Reply to referee #3

The authors thank the referee for the valuable time spent to thoroughly read the manuscript and provide valuable comments which contributed to improvement of this revised version. Below we provide our point-to-point responses, together with the revisions made, where appropriate.

(Referees' comments in red, author responses in black, and adjustments of manuscript in blue.)

Review of Liu et al. "Evaluation of the first year of Pandora NO_2 measurements over Beijing and application to satellite validation"

This paper introduces one year of NO_2 data measured by the AIRCAS Pandora site in Beijing. The diurnal and seasonal changes are analyzed. Comparisons with in-situ and satellite observations of NO_2 are carried out. The impact of atmospheric transport and the emission control policies have also been examined. This paper is well structured and the topic fits with the AMT journal.

Here are my comments:

1. In the abstract, need to brief mention that the Pandora data include total and tropospheric NO_2 VCD.

   Thank you for this suggestion. To be more clearly and in accordance with the reviewer concerns, we have added an interpretation in abstract, text "In this paper, an overview is presented of the Pandora NO_2 data collected during the first year of operation, i.e., from August, 2021, to July, 2022." has been revised to "In this paper, an overview is presented of the Pandora total and tropospheric NO_2 vertical column densities (VCDs) and surface concentrations collected during the first year of operation, i.e., from August, 2021, to July, 2022." in line 21-23.

2. Line 18, full name for "VCD" at its first appearance.

   Thank you for this comment. We have written "vertical column densities (VCDs)" at first appearance in both the abstract (line 22) and the main text (line 85).

3. Line 28-29, how about winter?

Thank you for this comment. We apologize for the mistake in the abstract and corrected the sentence to reflect the results presented in Section 3.3. It now reads "The contribution of tropospheric NO_2 to the total NO_2 VCD varies significantly on daily to seasonal time scales, i.e., monthly averages vary between 50% and 60% in the winter and between 60% and 70% in the spring and autumn." in line 28-30.

4. Line 35, define the unit "Pmolec"

Thank you for this comment. We have added "($1\ \mathrm{Pmolec \cdot cm^{-2}} = 1 \times 10^{15}\ \mathrm{molec \cdot cm^{-2}}$)." in line 36 of the abstract at the first occurrence. In the main text, first occurrence of $\mathrm{Pmolec \cdot cm^{-2}}$ was at the end of Section 2.2.1, where it was explained: " ($1\ \mathrm{Pmolec \cdot cm^{-2}} = 1 \times 10^{15}\ \mathrm{molec \cdot cm^{-2}} = 3.745 \times 10^{-2}\ \mathrm{DU\ (Dobson\ Unit)} = 7.639 \times 10^{-7} \mathrm{kg \cdot m^{-2}}$) (Herman et al., 2009)." (lines 171-172)

5. Line 123, capital

Thank you. We changed the text "…as the capitol of China" in line 123 to "…as the capital of China".

6. Line 171-173, there are two precision estimates mentioned here, are they both for the total VCD product? Also, please explain the DU unit here. Please also quantify the retrieval error in fraction, which is the error divided by the mean NO_2.

Thank you for this comment. In fact, the first one is precision and the second one is accuracy. Considering that readers' understanding of precision and accuracy can easily lead to bias and that accuracy is more concerned about Pandora also reader, we only retain relevant descriptions of accuracy in the manuscript.

As to the "Dobson Unit (DU)", it is usually used unit to indicate how much of a given trace gas, especially O_3, is in the atmosphere, and is also commonly used in many research for NO_2. The Dobson unit is defined as the thickness (in units of 10 μm) of that layer of pure gas which would be formed by the total column

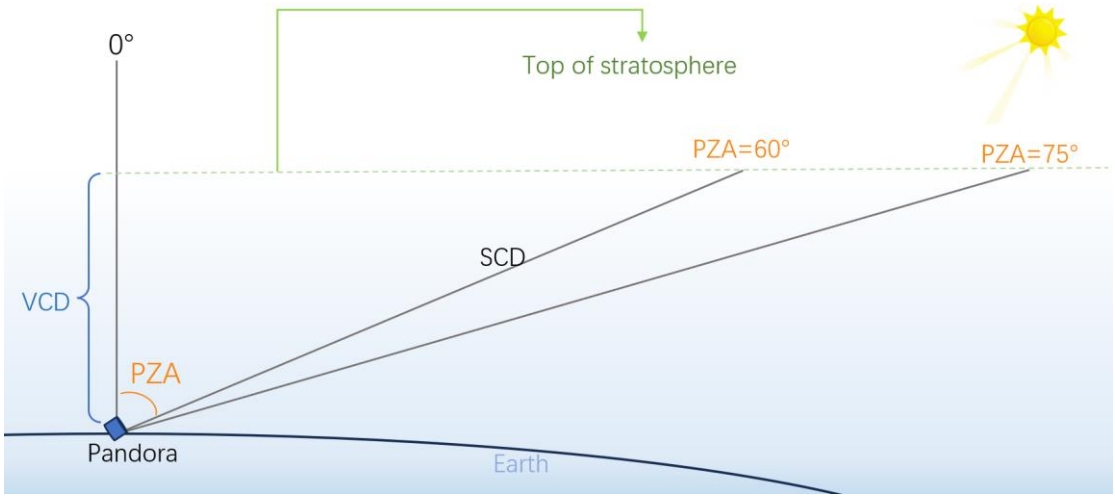
amount at standard conditions for temperature and pressure. To have a better understanding of DU, we add '(Dobson Unit)' after DU and an International System Unit, kg/m^2, in manuscript.

The absolute value of the deviation will change in different scenarios, such as high-concentration and low-concentration scenarios, so here we use the mean fraction of retrieval error in typical cases from Pandora official paper.

Corresponding text in line 171-173 now reads 'The estimated nominal accuracy is about $\pm 2.67\ \text{Pmolec} \cdot \text{cm}^{-2}$ (error in fraction for 5.33%). ($1\ \text{Pmolec} \cdot \text{cm}^{-2} = 1 \times 10^{15}\ \text{molec} \cdot \text{cm}^{-2} = 3.745 \times 10^{-2}\ \text{DU(Dobson Unit)} = 7.639 \times 10^{-7} \text{kg} \cdot \text{m}^{-2}$) (Herman et al., 2009).'

7. Section 2.2.1, the total NO_2 VCD retrieval from direct sun measurement is straightforward to understand. However, the retrieval of tropospheric partial column using scattered light with different angles is not. Please explain here how the tropospheric component is retrieved from the measurements. What are the assumptions for this retrieval?

In this method for getting the tropospheric VCD of trace gas, such as O_3, NO_2, HCHO, used by ground-based MAX-DOAS instruments, is assumed that the stratospheric slant column density (SCD) only varies with SZA and is independent of the pointing zenith angle (PZA) of MAX-DOAS. With this assumption, the contribution of stratospheric SCD to total SCD can be removed by subtracting the SCD at PZA=0 from the SCD at PZA=α, also referred to as the differential slant column density method. Using the air mass factor (AMF) calculated with an atmospheric model, the SCD can then be converted to the tropospheric VCD. In (Cede et al., 2021) (the Pandora ATBD), the method for removing the contribution from stratospheric, mentioned above, is also employed. Please note, Pandora assumes that O_2 concentrations in atmosphere are weakly variable and therefore could be used to characterize atmospheric background concentrations. Differ from MAX-DOAS, Pandora uses both differential slant column density O_2 observed by Pandora and climatological O_2 VCD as the atmospheric air background to obtain NO_2 volume ratios rather than AMF, hence it is considered the variation of atmospheric density, and therefore also atmospheric boundary layer height. To have a better understanding of the retrieval principle of Pandora, we extract the relevant formulas from Pandora algorithm using the schematic in the following figure:



Schematic of Pandora observation geometry.

Cede et al., (2021) use the following formula to obtain the tropospheric vertical column density (VCD_{trop,NO_2}).

$$VCD_{trop,NO_2} = \frac{\left(SCD_{75,NO_2} - SCD_{0,NO_2}\right) \cdot VCD_{CLM,AIR}}{SCD_{75,AIR} - SCD_{60,AIR} + VCD_{CLM,AIR}} \quad (1)$$

Where VCD_{trop} is NO_2 tropospheric VCDs.

SCD_{75,NO_2} is slant column density at PZA 75° observed by Pandora.

$SCD_{75,AIR}$ is the slant column density of air-gas (background air) with PZA=75° observed by Pandora.

$VCD_{CLM,AIR}$ is the total VCDs of air-gas calculated by climatology, and is the integral of effective air-gas height and climatological concentration in per layer of total column.

According to the triangle function theorem, $Cos60° = \frac{VCD_{CLM,AIR}}{SCD_{60,AIR}}$, then:

$$= \frac{\left(SCD_{75,NO_2} - SCD_{0,NO_2}\right) \cdot VCD_{CLM,AIR}}{SCD_{75,AIR} - \frac{VCD_{CLM,AIR}}{Cos60°} + VCD_{CLM,AIR}} \quad (2)$$

$$= \frac{\left(SCD_{75,NO_2} - SCD_{0,NO_2}\right) \cdot VCD_{CLM,AIR}}{SCD_{75,AIR} - VCD_{CLM,AIR}} \quad (3)$$

$$= \frac{\mathrm{SCD}_{75,\mathrm{NO_2}} - \mathrm{SCD}_{0,\mathrm{NO_2}}}{\frac{\mathrm{SCD}_{75,\mathrm{AIR}}}{\mathrm{VCD}_{\mathrm{AIR}}} - 1} \quad (4)$$

$$= \frac{\mathrm{SCD}_{75,\mathrm{NO_2}} - \mathrm{SCD}_{0,\mathrm{NO_2}}}{\frac{1}{\mathrm{Cos}75} - 1} \quad (5)$$

Based on the Equation $\mathrm{VCD}_{trop} = \frac{\mathrm{dSCD}_{\alpha\neq 0} - \mathrm{dSCD}_{\alpha=0}}{\mathrm{AMF}_{\alpha\neq 0} - \mathrm{AMF}_{\alpha=0}} = \frac{\Delta\mathrm{SCD}}{\Delta\mathrm{AMF}} = \frac{\Delta\mathrm{SCD}}{\frac{1}{\cos\alpha} - \frac{1}{\cos 0^\circ}} = \frac{\Delta\mathrm{SCD}}{\frac{1}{\cos\alpha} - 1}$ from (Tian et al., 2019) for MAX-DOAS of retrieval method of tropospheric VCD, hence, the above proof is completed.

8. Section 2.2.3, ERA5 has wind data for different heights, what altitude do you use for you analysis and why?

Thank you for this comment. Here we followed earlier publications (Ialongo et al., 2020; Zhao et al., 2022) where wind data at four pressure levels (925, 950, 975 and 1000 hPa) were averaged. We added the following text: "ERA5 hourly wind speed data at four pressure levels: 925, 950, 975 and 1000 hPa) were downloaded from the ECMWF website (ERA5 web: https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-pressure-levels?tab=form, last accessed: 11th July 2023) and averaged (following, e.g., Stein et al., 2015; Ialongo et al., 2020; Zhao et al., 2022) for use in the analysis presented below." (Section 2.2.4, lines 213-217) (as advised by Referee#1 the section numbering has been changed).

9. Section 3.1.1, "The NO_2 VCDs decrease in the morning to reach a daily minimum around local noon and then increase." Does this just depend on the diurnal change of boundary layer height, can you see the contribution from traffic/industries? The anthropogenic should play an important role here in regulating the diurnal change.

Thank you for this comment. The diurnal variation is briefly addressed in Section 3.3 in relation to the variable contribution of tropospheric NO_2 to the total NO_2 VCD and in Section 3, 4 where we compare Pandora-derived surface concentrations with in situ measurements. In response to your comment we refer to the text in the first paragraph below Figure 7. We further note that other papers report enhanced NO_2 concentrations during local rush hours, i.e. from high traffic intensity (Herman et al., 2009; Liu et al., 2023; Di Bernardino et al.,

2023). In our data this signal may be present but is relatively weak in comparison to other studies.

Referee# 2 also commented on the observations in Section 3.3. and in response we added the following text (lines 369-374): " This is due to a combination of processes including sources and sinks, of (photo)chemical nature (Herman et al. 2009), transport influenced by meteorological phenomena such as variations in wind speed and wind direction (discussed above in Section 3.2) and variations in boundary layer height, while also the temperature profile changes throughout the day, influencing reaction rates and chemical balance (cf. Kang et al., 2022, for a brief overview). Likely all of these are different between the troposphere and above and therefore influence the ratio tropospheric / total NO_2 VCD and its daily evolution." Disentangling these processes would require a detailed model study, but this is out of the scope of this study.

10. In figure 4, please indicate the height of the wind speed. You may need to show wind speed at different elevation.

Thank you for this comment. In this study we only considered the wind speed and wind direction at the height level for 925, 950, 975 and 1000hPa, referenced from Ialongo et al., 2020; Zhao et al., 2022. This comment is also similar to your comment 8, you also could see our response to that comment there.

11. Line 361, ratio

Thank you for noting this. We have corrected this typo.

12. Line 363-364 "Also, similar to ozone, stratospheric intrusion could be a possible reason for the springtime increase in tropospheric NO_2 concentrations (Lin et al., 2015)". This is highly speculative. Can you provide paper reference that show more solid evidences?

Thank you for pointing this out. We note that there have been a number of outstanding studies on NO_2 tropospheric and stratospheric profiles. They report that there is a zone of high values of NO_2 at 20-30 km (Sioris et al., 2003; Hendrick et al., 2004; Preston et al., 1998), whereas most of the tropospheric NO_2 is distributed within the boundary layer, about 1-2 km below (Lin et al., 2014; Wang et al., 2019). Therefore, when the bottom of the stratosphere

collapses with the tropopause in spring (concurrent with the ozone stratospheric intrusion), there may be an effect on the tropospheric column concentration of NO_2. Although NO_2 is quickly converted to secondary pollutants (ozone, particulate matter, etc.) by photochemical reactions, the conversion of NO_2 may be lower than within that in the boundary layer due to the relatively low concentrations of VOCs at the top of the troposphere. Certainly, near-surface anthropogenic emissions result in a dominant NO_2 concentration within the boundary layer (~15 ppb, Wang et al., 2019), while stratospheric NO_2 concentrations (~5-8 ppb, Preston et al., 1998) may only contribute to tropospheric NO_2 concentrations to some extent. However, we would like to state that this is one possible reason for the increase in spring RATIO, and we do not exclude other reasons for this phenomenon, e.g., due to enhanced stratospheric NO_2 photolysis by solar radiation in spring. We have modified the original text in the manuscript for greater rigorous as follows in lines 384-391:

"The smaller ratio in the winter may be related to the frequent occurrence of haze days when tropospheric NO_2 is converted to fine particulate matter (e.g., Zheng et al., 2015; Xie et al., 2015; Wang et al, 2020), whereas the larger ratio in spring may be derived from reduced stratospheric concentrations due to enhanced solar shortwave radiation (Cheng et al., 2016; Müller, 2021). Similar to ozone, stratospheric intrusion could be a possible reason for the springtime increase in tropospheric NO_2 concentrations (Lin et al., 2015), because the higher values in the stratosphere have been observed in many studies (Sioris et al., 2003; Hendrick et al., 2004; Preston et al., 1998). Also, the larger standard deviations in spring (especially in March when it was larger than 0.2) indicate a larger day-to-day variability than in other seasons, which may be due to more active photochemical reactions in response to enhanced radiation intensity."

13. Line 480: although the absolute values increase with increasing NO_2 VCD, the fraction (bias divided by the mean NO_2) may be similar.

Thank you for pointing this out. The absolute difference is growth with the increasing of NO_2 concentration, but, the fraction, a good evaluation metric, may be not similar to absolute difference but changes little/weak. Given that previous text in section 3.5 have descripted the trend of comparison between TROPOMI and Pandora for Figure 9. Hence, we decide to remove the text, 'In

other words, the uncertainties in the TROPOMI-derived NO_2 total VCDs increase with increasing VCD.', out of manuscript.

14. Line 554, please mention that "0.2" and "1" are fractions (so they are unitless).

Thanks for your comment. Text "…varies between 0.2 to 1 with large diurnal to …" has been revised to "The fraction of tropospheric NO_2 contributing to the total NO_2 VCDs varies between 0.2 to 1, with large diurnal to seasonal variations, is high in the morning and afternoon with a minimum around noon." in line 578-579.

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