISAT/SCIAMACHY and solar FTIR at the Permanent Ground-Truthing Facility Zugspitze/Garmisch, *Atmos. Chem. Phys.*, 5, 2657–2677, doi:10.5194/acp-5-2657-2005, 2005.

Deleted: https://

Deleted: .org/

[Thalman, R., and Volkamer, R.: Temperature dependent absorption cross-sections of O<sub>2</sub>-O<sub>2</sub> collision pairs between 340 and 630 nm and at atmospherically relevant pressure](#), *Phys. Chem. Chem. Phys.*, 15, 15371–15381, doi:10.1039/C3CP50968K, 2013.

760 Toledano, C., González, R., Fuertes, D., Cuevas, E., Eck, T. F., Kazadzis, S., Kouremeti, N., Gröbner, J., Goloub, P., Blarel, L., Román, R., Barreto, Á., Berjón, A., Holben, B. N., and Cachorro, V. E.: Assessment of Sun photometer Langley calibration at the high-elevation sites Mauna Loa and Izaña, *Atmos. Chem. Phys.*, 18, 14555–14567, doi:10.5194/acp-18-14555-2018, 2018.

Deleted: https://

Deleted: .org/

765 [Vandaele, A. C., Fayt, C., Hendrick, F., Hermans, C., Humbled, F., Van Roozendael, M., Gil, M., Navarro, M., Puentedura, O., Yela, M., Braathen, G., Stebel, K., Tørnkvist, K., Johnston, P., Kreher, K., Goutail, F., Mieville, A., Pommereau, J. P., Khaikine, S., Richter, A., Oetjen, H., Wittrock, F., Bugarski, S., Frieß, U., Pfeilsticker, K., Sinreich, R., Wagner, T., Corlett, G., and Leigh, R.: An intercomparison campaign of ground-based UV-visible measurements of NO<sub>2</sub>, BrO, and OClO slant columns: Methods of analysis and results for NO<sub>2</sub>](#), *J. Geophys. Res. Atmos.*, 110, doi:10.1029/2004JD005423, 2005.

770 Wang, S., Pongetti, T. J., Sander, S. P., Spinei, E., Mount, G. H., Cede, A., and Herman, J.: Direct Sun measurements of NO<sub>2</sub> column abundances from Table Mountain, California: Intercomparison of low- and high-resolution spectrometers, *J. Geophys. Res. Atmos.*, 115, D13305, doi:10.1029/2009JD013503, 2010.

Deleted: https://

Deleted: .org/

[Wang, S., Li, K.-F., Zhu, D., Sander, S. P., Yung, Y. L., Pazmino, A., and Querel, R.: Solar 11-Year cycle signal in stratospheric nitrogen dioxide—Similarities and discrepancies between model and NDACC observations](#), *Solar Phys.*, 295, 117, doi:10.1007/s11207-020-01685-1, 2020.

775 Woolard, E. W.: Theory of the rotation of the Earth around its center of mass, *Astron. Pap. Amer. Ephem. XV, Part I*, 1–165, 1953.

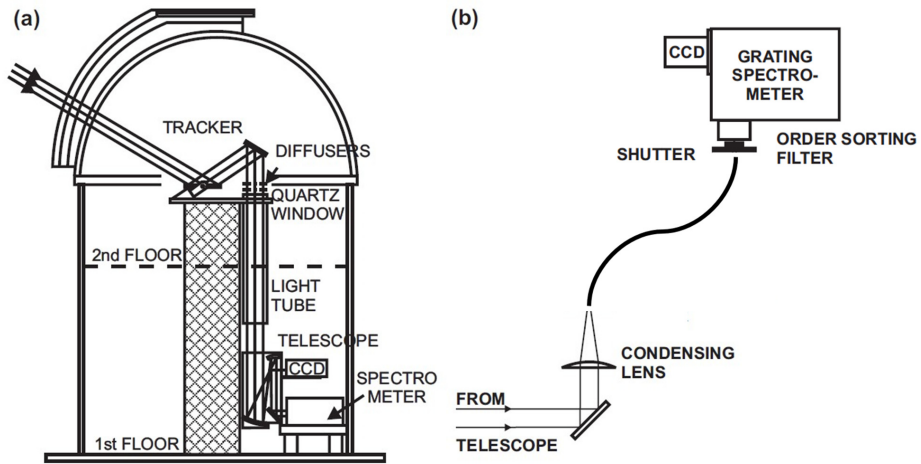
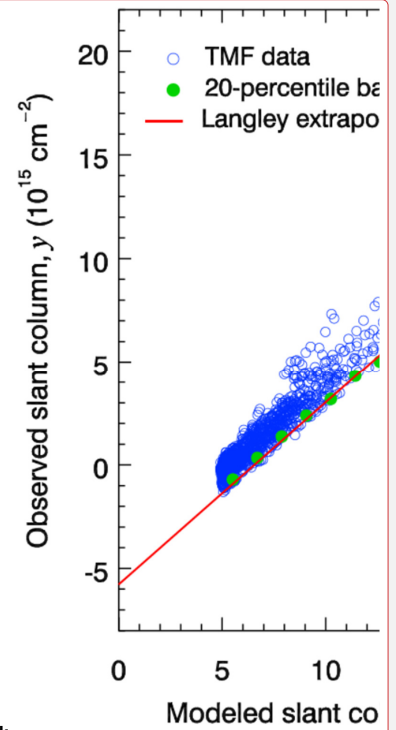
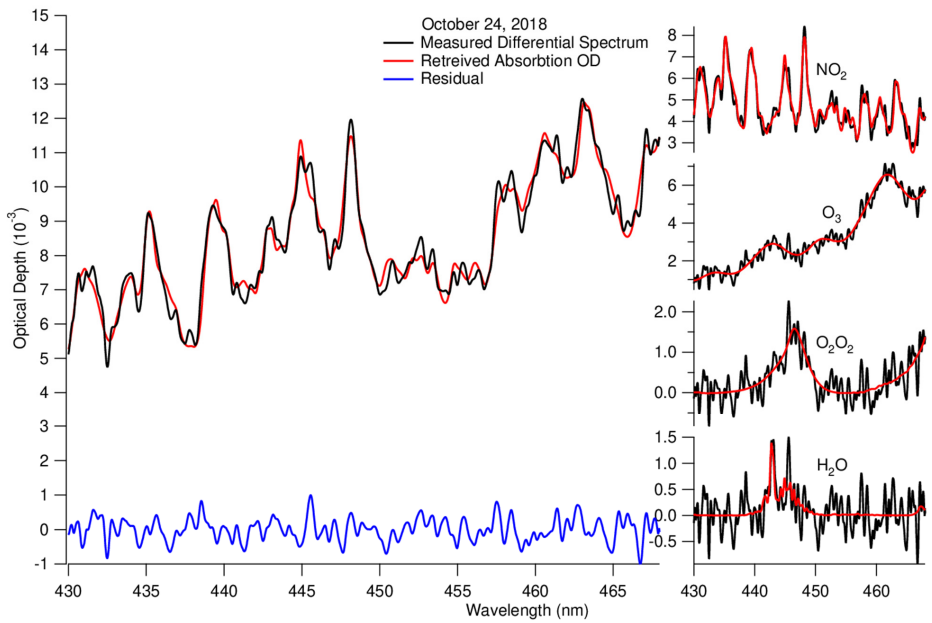


Figure 1: Schematic of the instrument light path over the Table Mountain Facilities (TMF, 2.286 km above mean sea level, 34.38°N, 117.68°W), Wrightwood, California, USA. (a) Light is collected by the primary of the heliostat (tracker), reflected down to the telescope on the first floor which conditions it to a 7-cm diameter beam. (b) The light is then reflected to a condensing lens into a fibre optic bundle, past a shutter, order-sorting filter and then into the spectrometer. The fibre bundle contains 19 fibres in a round pattern at the entrance, and at the exit fibres are arranged in a line pattern that is set parallel to the spectrometer slit.

795

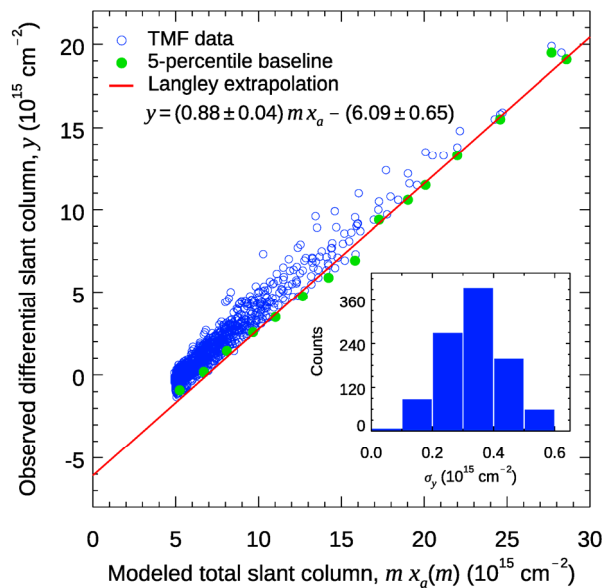


Deleted:  
Figure 2. The model-based minimum-amount Langley extrapolation.



**Figure 2. An example of the QDOAS spectral fit on October 24, 2018.** The measured spectrum is shown by the black curve on the left panel. The fitted spectrum (red) is overlaid and the residual spectrum (blue) is shown at the bottom. Four species are considered in the spectral fit: NO<sub>2</sub>, O<sub>3</sub>, O<sub>2</sub>, and H<sub>2</sub>O. The spectral fits are performed simultaneously in QDOAS. The red lines on the right column are the fitted spectra of the corresponding species. To visualize the signal-to-noise ratios, we add the residual spectrum (blue on the left panel) to individual fitted spectra, which are shown as the black spectra in the subpanels on the right.

805



**Figure 3. The modified minimum-amount Langley extrapolation (MMLE).** The blue circles are the observed differential slant columns during our campaign over TMF from October 23 to October 28, 2018. Each observational value is plotted against the total slant column modelled at the same time of the day (e.g. 11:05 AM PST). The green dots are the 5-percentile of 20 uniform bins on the  $x$ -axis. The red line is a linear regression of the green dots, which is taken as the background diurnal cycle in a clean atmosphere. The linear fit is  $y = 0.88 m x_a(m) - 6.09 \times 10^{15}$ . The  $2\text{-}\sigma$  uncertainties of the slope and the intercept are  $0.04$  and  $0.65 \times 10^{15}$ , respectively. The  $y$ -intercept thus gives a reference column,  $y_0 = 6.09 \times 10^{15}$  molecules  $\text{cm}^{-2}$ . The inset shows the distribution of the  $2\text{-}\sigma$  uncertainty of the observed differential slant columns.

810

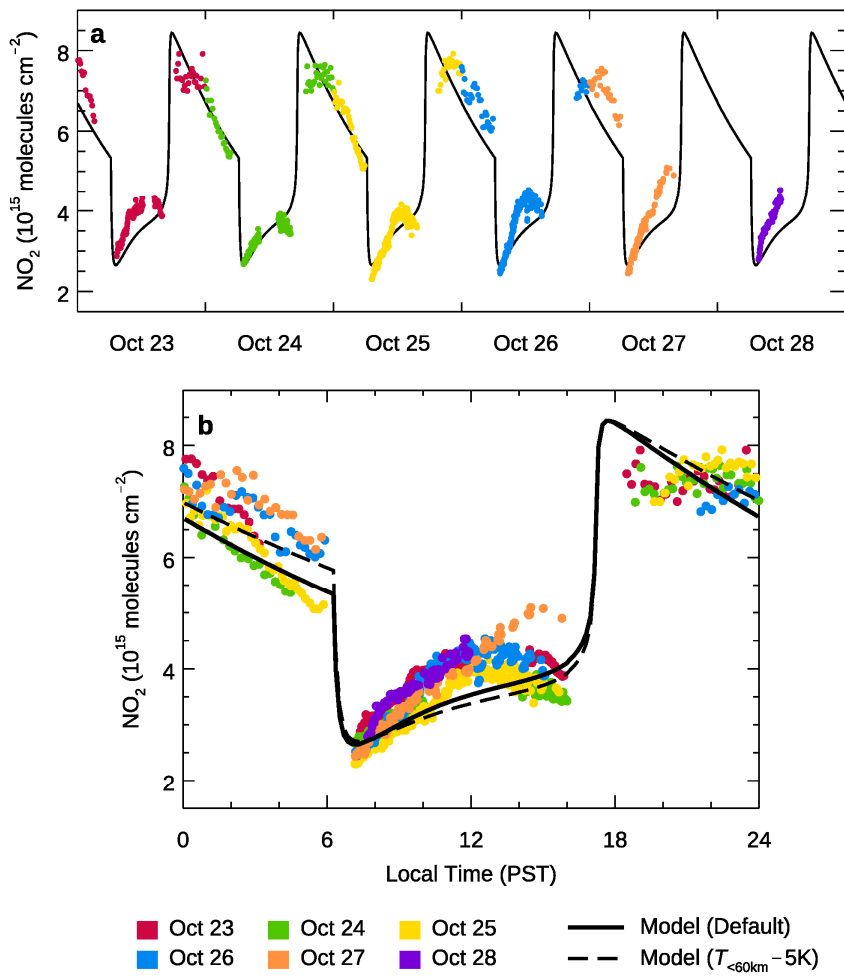
815

Deleted: 20

Deleted: 5.77

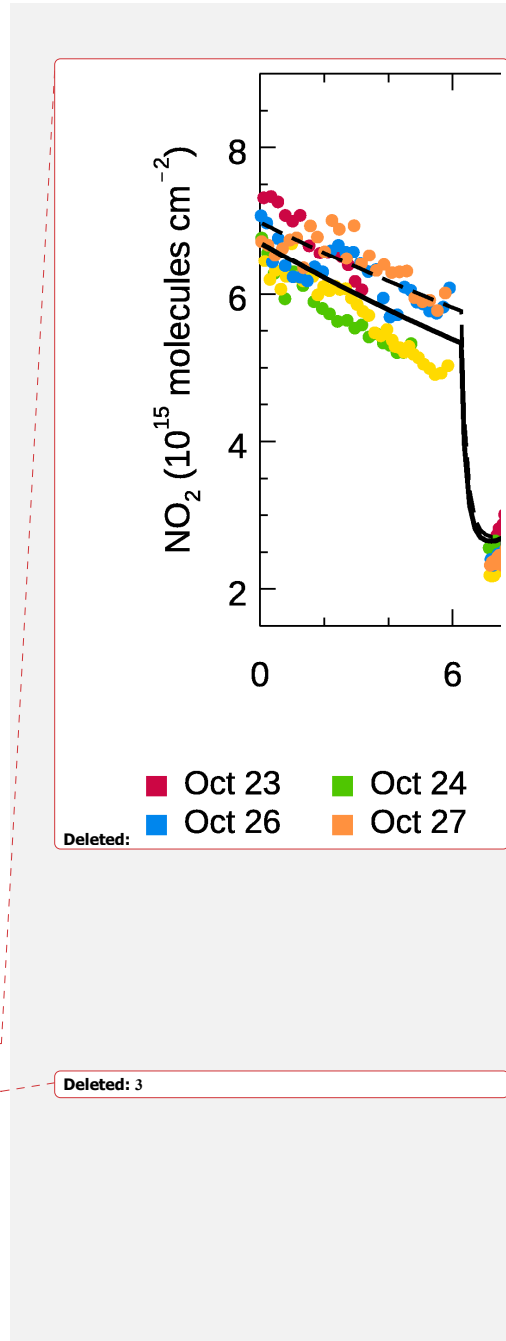
Deleted: the

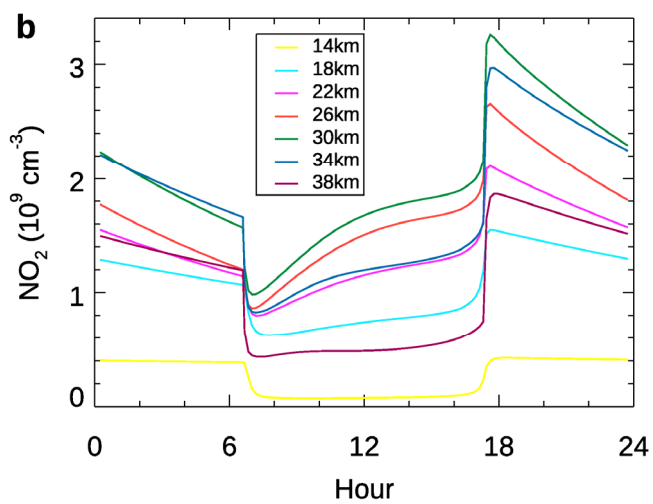
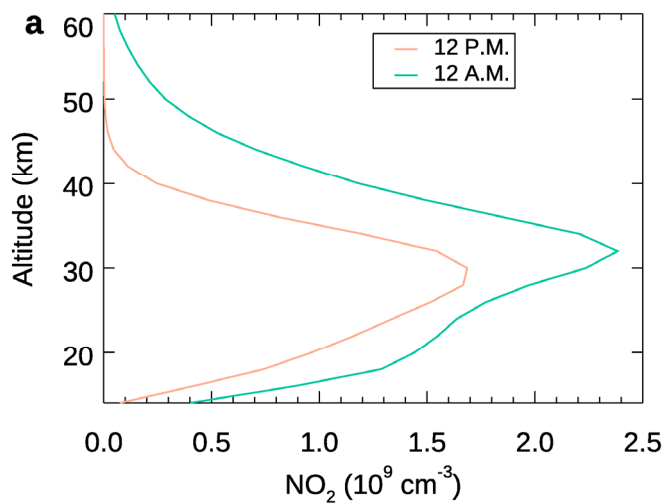
Deleted: 5.77



**Figure 4:** The total column NO<sub>2</sub> abundance measured over TMF on October 23–28, 2018, represented by the color dots. The 1-D model simulation, with default input temperature and surface N<sub>2</sub>O being 330 ppb, representing October 26 is shown as the solid black line. (a) The total column NO<sub>2</sub> measurements on individual dates. (b) The aggregated total column NO<sub>2</sub> measurements as a function of local time. An additional 1-D model simulation with temperature below 60 km reduced by 5 K, is shown as the dashed line.

825

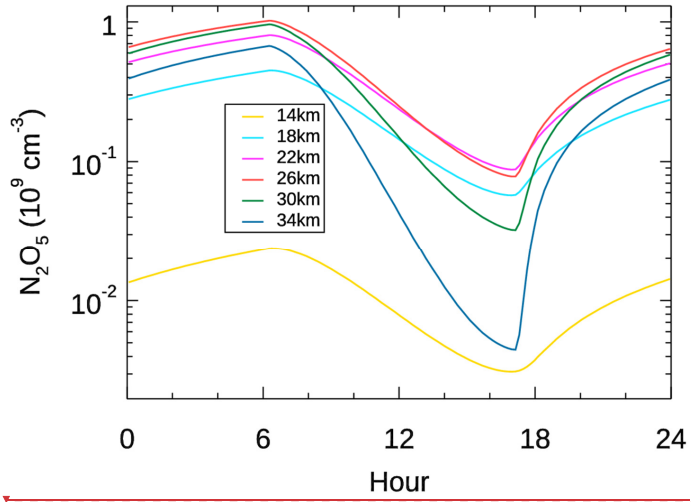




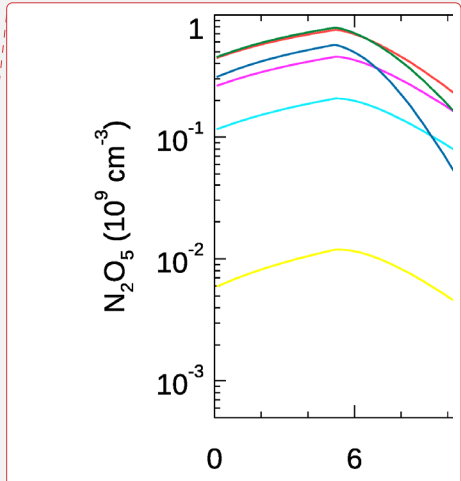
830 **Figure 5: Simulated vertical NO<sub>2</sub> concentration.** (a) The simulated NO<sub>2</sub> vertical concentration between 14–38 km at 00:00 PST (green) and 12:00 PST (orange) corresponding to October 27 in the 1-D photochemical model. (b) Same as (a) except the simulated NO<sub>2</sub> variation over the 24 hours at selected altitudes.

Deleted: 4





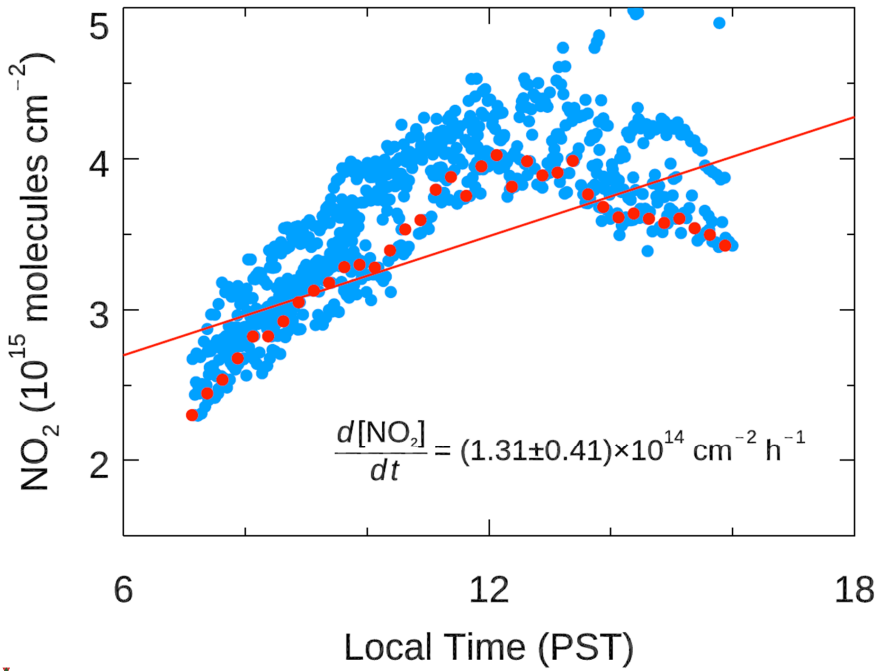
835 Figure 6. Same as Figure 5(b) except for  $N_2O_5$ .



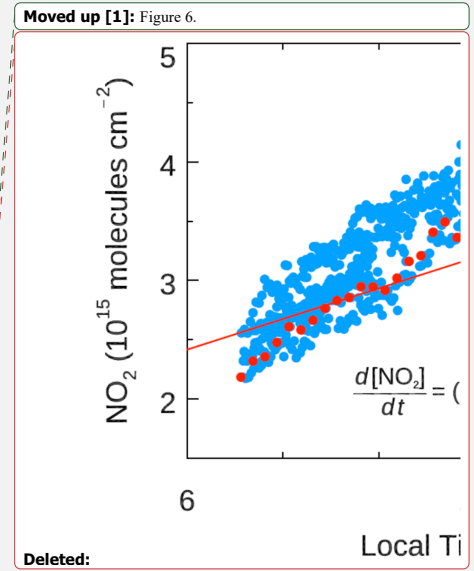
Deleted:  
Figure 5.

Moved (insertion) [1]

Deleted: 4



840 **Figure 7.** The daytime NO<sub>2</sub> increase obtained from the baseline of the observed diurnal variability. The blue points are the same as the daytime data shown in Figure 4. The red points are the 20-percentile of the daytime data in 15-minute intervals between 7 AM to 4 PM, which form a baseline of the daytime variability. The daytime NO<sub>2</sub> increase rate, obtained from the linear regression of the red points, is  $(1.31 \pm 0.41) \times 10^{14} \text{ cm}^{-2} \text{ h}^{-1}$ .



- Deleted: 3
- Deleted: 29
- Deleted: 30
- Formatted: Font: Not Bold

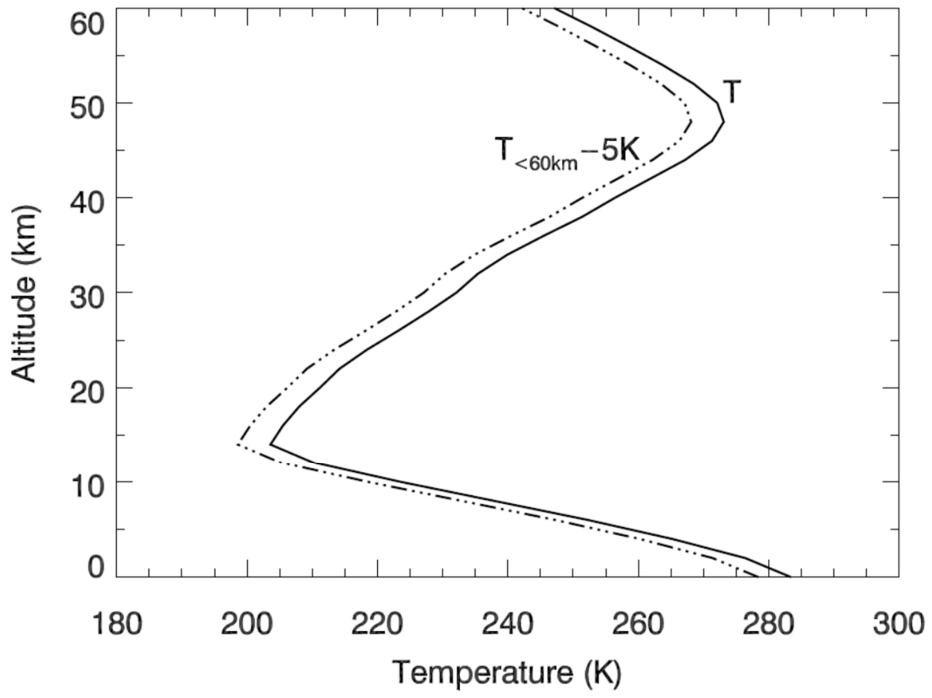
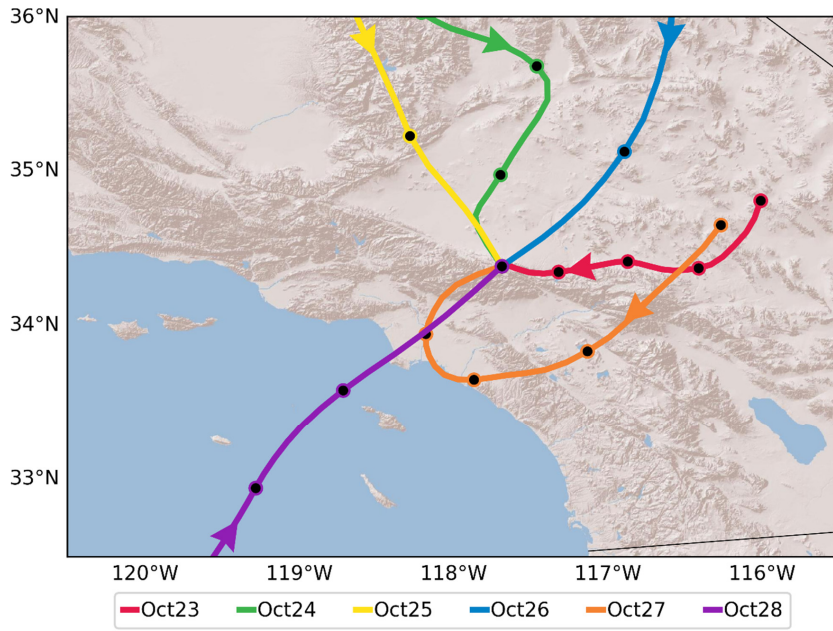


Figure 8: The temperature profiles used in the 1-D Caltech/JPL photochemical model: the baseline profile (solid line) based on the equinox zonal average at 30° latitude and the modified profile where the temperature below 60 km is reduced by 5 K (dash-dotted line).

855

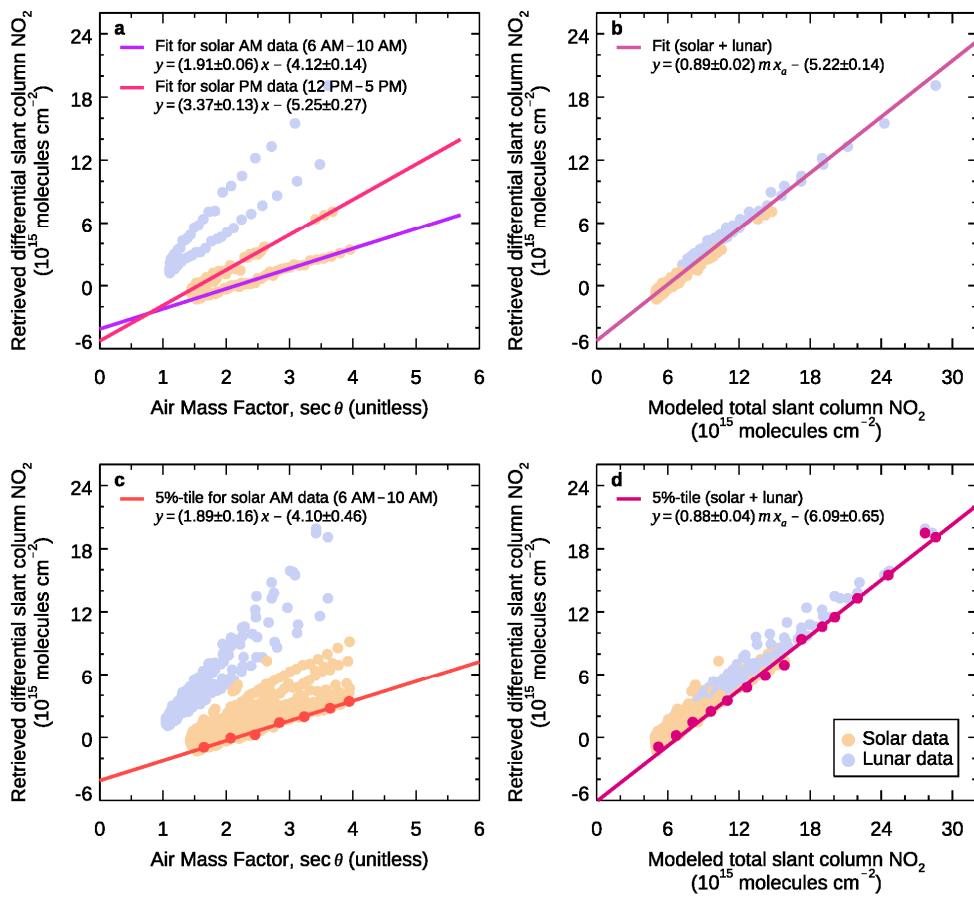
Deleted: 7



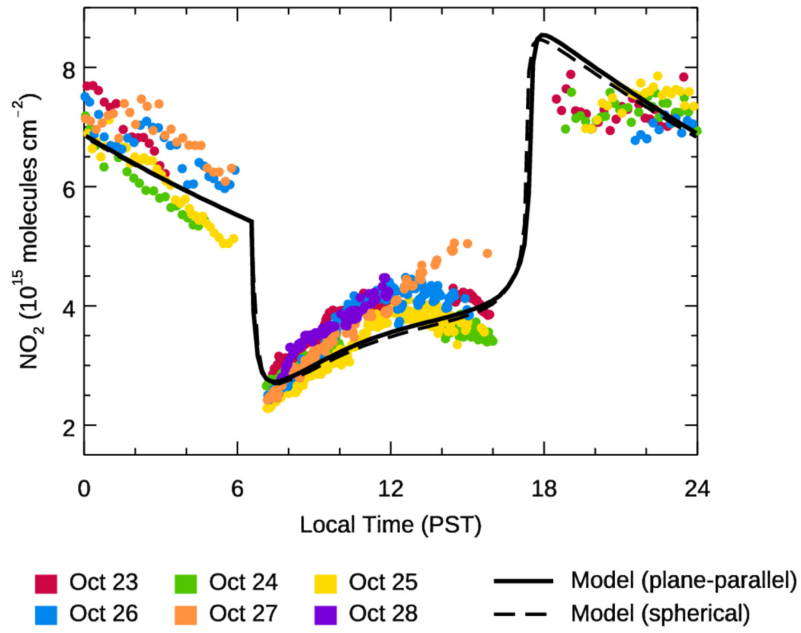
**Figure 2:** The 24-hour back-trajectories of ambient air flow that reached TMF at 15:00 PST on each day from October 23 to October 28, 2018. The colour codes are the same as those used in Figure 4. The black dots represent the 6-hour intervals on the trajectories.

Deleted: 8  
 Deleted: 3

860



865 [Figure A1. Comparison of the standard MLE \(a, c\) and the modified MLE \(MMLE\) \(b, d\) introduced in this work for single-day \(a, b\) and multiple-day data \(c, d\). Panel d is the same as Figure 3 except for the separation of the daytime and nighttime data.](#)



870 **Figure B1.** Comparison of the simulated diurnal cycles of the total column  $\text{NO}_2$  in a plane-parallel atmosphere and a spherical atmosphere. The data points are the same as in Figure 4b.

**Formatted:** Font: Bold