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RC1

A Review of "The Antarctic stratospheric Nitrogen Hole: Southern Hemisphere and Antarctic springtime total nitrogen dioxide and total ozone variability as observed in Sentinel-5p TROPOMI data" by A. de Laat et al.

General Comments

This paper describes a new analysis of stratospheric "Nitrogen Hole" using TROPOMI nitrogen dioxide (NO2) data and assimilated ozone (O3) data. The analysis idea is somewhat new and found some new aspects on springtime cross-vortex chemistry/dynamics on NO2 and O3. However, since the stratospheric photochemical lifetime of NO2 (10-100 s) is much shorter than that of HNO3 (105-106 s), special care is needed to treat the stratospheric NO2 data. The authors need to more carefully treat this point in the paper, as is pointed out in the following comments. When the modification of these points is completed in the paper, I think that the paper is worth published in Atmospheric Chemistry and Physics.

Response: we thank the referee for the review efforts and the comments that have helped improve the paper. Below follows a detailed response to the comments including for each comment a description of the modifications that have been made.

Major Comments

1) P.6, L.160: The authors first tried to validate the TROPOMI SNO2 data with ground-based SAOZ data. However, the TROPOMI SNO2 data are acquired at 13:30 local time, while SAOZ data are acquired at local sunrise. The authors claim that "a diurnal cycle correction is applied based on model calculations". Since this is a critical point for comparison, more detailed description is needed for this "diurnal cycle correction".

Action: we added this literal quote from Compernolle et al. [2021] that is also in Lambert et al. [2023]:

"the SAOZ measurements are adjusted to the TROPOMI overpass time using a model-based factor. This is calculated with the PSCBOX 1D stacked-box photochemical model (Errera and Fonteyn, 2001; Hendrick et al., 2004), initiated with daily fields from the SLIMCAT chemistry transport model (CTM). The amplitude of the adjustment depends strongly on the effective SZA assigned to the ZSL-DOAS measurements; it is taken here to be 89.5°. The uncertainty related to this adjustment is of the order of 10 %. To reduce mismatch errors due to the significant horizontal smoothing differences between TROPOMI and SAOZ measurements, TROPOMI SNO2 values (from ground pixels at high resolution) are averaged over the air mass footprint where ground-based zenith-sky measurements are sensitive."

2) If ascending node crossing local time of Sentinel-5P is 13:30, the descending node crossing local time is 01:30. However, there is no description on whether the authors are using only ascending part of the orbit, or using both ascending and descending parts (full parts) of the orbit. Since the measurement local time is important for NO2 analysis, please clarify this point.

Response: For this paper all TROPOMI SNO2 observations that are sufficiently accurate (qa value > 0.5) are included in the averaging at the 0.4×0.8 degree grid. Note that the qa_value threshold of 0.5 is defined such that effectively only measurements with SZA > 81.2 degrees are excluded. Overall it means that data from ascending and descending orbits are used in the calculation of daily mean TROPOMI SNO2. The average is arithmetic without any weighting.

We also added a brief discussion on SNO2 diurnal cycle effects on both TROPOMI SNO2 retrievals and validation results. Although this is not expected to materially affect the results of this paper there are clear indications that effects are not marginal. Which supports the need for an assessment of diurnal cycle effects. As we present a more-or-less new SNO2 application for a region (Polar) that otherwise has been largely ignored there is little information – if any – about diurnal cycle effects. What has been published indicates what effects can be sufficiently large that they cannot be simply ignored but not large enough to materially affect the results presented here.

Note in support that the 10-20% SNO2 diurnal cycle adjustment effects reported in Dubé et al. [2021] are consistent with the SAOZ 10% SNO2 diurnal cycle correction effects mentioned in Compernolle et al. [2021].

Action: the following was added to the discussion section 4.

"In addition, although the diurnal cycle in SNO2 is relatively small compared to its seasonal cycle it nevertheless can affect satellite retrievals and validation results. Dube et al. [2021] reported order of magnitude 10-20% effects for SAGE III/ISS solar occultation limb retrievals with larger effects for higher latitudes. Although their results are not one-on-one applicable to the results presented here they clearly indicate the need for properly assessing diurnal cycle effects on TROPOMI SNO2 measurements and validation."

We also added the following to the end of section 2.1.

"A qu_value > 0.5 excludes any TROPOMI observation with a solar zenith angle > 81.2°. During the Antarctic summer this leads to some observations from the descending TROPOMI orbit over Antarctic to be include in the daily average (TROPOMI orbits the sunlit part of the earth from south to north)."

3) The authors use the term "Noxon cliff" for both the cliff for NO2 and that of O3. However, as far as I understand, the "Noxon cliff" can be used only for the cliff of nitrogen species (NOx, HNO3, N2O5, etc.), but not for O3. Therefore, all the description after Section 3.4, where the authors use the terminology "Noxon cliff for TCO3" should be re-worded.

Response: we agree, originally the Noxon cliff was indeed associated with nitrogen oxides and the strong-cross-vortex-edge gradient that was observed in nitrogen oxides. We do want to note in passing that several subsequent publications have connected the Noxon cliff to similar cross vortex trace gas gradients observed for other trace gases. Which should not surprise anyone as there are other trace gases involved in the catalytic ozone destruction cycle that will show strong similar gradients (HOx, CLOx or BROx cycle gases) while the mixing barrier across the winter vortex may also lead to significant gradients in other trace gases not involved in catalytic ozone destruction cycles.

Action: changed the description to "cross-vortex TCO3 gradient" (or similar) and checked/ensured that the use of the phrase "Noxon cliff" was exclusively used in conjunction with stratospheric nitrogen cycle trace gases.

Minor Comments

4) P.6, Figure 1A: Please explain why there are differences in darkness both in S5p total NO2 data points and reference total NO2 data points in this plot.

Response: the data points are semi-transparent circles (with darker outline) to provide the reader with some idea of where TROPOMI and SOAZ data overlap. Due to the strong seasonal cycle and relatively small differences between both datasets points frequently overlap. The plots on the S5p VDAF server consist of non-transparent filled markers. This has the consequence that many data points become invisible - either overlapping data points from the same instrument or overlapping TROPOMI and SAOZ data points. We thought that using semi-transparent data points was visually a bit more appealing. The consequence is that overlapping data points will show up with a different transparency. Note that for each SAOZ data point there is a corresponding TROPOMI data point.

Action: We added a clarification to the figure caption.

5) P.6, Figure 1B: There is no explanation on different three regression lines. Please explain them either in caption or in the legend. Also, no color bar is shown in the figure. Please add a color bar.

Response: we indeed forgot to describe which line is which (although the color of the value of the regression coefficients provide in the upper left corner of the plot provide a visual clue). The dotted grey line is the 1:1 line, the solid grey line is the Ordinary Linear Regression line, the solid red line is the Orthogonal Distance Regression line.

Action: We added a clarification to the figure caption.

6) P.6, Table 1: Why there are relatively large biases (< -10 %) in Rio Gallegos data? Please add some explanation.

Response: Comparison between TROPOMI and Pandora total NO2 column data and separating stations by (tropospheric NO2) pollution levels reveals a systematic small positive "bias of +5.8 % for the 28 lower polluted stations and -17.9 % for the 42 higher polluted stations" (ground-based measurements larger than TROPOMI), see Lambert et al. [2023]. This negative bias for polluted stations is consistent with the negative bias for Rio Gallegos and of similar order of magnitude.

Although the Pandora network does not cover high southern latitudes, the possibility exists that Rio Gallegos measurements are affected by air pollution from the city of Rio Gallegos itself (population of approximately 80,000). The location of the SAOZ instrument at "Observatorio Atmosférico de la Patagonia Austral" is west-north-west to the city and bordering the airport (see Google Maps image below). The physical distance to the city border is approximately 5 km and to the city center approximately 10 km, sufficiently nearby for combustion NO2 from the city to affect the SAOZ observations.

The validation report by Lambert et al. [2023] does not find biases due to the satellite solar zenith angle (SZA), the satellite cloud fraction and satellite surface albedo large enough to explain the relatively large bias for Rio Gallegos. Note that Lambert et al. [2023] does not specifically discuss comparisons for individual locations.

An analysis of SAOZ NO2 data at Rio Gallegos by Raponi [2012] reveals that the lower envelope of the NO2 seasonal cycle is well and sharply defined – suggesting a clean troposphere with the stratospheric seasonal cycle dominating. The upper envelope, however, shows a lot of scatter and spikes – which are absent at clean Southern Hemisphere locations like Neumayer suggesting emission plumes passing over the SAOZ station under favorable conditions. Note that Raponi [2012] does not discuss the causes of these spikes.

Overall, contamination of Rio Gallegos measurements by local tropospheric pollution would be a possible and plausible explanation but would require more research. Note that even with the bias the difference remains within the TROPOMI mission requirement targets.

Action: a brief summary/explanation based on the response above was added to section 2.2

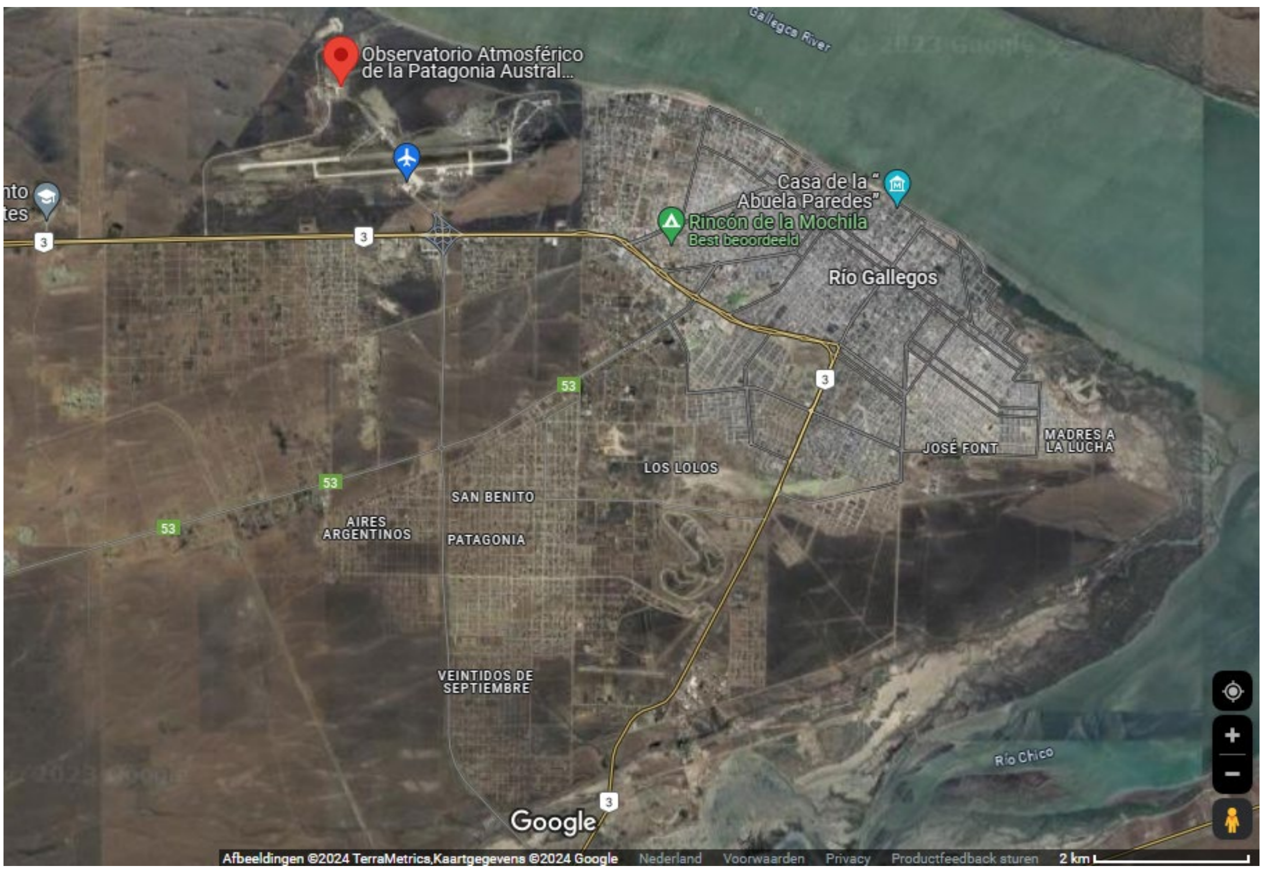
reference

Measurements of NO2 and O3 vertical column densities over Río Gallegos, Santa Cruz province, Argentina, using a portable and automatic zenith-sky DOAS system

Optica Pura y Aplicada 45(4):397-403

DOI:10.7149/OPA.45.4.397

https://www.researchgate.net/publication/272963549_Measurements_of_NO2_and_O3_vertical_column_densities_over_Rio_Gallegos_Santa_Cruz_province_Argentina_using_a_portable_and_automatic_zenith-sky_DOAS_system



7) P.6, Table 1: The order of stations in the table should be not in alphabetical order, but from lower latitude to higher latitude.

Action: changed accordingly

8) P.7, L.195: "MSR-2" first appeared in the text which is not explained elsewhere, nor any reference is shown. Please explain MSR-2 and add some references.

Action: a brief description of MSR-2 and some references were added to section 2.3 (Global Ozone field data).

9) P.7, L.197: "TEMIS" first appeared in the text which is not explained elsewhere, nor any reference is shown. Please explain TEMIS and add some references.

Action: we removed "TEMIS" and rather refer to the "KNMI operational daily global assimilated TCO3 field". We also added that this operational assimilated TCO3 field is produced for operational daily worldwide UV index predictions and that these TCO3 analyses and predictions – input for the UV index predictions - are always in real time available – unlike MSR-2 which is updated once a year or so.

10) P.7, L.203: The authors claimed "longitude-latitude grid of 1.5°x1.0° and is re-gridded to 0.8°x0.4° to match …". How they re-grid the data into finer resolution grid? Please explain.

Response: This is correct, the TCO3 data is regridded to a finer resolution using a standard bilinear interpolation. Obviously it could have been decided to retain the lower TCO3 resolution and average the TROPOMI NO2 data to on that grid. TROPOMI NO2 data has a much finer resolution (3.5x5.5 km sub-satellite) so the 0.8x0.4 grid already involves and averaging step. The 0.8x0.4 grid is then somewhere between the TROPOMI NO2 resolution and the TCO3 resolution. This could have been done differently but each choice comes with its pros and cons. We did, however, check for a single day what results looked like using TROPOMI TCO3 pixel data – so at a spatial resolution similar to TROPOMI NO2 – and we did not find significant differences in the overall outcomes (this is mentioned at the end of discussion section 4): "results … are robust relative to using gridded data or pixel data or even data from different satellites". Obviously this is a point for further attention in the future but sufficient for the purpose of this paper.

Action: we changed this to "re-gridded (bi-linear interpolation) to a finer 0.8 ..."

11) P.7, L.205: "GOME-2 has a 4 DU bias". Is this a positive bias or a negative bias? Please explain.

Response: The bias (offset) is positive relative to ground-based observations (see van der A et al., 2015)

Action: the text was modified accordingly

12) P.8, Figure 4: The panel for 2020 is wrong (the one shown here is for 2019). Please add a panel for 2020.

Action: figure was updated

13) P.8, Figure 5: Please add panel numbers [A]-[F] in Figure 5. In the figure caption, use [A]-[F] for the corresponding explanation.

Action: figure was updated and the text modified accordingly

Grammar/Typos

Action: all grammar issues and typos have been changed accordingly

14) P.1, L.28: This process depletes the Antarctic … --> This process depletes nitrogen oxides (denitrification/denoxification) in the Antarctic stratospheric vortex (Farman …

15) P.2, L.29: Farman et al., 1995 --> Farman et al., 1985

16) P.2, L.31: during Antarctic spring to the then denitrified … --> during Antarctic spring to the denitrified …

17) P.2, L.45: Struthers et al 2004 --> Struthers et al., 2004

18) P.6, L.170: regression coefficients equal 0.94 --> regression coefficients equal to 0.94

19) P.11, L.336: And complex relationships between (long-lived) … --> And complex relationships among (long-lived) …

20) P.14, L.416: J d.L. --> A.d.L.

21) P.15, L.417: P.V. --> J.P.V.

RC2

General comments:

> "The Antarctic stratospheric Nitrogen Hole: Southern Hemisphere and Antarctic springtime total nitrogen dioxide and total ozone variability in Sentinel-5p TROPOMI data" provides a scientifically useful analysis of a TROPOMI measurements of nitrogen dioxide during the Antarctic ozone hole. The study demonstrates that co-located TROPOMI NO_2 and O_3 observations can be used to clearly identify the evolution of chemical differences between inner and outer polar vortex air masses throughout the springtime. While demonstrating the viability of a new dataset for the analysis of the Antarctic ozone hole is scientifically important, improvements to the presentation of the data and details about the design of the analysis are needed.

Response: we thank the referee for the review efforts and the comments that have helped improve the paper. Below follows a detailed response to the comments including for each comment a description of the modifications that have been made.

Specific comments:

1. The introduction could be improved by focusing on the advances offered by the TROPOMI dataset and the authors' analysis, specifically:
    a. What improvements or unique capabilities does this satellite dataset offer?
    b. What problem or scientific question does the dataset answer?
    c. The background on prior satellite studies could be condensed.

Response

1a. The TROPOMI satellite instrument builds on the legacy of hyperspectral UV/VIS satellite instruments like GOME, SCIAMACHY, OMI, and GOME-2. TROPOMI provides satellite observations with unprecedented spatial resolution, accuracy and precision compared to its predecessors. Although designed for improved monitoring tropospheric pollution, it nevertheless also equally improves stratospheric NO2 and/or total NO2 column observations.

Action: we add the following to the introduction:

"The TROPOspheric Monitoring Instrument (TROPOMI) is the first of the next generation of hyperspectral UV/VIS satellite instruments. Designed and developed based on experience with satellite instruments like GOME, SCIAMACHY, GOME and GOME-2 it provides satellite observations of unprecedented spatial resolution and accuracy."

1b. Apart from providing measurements of a trace gas relevant for stratospheric ozone and catalytic ozone depletion at an unprecedented scale and with unprecedented accuracy (as explained in **1a**), a key aspect is that these measurements add some new stratospheric monitoring capacity that otherwise currently is suffering from aging satellites and steady decline in the number of such satellites. The scientific community has a commitment towards continued monitoring of the stratosphere and the ozone layer as part of the Montreal Protocol "for the protection of the ozone layer". Satellite measurements have been crucial for this commitment. Fewer satellite and deteriorating satellites are making meeting this commitment more difficult. Developing new satellite data applications is therefore very much welcomed. Especially is they are based on satellite instruments that are expected and planned to be operational for many decades ahead in time.

Action. We added the following paragraph to the introduction:

"Furthermore, the current suite of satellites that can be used for stratospheric monitoring is aging and the number of such satellites is dwindling. This is a significant concern for the scientific community and their commitment towards monitoring the ozone layer as part of the Montreal Protocol for "Protection of the Ozone Layer". Recovery due to the phase out of emissions of ozone depleting substances is a slow process and full recovery is only expected in the second half of the 21st century. However, unusual stratospheric events can strongly affect the ozone layer thickness from year to year. Whether such year-to-year changes in stratospheric ozone are anomalous or the result of natural variability is crucial for confident statements whether recovery is progressing as expected (or not). Satellite instruments measuring the stratospheric chemical composition other than ozone have been essential for understanding this year-to-year variability and thus meeting the commitment of the scientific community towards monitoring the ozone layer support of the Montreal Protocol. Given the aging suite of stratospheric monitoring satellites and their dwindling numbers, identifying new stratospheric monitoring applications is more than welcome for continued stratospheric monitoring. Especially if these applications are based on satellite instruments that are planned to remain available for many decades into the future."

1c. Because the topic and application introduced in this paper in essence is new – with the exception of the two exploratory research papers based on the earliest generation of hyperspectral UV/VIS satellite instruments in the mid-2000s – our thinking was to provide an as complete as possible earth observation context of stratospheric NO2 observations - taking limitations in publication length into account.

Hence the lengthy "background on prior satellite studies". We are pretty confident that knowledgeable people in the field will ask – just like we did – as to why this has not been published before and how this related to the extensive research done on stratospheric chemistry.

Furthermore, given that this paper could be the start of a series of new publications an overview with a "background on prior satellite studies" would provide a good starting point for anyone building on our paper.

Hence out preference to keep the section on the “background on prior satellite studies”. We could do otherwise but would prefer for the editor to make a decision on this.

Action: we leave it up to the editor to decide if the “background on prior satellite studies” should be shortened or not.

2. Additional details in the methods describing the range of latitudes used in each analysis are needed.

Response. See comment (2) by referee #1 for a similar question and our response that comment.

Action: the following was added to the discussion section 4.

“In addition, although the diurnal cycle in SNO2 is relatively small compared to its seasonal cycle it nevertheless can affect satellite retrievals and validation results. Dube et al. [2021] reported order of magnitude 10-20% effects for SAGE III/ISS solar occultation limb retrievals with larger effects for higher latitudes. Although their results are not one-on-one applicable to the results presented here they clearly indicate the need for properly assessing diurnal cycle effects on TROPOMI SNO2 measurements and validation.”

We also added the following to the end of section 2.1.

“A qu_value > 0.5 excludes any TROPOMI observation with a solar zenith angle > 81.2°. During the Antarctic summer this leads to some observations from the descending TROPOMI orbit over Antarctic to be include in the daily average (TROPOMI orbits the sunlit part of the earth from south to north).”

3. In the analysis of NO_2/O_3 correlations, how are the mask boundaries determined? What effects are there, if any, on the conclusions of the analysis if the boundaries are varied?

Response: the boundaries between the three different masks are the result of a manual iterative process. We came to these boundary after some experimenting and testing. The main reason for them is that these three masks consistently separate the inner-edge-outer vortex regions, regardless of the time period start, the time period end and the timp period duration. In that sense these boundaries are robust, although they are purely empirical. We have entertained the thought to distinguish between two distributions in vortex edge region (see answer to next question) but decided against it to keep it simple.

Action:

4. Can the “mixing lines” be geographically and temporally isolated into discrete eddies/filaments?

Response: this continues/builds on the answer to comment (4) above.

In short: good question, in all honesty we don't really know, it surely looks like it could be the case but that requires much more research.

There is at least an easy separation possible for the MASK-3 region – as is also obvious from the phase diagrams. There is almost always a vortex edge section with reduced NO2 and reduced O3. This is likely explained by total ozone over Antarctic during Antarctic springtime generally following a wave-1 pattern (maximum-minimum-maximum along a full longitude circle). The location of the minimum and maximum rotates throughout spring in a clockwise fashion and with a time scale of two weeks or so (if I recall correctly). We believe that these locations might be areas of something one could call "vortex leakage", areas where cross-vortex edge mixing takes place

Given the multiple TROPOMI overpasses per day – including ascending and descending orbits – could be the reason that during daytime there appear multiple "mixing lines" in the phase diagram (Figure 5). Simply a case of the vortex edge regions having spatially moved during the 12 hours between the previous and next overpass during late Antarctic spring. For the phase diagrams covering longer periods it becomes more and more difficult to distinguish these mixing lines, as evidence by many figures in the paper. Rather they developing into a continuous distribution: the vortex edge continuously changing locations and thereby NO2-O3 ratios due to different dynamics and advection and different altitudes.

However, to fully understand and explore vortex edge dynamics requires much more extensive research, something we felt more suitable for a follow-up paper and/or research proposal. That includes the question whether mixing lines could be "geographically and temporally isolated into discrete eddies/filaments". Like stated above, yes, a possibility, looks like it, but for now we don't know. Furthermore, we have done much more analysis and made many more plots than ever would be possible to show in a paper (see as an example the animation in the supplement) so we already had to condense a lot of material for this paper.

Action: no action

a. Can the simple phase analysis of "mixing lines" recreate a similar structure on a 2-d plot? Figure 9 is not convincing on its own. Consider including actual seasonal trends.

Response: see also previous answer. We are not sure what the referee means here: the aim of this conceptual figure is to highlight that shifts in (spatial) phasing in even simple distributions with different locations spatially of minimum and maximum values lead to variations in a phase-diagram that is not dissimilar from what is observed.

We constructed Figure 8 based on an extensive series of TROPOMI SNO2-TCO3 phase diagrams along a range of latitudes and for a range of dates that show more or less similar albeit more complex patterns that nevertheless in essence come down to the same point: phase differences in collocated data with different locations of their minimum and maximum.

But as in previous answers: space limitations in a research paper do not allow us to present most of the analyses and figures we made.

Hence why we prefer to keep Figure 9 as it is.

Note that obviously latitude is not the best coordinate here – equivalent latitude would be preferred but that is also something for a future project.

Action: no action

Technical comments:

1. Subscripts for the common notation of SNO_2 and TCO_3

Action: changed through the document

2. Improve the figure labels, especially dates

Action: figures have been updated also in accordance with a number of comments from referee #1

3. Figure 4 is redundant

Response: without further explanation it is not clear why figure 4 is redundant. We would argue Figure 4 provides necessary spatiotemporal global (zonal mean) information on the seasonal cycle in SNO2. No other figures contain similar information. Also, as this paper are in part is inspired by Wespes et al. (2022) who present a similar figure for IASI HNO3 this allowing a visual direct comparison with their results (the TCO3-SNO2 phase-diagrams are something new and not available for other trace gas combinations).

Hence we have a strong preference to keep Figure 4.