

Reply to referee #2

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.)

This paper presents the NO₂ observations from the Pandora spectrometer in Beijing from August 2021 to July 2022. The authors quantitatively discuss the temporal variations of NO₂ observations on different time scales, and analyze the influences of the wind on NO₂ VCDs using reanalysis data. The Pandora NO₂ measurements are compared with ground-based in-situ measurements, and the reasons behind their differences are further explained. Finally, the authors use the Pandora NO₂ data to validate TROPOMI v1.4 tropospheric NO₂ VCDs, and give an estimation of the spatial representativeness of Pandora NO₂ measurements.

Overall, I think this paper is clear and well structured. I recommend it be published after addressing the comments listed below.

Specific Comments:

1.Line 237-239: Why do you use the defined “standard deviation” instead of covariance, which seems more appropriate, to evaluate TROPOMI and Pandora data sets?

Thank you for this comment. The evaluation metrics are described in Section 2.3 Methodology and are used throughout the manuscript. We have considered your suggestion and also checked some relevant papers (Verhoelst et al, 2020; Ialongo et al., 2021; Lange et al., 2023) that they all use Pearson correlation R. Therefore we decided to continue using the Pearson correlation R and add the equation for R in Section 2.3 (lines 241-242):

“The Pearson correlation R (Pearson., 1895) is defined in Eq. (4).

$$R = \frac{\sum_{i=1}^n (\text{VCD}_{\text{TROPOMI},i} - \overline{\text{VCD}_{\text{TROPOMI}}}) (\text{VCD}_{\text{Pan},i} - \overline{\text{VCD}_{\text{Pan}}})}{\sqrt{\sum_{i=1}^n (\text{VCD}_{\text{TROPOMI},i} - \overline{\text{VCD}_{\text{TROPOMI}}})^2} \sqrt{\sum_{i=1}^n (\text{VCD}_{\text{Pan},i} - \overline{\text{VCD}_{\text{Pan}}})^2}}, \quad (4)$$

”

2. Line 294: The number of days for December is reduced to 12 or 9? The “Number of days with high quality data” for December in Table 1 is 9.

We thank the reviewer for pointing this out. We rechecked the numbers in our script output as well as the text in the tables and the main text, and we have corrected “the number of days is reduced from 31 to 12” to “the number of days is reduced from 31 to 9” in line 302 of this manuscript.

3. Line 323-324: “Because of the large diurnal variation of the NO₂ VCDs, only data have been selected at the TROPOMI overpass time at 13:00 BJT”. The causal relationship here is unreasonable. If you select the TROPOMI overpass time, it is expected that you also analyze the TROPOMI NO₂ VCDs for comparison. Please consider adding the comparison results with TROPOMI observations, or explaining reasonably your thoughts about the time selection.

Thank you for this comment. Indeed this wording may lead to misunderstanding. The NO₂ concentrations (here tropospheric VCD) are very variable and plotting all data throughout a day for analysis of effects of certain parameters influencing the concentrations is not conclusive because the effects are hidden in much larger diurnal variations. Therefore, we selected a certain time to exclude the diurnal effect, and selected 13:00, around the time when the daily concentration is at a minimum. That this is also the TROPOMI overpass time, but that is not relevant. The sentence has been changed to: “To separate effects of wind direction and wind speed on NO₂ VCDs from the large diurnal variations (Figure 2), only data have been plotted at 13:00 BJT when the concentrations are close to their daily minimum.”. We also referred to the TROPOMI overpass time in section 3.4 and have removed these words (line 332-334).

4. Line 348-350: what are the reasons for the diurnal variations of the tropospheric / total ratio? Are they related to the diurnal variations of NO_x emissions, photochemistry or stratospheric NO₂? Please specify.

Thank you for this comment. The goal of this paper is to describe the first year of observations of NO₂ using Pandora and we noticed the difference in time series of tropospheric and total VCDs, which are determined by independent methods. Therefore, we decided to plot the ratio of tropospheric /total and describe the results. Likely these provide information on atmospheric processes,

but we do not know which process is most important. We did a literature search but did not find an explanation for our observations: For line 367-369, “The data show that the tropospheric / total ratio decreases to a minimum around the middle of the day, i.e., early in the day the tropospheric NO₂ VCDs decrease faster than the total, before it increases in the afternoon.” This is due to a combination of processes, and we added to the 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 (Kang et al., 2022). Likely all of these are different between the troposphere and above and therefore influence the ratio tropospheric / total NO₂ VCD and its daily evolution.”

We also changed the second sentence of Section 3.3 to (lines 358-359) “Hence the total and tropospheric NO₂ VCDs are independently determined, and can be used to obtain information on atmospheric processes.”

5. Line 362-363: please specify the reasons why enhanced solar shortwave radiation (more active photochemical reactions) can result in higher ratio in the spring.

Thank you for this comment. This sentence was not accurate. What we are trying to describe is that the larger change in standard deviation is due to enhanced solar radiation in the spring, not that the higher absolute values are due to enhanced radiation. We have corrected the original text in the manuscript to (lines 384-391):

“The smaller ratio in the winter may be related to the frequent occurrence of haze days when tropospheric NO₂ 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 NO₂ 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 related to more active photochemical reactions in response to enhanced radiation intensity."

6. Line 395-399: How do you know the variations of the tropospheric NO₂ VCDs from Figure 7? Only total VCDs are shown in this figure.

Thank you for this comment. We need to apologize for a mistake in the text of this paragraph. We described the observations plotted in Figure 7, i.e. total VCD as we wrote the first time, but by mistake we wrote tropospheric VCD in the following lines. In the revised version this has been corrected. (lines 414-424)

7. Section 3.6: The quantification of the spatial representativeness of the Pandora observations at the Beijing-RADI site is based on TROPOMI v1.4 tropospheric NO₂ VCDs. However, it has been well known that TROPOMI v1.x data are significantly underestimated, especially for polluted regions. Please use updated TROPOMI PAL v2.3.1 or reprocessed TROPOMI v2.4.0 tropospheric NO₂ VCDs to validate the robustness of your conclusion.

Thank you for this comment. We have checked the TROPOMI version we used. Our study covers the period 1 August 2021 to 31 July 2022. For the period from 1 August 2021 to 14 November 2021, the data were processed using version 2.2.0. For the period from 15 November 2021 to 17 July 2022, the data were processed using version 2.3.1. For the period 18 July 2022 onwards, the data were processed using version 2.4.0. The ATBD (Cede, 2021) mentions that the change from version 1.4 to version 2.2 is a big upgrade due to the treatment of surface albedo. As noted by Referee#2 and also in the TROPOMI NO₂ ATBD (van Geffen, et al., 2022b), the underestimation, especially in contaminated areas, has been weakened since version 2.2. Unfortunately, when we did this study, only the versions mentioned above were available during the indicated time periods at the indicated website (see data availability).

We have added the above information on the data versions to the text 'Section 2.2 Instrumentation and auxiliary data' (lines 193-195):

"The TROPOMI OFFL data used in this study were retrieved using retrieval processor version 2.2.0 from 1 August 2021 to 14 November 2022, version 2.3.1 from 15 November 2021 to 17 July 2022 and version 2.4.0 after 18 July 2022 (van Geffen et al., 2022a, van Geffen et al., 2022b)."

Technical comments:

8. Figure 2 and Figure 5: I find these two figures are nearly impossible to read the characteristics of diurnal variations. If the discussion of diurnal variations is important, please add additional figures clearly showing the details.

Thank you for this comment. We agree that Figure 2 and 5 are difficult to read and do not show detail, except for the overall variation. However, they only serve to present an overall overview of the data and the diurnal variation is discussed in Section 3.4. Therefore we have selected 2 months (November and December) as examples which we enlarged to landscape and moved Figure 2 to the Supplementary as Figure S1. This is explained in the text in lines 266-267: “The data in Figure 2 show the total VCDs are larger than the tropospheric VCDs. The data also show the diurnal variation of these parameters and the surface concentrations derived from Pandora.”.

The first sentence of Section 3.1.1 has been changed to “The data in Figure 2 show the total VCDs are larger than the tropospheric VCDs. The data also show the diurnal variation of these parameters and the surface concentrations derived from Pandora.”

Likewise, Figure 5 has been moved to the Supplementary as number S6 and we only show February as an example in Figure 5. This is explained in the text in lines 360-361: “the time series of the ratio of the tropospheric to the total NO₂ VCD (see e.g., Figure 5, where the ratios for February are shown as an example, and Figure S6 for all months)”

9. Line 35: add a period after “VCD_{trop}”.

Thank you for this comment. The text “...error for TROPOMI of 0.5 Pmolec · cm⁻² + (0.2 to 0.5) · VCD_{trop}” have been corrected to “...error for TROPOMI of 0.5 Pmolec · cm⁻² + (0.2 to 0.5) · VCD_{trop}.” in line 36.

10. Line 123: change “capitol” to “capital”.

Thank you for this comment. The text in Line 123 have been revised to “...as the capital of China” in line 123.

11. Line 312: change “NO2” to “NO₂” in the subheading.

Thank you for this comment. NO2 has been changed to NO₂ in line 321, and we

have checked also the rest of the text.

12. Line 361: change “ration” to “ratio”

Thank you for this comment. The text in line 384 has been corrected to “[The smaller ratio in the winter may be related to...](#)”.

lalongo, I., Virta, H., Eskes, H., Hovila, J., and Douros, J.: Comparison of TROPOMI/Sentinel-5 Precursor NO₂ observations with ground-based measurements in Helsinki, *Atmos. Meas. Tech.*, 13, 205-218, 10.5194/amt-13-205-2020, 2020.

Kang, H., Zhu, B., de Leeuw, G., Yu, B., van der A, R. J., and Lu, W.: Impact of urban heat island on inorganic aerosol in the lower free troposphere: a case study in Hangzhou, China, *Atmos. Chem. Phys.*, 22, 10623–10634, <https://doi.org/10.5194/acp-22-10623-2022>, 2022.

Lange, K., Richter, A., Schönhardt, A., Meier, A. C., Bösch, T., Seyler, A., Krause, K., Behrens, L. K., Wittrock, F., Merlaud, A., Tack, F., Fayt, C., Friedrich, M. M., Dimitropoulou, E., Van Roozendaal, M., Kumar, V., Donner, S., Dörner, S., Lauster, B., Razi, M., Borger, C., Uhlmannsiek, K., Wagner, T., Ruhtz, T., Eskes, H., Bohn, B., Santana Diaz, D., Abuhassan, N., Schüttemeyer, D., and Burrows, J. P.: Validation of Sentinel-5P TROPOMI tropospheric NO₂ products by comparison with NO₂ measurements from airborne imaging DOAS, ground-based stationary DOAS, and mobile car DOAS measurements during the S5P-VAL-DE-Ruhr campaign, *Atmos. Meas. Tech.*, 16, 1357–1389, <https://doi.org/10.5194/amt-16-1357-2023>, 2023.

Müller, R.: The impact of the rise in atmospheric nitrous oxide on stratospheric ozone : This article belongs to Ambio's 50th Anniversary Collection. Theme: Ozone Layer, *Ambio*, 50, 35-39, 10.1007/s13280-020-01428-3, 2021.

Pearson, K. Notes on Regression and Inheritance in the Case of Two Parents, *Proceedings of the Royal Society of London*, 58, 240-242. <https://doi.org/10.1098/rspl.1895.0041>, 1895.

Sillman, S. and He, D.: Some theoretical results concerning O₃-NO_x-VOC chemistry and NO_x-VOC indicators, 107, *ACH 26-21-ACH 26-15*, <https://doi.org/10.1029/2001JD001123>, 2002.

Verhoelst, T., Compernelle, S., Pinardi, G., Lambert, J.-C., Eskes, H. J., Eichmann, K.-U., Fjæraa, A. M., Granville, J., Niemeijer, S., Cede, A., Tiefengraber, M., Hendrick, F., Pazmiño, A., Bais, A., Bazureau, A., Boersma, K. F., Bogner, K., Dehn, A., Donner, S., Elokhov, A., Gebetsberger, M., Goutail, F., Grutter de la Mora, M., Gruzdev, A., Gratsea, M., Hansen, G. H., Irie, H., Jepsen, N., Kanaya, Y., Karagkiozidis, D., Kivi, R.,

Kreher, K., Levelt, P. F., Liu, C., Müller, M., Navarro Comas, M., Piters, A. J. M., Pommereau, J.-P., Portafaix, T., Prados-Roman, C., Puentedura, O., Querel, R., Remmers, J., Richter, A., Rimmer, J., Rivera Cárdenas, C., Saavedra de Miguel, L., Sinyakov, V. P., Stremme, W., Strong, K., Van Roozendaal, M., Veefkind, J. P., Wagner, T., Wittrock, F., Yela González, M., and Zehner, C.: Ground-based validation of the Copernicus Sentinel-5P TROPOMI NO₂ measurements with the NDACC ZSL-DOAS, MAX-DOAS and Pandonia global networks, *Atmos. Meas. Tech.*, 14, 481–510, <https://doi.org/10.5194/amt-14-481-2021>, 2021.