Author reply to Referee #1

Lisa K. Behrens et al.

March 6, 2018

We thank Referee #1 for carefully reading our manuscript and for the helpful comments which will improve the quality of our manuscript. We will reply to the comments point by point.

Legend:
- referee comments
- authors comments
- **changed text in the manuscript**

The paper "Investigation of NO2 vertical distribution using two DOAS retrievals for GOME-2A measurements in the UV and vis spectral range" by Behrens et al. presents a retrieval of NO2 vertical columns in the UV spectral range and discusses how far the comparison to the "standard" retrieval in the blue spectral range provides information on the vertical distribution of NO2 within the troposphere. The manuscript is well written, clearly structured and overall convincing in its conclusions. It matches well in the scope of AMT.

Thank you very much for the positive comments.

I have two fundamental comments:

1. The goal of investigating the vertical distribution of NO2, as stated in the title, seems quite ambitious to me; one measured spectrum just provides information on the integrated column (SCD), without any information on the vertical distribution. It is not clear to me why the authors seem to have expected to get direct quantitative information on the vertical distribution by just adding one further piece of information (the SCD at a different wavelength). ...

We agree with the referee that the investigation of the vertical distribution is ambitious and the title can be confusing, because we are not able to give a real profile shape. Therefore, we will change the title to: "GOME-2A retrievals of tropospheric NO_2 in different spectral ranges - influence of penetration depth". Furthermore, we will add maps with retrieved top-altitudes of NO_2 layer height (Fig. 1) in the revised manuscript in Sect. 3.1. For the altitude retrieval simple box profiles are assumed for tropospheric NO_2. A seasonal dependency of the retrieved altitude can be clearly observed in the global maps.

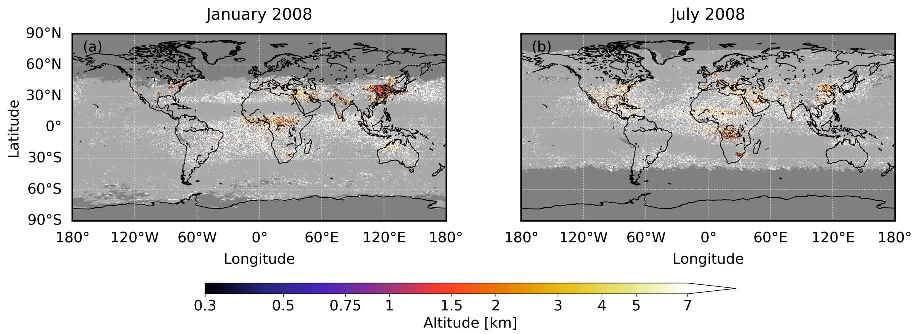

Figure 1: Monthly mean top-altitudes retrieved from the ratio between the UV and blue spectral range. To retrieve the altitude, box profiles are assumed for the tropospheric NO_2. The light grey coloured values indicate values which are below the threshold defined for the ratio (see Fig. 8 manuscript; will be added in a revised version)

... So the aim of deriving vertical information in the troposphere seems to be rather a second step; as first step, I would have expected improved stratospheric estimates. The separation of stratospheric and tropospheric column is still a fundamental challenge for the retrieval of tropospheric NO2 VCDs. While it is often no problem over highly polluted regions, it is still a crucial prerequisite for accurate emission estimates of large-scale sources such as soil emissions. Thus I miss some discussion about how far a UV retrieval might improve stratospheric estimates. Empirical approaches such as the RSM and modifications (allowing for longitudinal gradients) as well as assimilation approaches use the measured total column for the estimation of the stratospheric fraction. This requires some kind of a-priori knowledge on how large the tropospheric contribution is expected to be. For a UV retrieval, the sensitivity to the tropospheric column is weaker. Thus, a modified RSM approach might benefit from UV measurements since it can include more measurements over weakly polluted regions. This topic should be discussed in the manuscript.

We agree with the referee that the derivation of the vertical column is a second step and that it would be nice to improve the separation between troposphere and stratosphere which was indeed our original intention. Unfortunately, it was not possible to improve the stratospheric estimation with a UV NO_2 retrieval as this suffers not only from noise but also from systematic biases. However as shown by the BAMFs (Fig. 6 (Fig. 2, manuscript, will be replaced in a revised version)), the UV spectral range has still a small sensitivity to the lower troposphere and therefore, the tropospheric contribution can also be observed in the UV spectral range. This tropospheric pollution can be observed in the total SCDs in both spectral ranges (Fig. 2, will be added in a revised version) as well as an additional fitting window in the green spectral region.

BAMFs show the largest differences between the UV and blue spectral range close to the ground ($\sim$ factor 3). In higher altitudes of the troposphere, the differences are clearly reduced. As shown by Delon et al. (2008) and Stewart et al. (2008), also soil emissions (large-scale sources) are partly located in elevated layers which increases the visibility in the UV spectral range, and therefore, reduces the differences between the spectral ranges. A key issue here is the seasonal dependency between the spectral ranges (Fig. 3, Fig. 5; will be added in a revised version). In January, the $\mathrm{vis_{blue}}$ NO_2 values are higher than the UV NO_2 values especially above polluted areas (Fig. 3) whereas in July, both spectral ranges are similar or the UV NO_2 values are higher than the $\mathrm{vis_{blue}}$ NO_2 values. Similar offsets can be found between the blue and the green fitting window. Therefore by introducing an UV fitting window, improving the separation of stratosphere and troposphere is not possible and further investigations are needed for this special point. In our case, we are using tropospheric columns by subtracting the reference sector, and therefore, the differences are cancelled out to a large extent. We will add the following paragraph (between Sect. 2.4 and Sect. 2.5 in the old manuscript (2.6 in the new manuscript)):

2.5 Stratospheric NO_2
Figure 5 (will be added in a revised version) shows the latitudinal and seasonal dependency for the three NO_2 fitting windows. The seasonal dependency clearly differs between the three fitting windows also over regions dominated by stratospheric NO_2, especially for the green wavelength range strong interferences are observable. Although the differences are smaller between the UV and blue spectral range, they are clearly observable, for example at the equator (Figure 5 b; will be added in a revised version). In northern hemispheric summer the UV NO_2 values are higher than the NO_2 values derived from the blue spectral range whereas in northern hemispheric winter the NO_2 values from the blue spectral range are slightly higher. Therefore, it is currently not possible to improve the stratospheric NO_2 retrieval by using different wavelength ranges.

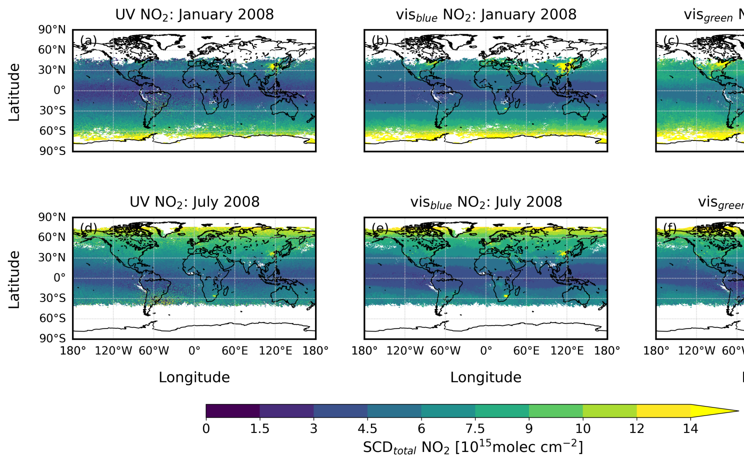

Figure 2: Monthly mean total NO_2 SCD for (a, b, c) January and (d, e, f) July 2008 for the (a, d) UV, (b, e) blue, and (c, f) green spectral range. (will be added in a revised version, supplement)

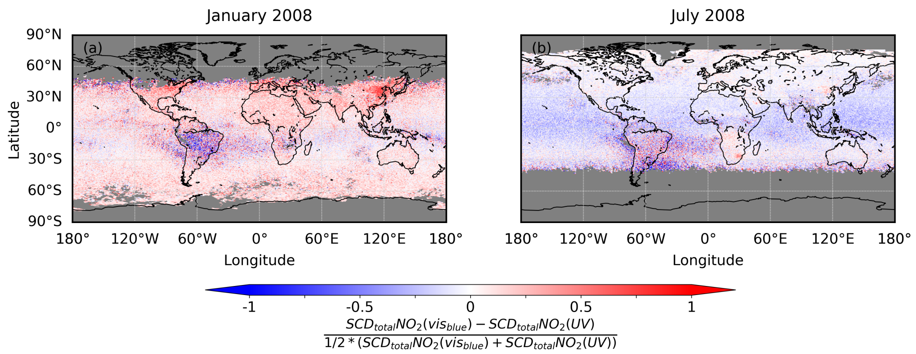

Figure 3: Relative difference between monthly mean total NO_2 SCDs in the blue and UV spectral range. Differences for (a) January and (b) July 2008. Dark grey shaded area: no NO_2 values available. (will be added in a revised version, supplement)

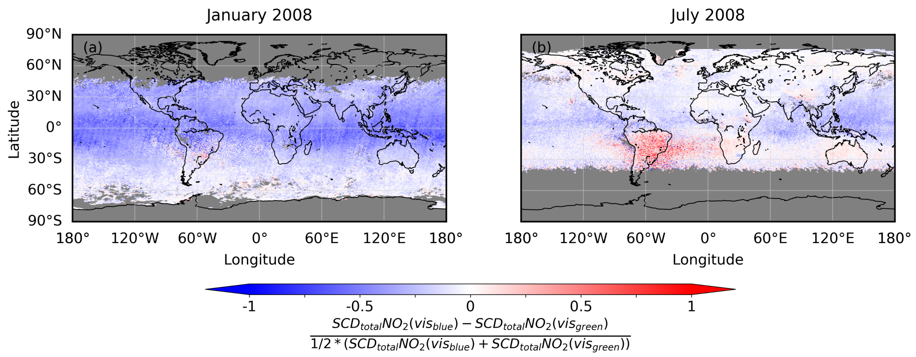

Figure 4: Relative difference between monthly mean total NO_2 SCDs for the blue and green spectral range. Differences for (a) January and (b) July 2008. Dark grey shaded area: no NO_2 values available. (will be added in a revised version, supplement)

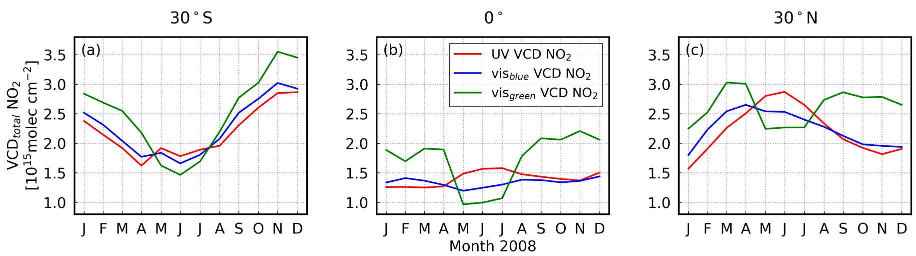

Figure 5: Time series of NO_2 total VCDs of 2008 for 30° S (averaged: 28° S – 32° S), 0° N (averaged: 2° S – 2° N), and 30° N (averaged: 28° N – 32° N) above the area of the reference sector for cloud free pixels. (will be added in a revised version)

2. The authors use the established blue spectral range plus a fit window in the UV. But what about the green spectral range? As shown in Fig. 1, the NO2 cross section still shows absorption bands above 550 nm. This would be another complementary piece of information, even more sensitive towards the lower troposphere than the standard retrieval. Of course the noise will be higher, and the choice of the fitting window and the water vapour cross section might be challenging. I understand that such a "green" retrieval would require major data processing; but still the authors should discuss the potential of adding additional wavelengths for the goal of assessing profile information, and I would appreciate if they could provide some sensitivity studies.

We calculated BAMF for three different wavelength 352 nm, 438 nm, and 515 nm. As can be seen in Fig. 6, the sensitivity for larger wavelength increases towards the surface compared to the standard fitting window. Therefore, in principle further information about the vertical profile can be gained from this spectral range as suggested by the reviewer.

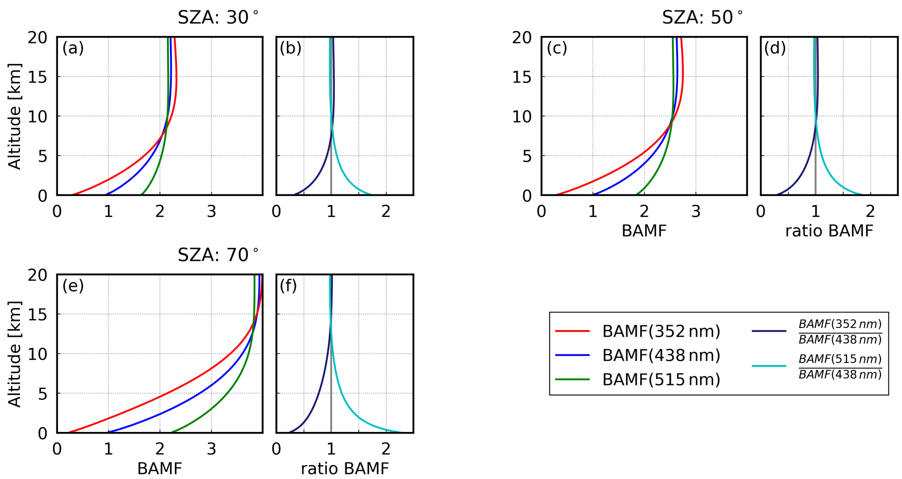

Figure 6: BAMF for three wavelengths and the ratio of BAMFs to the mean wavelength of the standard fitting window calculated with the radiative transfer model SCIATRAN. BAMFs converge at higher altitude (not shown). The BAMFs are calculated for 352 nm (UV), 438 nm (vis), and 515 nm at (a, b) 30° (c, d) 50° and at (e, f) 70° solar zenith angle (SZA). A surface spectral reflectance of soil is assumed. (Fig. 2, manuscript, will be replaced in a revised version)

An additional fitting window for the green spectral range was already presented in Richter and Burrows (2000). They used a fitting window from 490 – 540 nm for the GOME instrument. In combination with a UV fitting window, they tried to separate stratospheric and tropospheric NO_2 VCDs. They concluded that for GOME measurements it is not possible to retrieve global maps of NO_2 VCDs, because of the smaller signal to noise ratio and strong interferences with other absorbers which leads to systematic errors.
Here, we found similar results for GOME-2A. Large areas with liquid water absorption can be clearly identified. In our fit, we do not use a cross section for

liquid water, because this introduces further interferences over land where no liquid water absorption is expected. Furthermore, in the current fitting window, areas with clear water (see for example north of Australia, Fig. 8 (b); will be added in a revised version) and interferences with the surface in Africa can be observed (Fig. 7, 8; will be added in a revised version). These effects can also be observed in the ratio between the blue and green spectral range (Fig. 10; will be added in a revised version).

Compared with the fitting windows in the UV and blue spectral range, the fitting windows shows a similar distribution of total VCDs above the Pacific Ocean as the UV spectral range (Fig. 11 (Fig. 4, manuscript, will be replaced in a revised version)) with a small shift to negative values. Nevertheless, the NO_2 retrieval works quite well above highly polluted areas. Therefore, we will include a case study for China for the green spectral range and an additional section about the green fitting window in our revised manuscript.

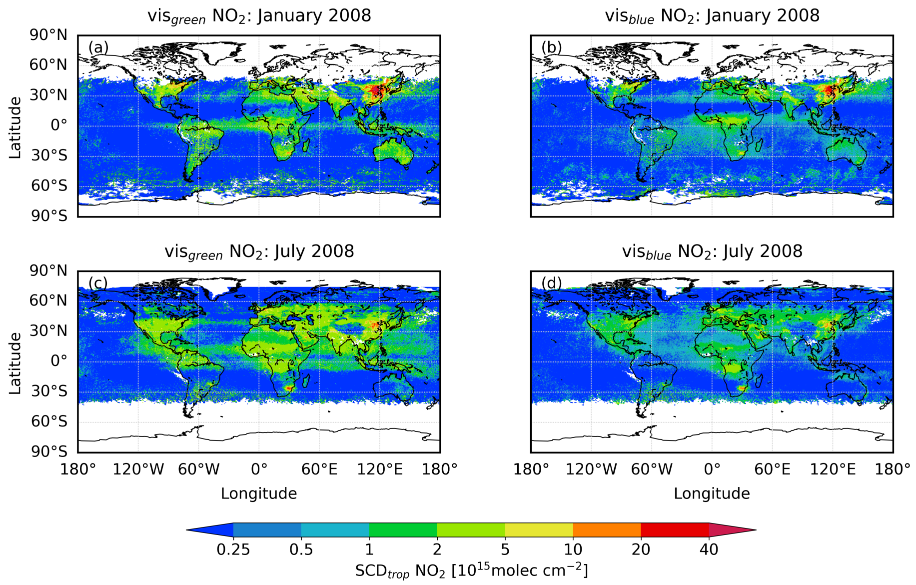

Figure 7: Monthly mean tropospheric NO_2 SCD for (a, c) January and (b, d) July 2008 for the (a, b) green and (c, d) blue spectral range. (will be added in a revised version, supplement)

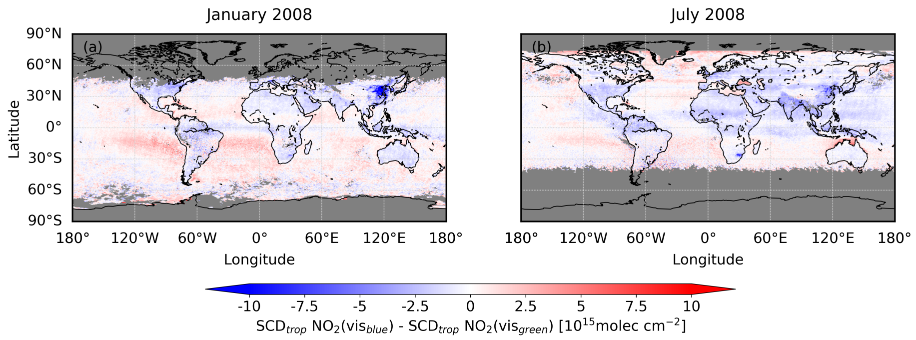

Figure 8: Absolute difference between monthly mean tropospheric NO_2 SCDs in the green and blue spectral range. Differences for (a) January and (b) July 2008. Dark grey shaded area: no NO_2 values available. (will be added in a revised version, supplement)

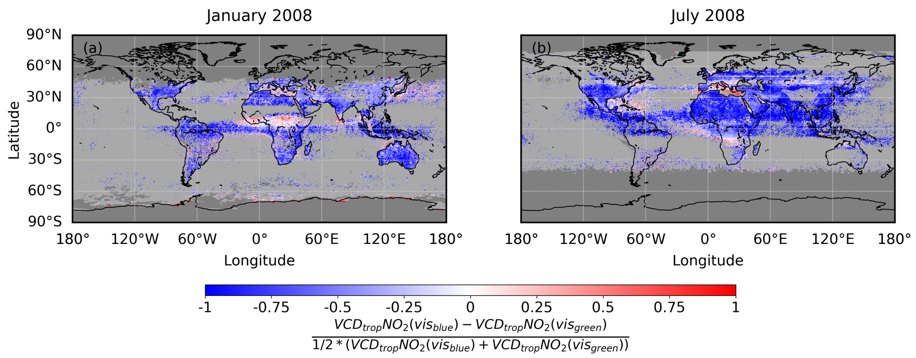

Figure 9: Relative difference between monthly mean tropospheric NO_2 SCDs in the green and blue spectral range. Differences for (a) January and (b) July 2008. Dark grey shaded area: no NO_2 values available. Light grey coloured values indicate values where the vis NO_2 is close to zero, which have been filtered out. (will be added in a revised version, supplement)

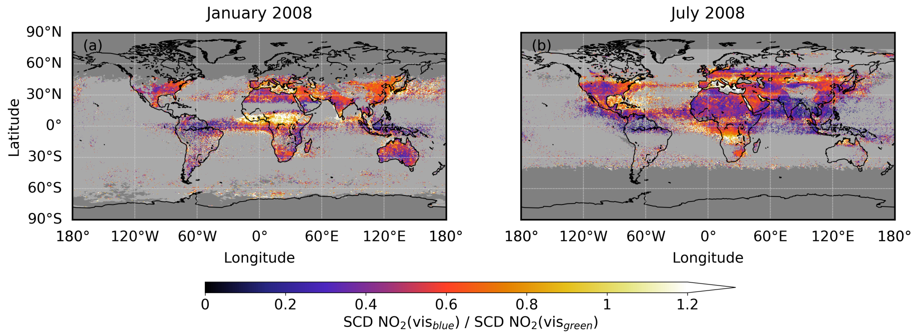

Figure 10: Ratio between monthly mean tropospheric SCDs of NO_2 in the blue and green spectral range. (a) January 2008 and (b) July 2008. Dark gray shaded area: no NO_2 values available. Light grey coloured values indicate values where the vis NO_2 is close to zero, which have been filtered out. (will be added in a revised version, supplement)

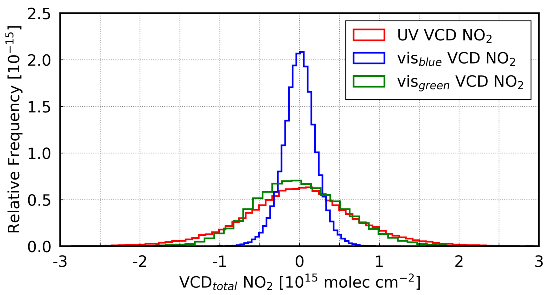

Figure 11: Distribution of total NO_2 VCDs over a clean region (equatorial Pacific: 5° S – 5° N and 150° E – 210° E) for the UV and vis spectral range for January 2008. Curves are normalised to unit area and centered on zero. (Fig. 4, manuscript, will be replaced in a revised version)

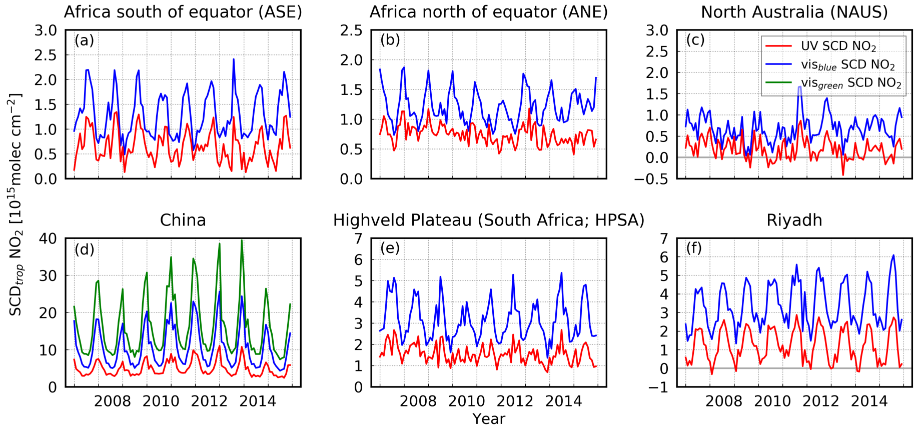

Figure 12: Time series 2007 – 2015 of tropospheric NO_2 SCDs for the UV (red line) and blue (blue line) spectral range for different regions. Additionally for China, the green (green line) spectral range is shown. Note the different y-axes. The vertical lines indicate January of the individual years. (a – c) biomass burning regions and (d – f) regions with high anthropogenic air pollution. (Fig. 9, manuscript, will be replaced in a revised version)

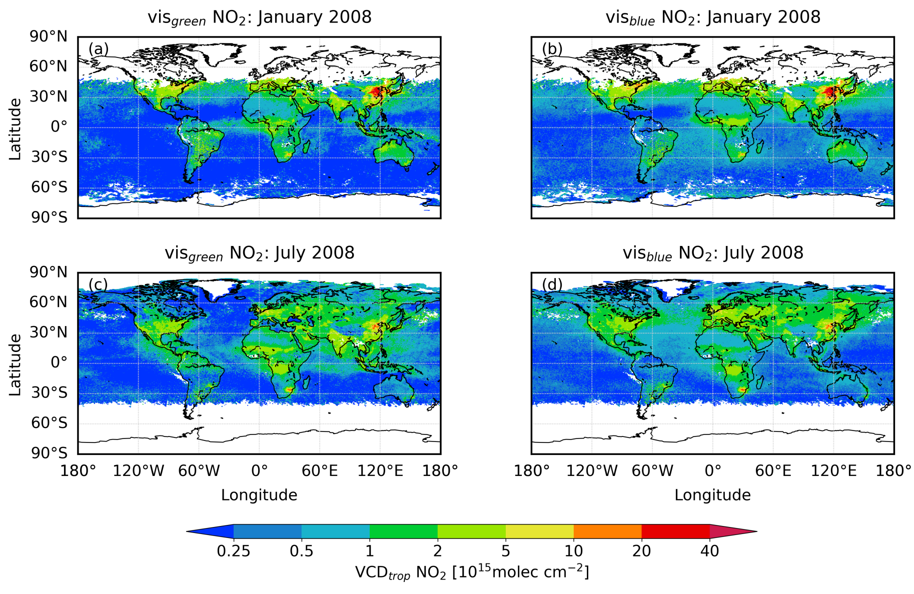

Figure 13: Monthly mean tropospheric NO_2 VCD for (a, c) January and (b, d) July 2008 for the (a, b) green and (c, d) blue spectral range. (will be added in a revised version, supplement)

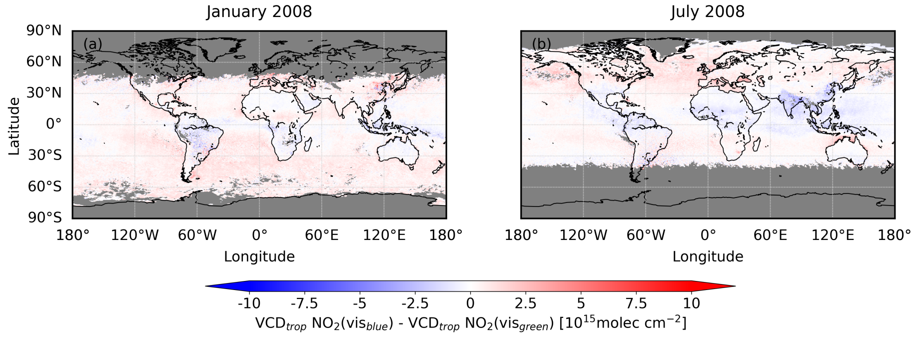

Figure 14: Absolute difference between monthly mean tropospheric NO_2 VCDs in the green and blue spectral range. Differences for (a) January and (b) July 2008. Dark grey shaded area: no NO_2 values available. (will be added in a revised version, supplement)

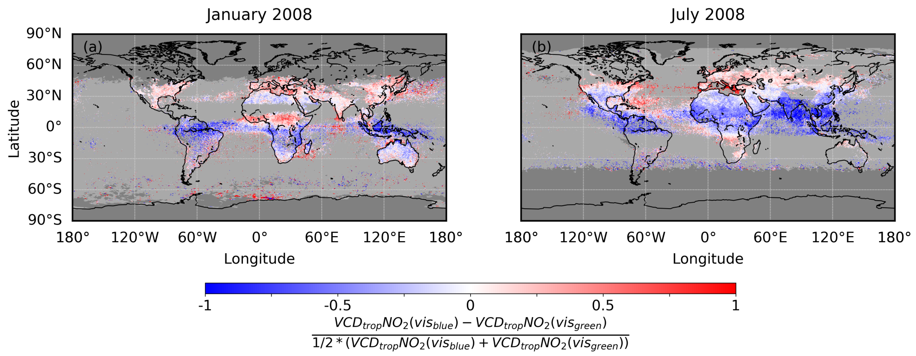

Figure 15: Relative difference between monthly mean tropospheric NO_2 VCDs in the green and blue spectral range. Differences for (a) January and (b) July 2008. Dark grey shaded area: no NO_2 values available. Light grey coloured values indicate values where the vis NO_2 is close to zero, which have been filtered out. (will be added in a revised version, supplement)

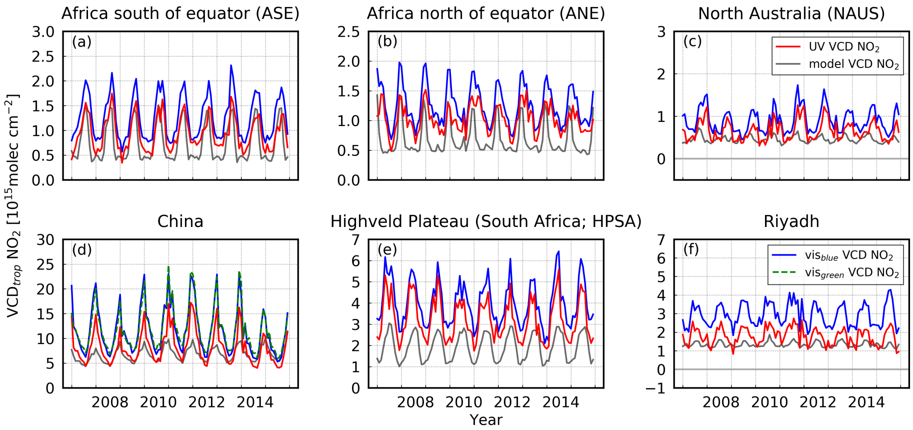

Figure 16: Time series 2007 − 2015 of tropospheric NO_2 VCDs for the UV (red line) and blue (blue line) spectral range as well as the TM5-model VCDs (gray line) for different regions. Additionally for China, the green (green line) spectral range is shown. Note the different y-axes, the same as in Fig. 12. The vertical lines indicate January of the individual years. (a − c) biomass burning regions and (d − f) regions with anthropogenic air pollution. (Fig. 13, manuscript, will be replaced in a revised version)

Minor comments:

Page 3 line 32: "can provide information about the accuracy": I would suggest a different formulation such as "allows to infere the validity of a-priori profiles".

Changed as suggested.

Page 4 line 12: should be "summary and conclusions".

Changed as suggested.

Section 2.1: Please add Munro et al. (2016) also as reference for GOME-2 A.

Done.

Page 4 line 30: add "before launch" or similar.

Done.

Section 2.2: The details of the cross sections and respective references might be shifted to Table 1.

Done — we changed the paragraph as follows:
For this study, we developed a NO_2 DOAS retrieval for the GOME-2A instrument in the UV which uses a fitting window between 342 and 361.5 nm, and a polynomial degree of four. In this retrieval, one NO_2 cross section measured with the GOME-2A instrument before launch as well as two O_3 cross sections are used with an additional $\mathbf{I_0}$ correction of $\mathbf{10^{20}}$ molec cm^{-2} (Platt et al., 1997; Richter, 1997). Additionally, cross sections for O_4, BrO, HCHO, the Ring effect and the instrumental cross section Zeta are included in the fitting procedure (see Tab. 1).

Table 1: Fit settings for the NO_2 retrievals in the UV and the vis spectral range.

	UV spectral range	vis spectral range
fitting window	342−361.5 nm	425−450 nm
polyn. degree	4	4
cross sections		
NO_2	223 K; Gür et al. (2005)	243 K; Gür et al. (2005)
O_3	223 K and 243 K; Serdyuchenko et al. (2014)	223 K; Gür et al. (2005)
O_4	Greenblatt et al. (1990)	Greenblatt et al. (1990)
H_2O	−	Rothman et al. (2010)
BrO	Wilmouth et al. (1999)	−
HCHO	Meller and Moortgat (2000)	−
Ring	calculated with SCIATRAN, Rozanov et al. (2014)	Vountas et al. (1998)
instr. func.	Zeta; EUMETSAT (2011)	−

Page 5 line 6: Which were the criteria for identifying "best results"?

Best results means smallest RMS — we changed the sentence as follows:
Among many different wavelength windows we tested, the selected window from 342 – 361.5 nm provided the smallest root mean squared error (RMS).

Page 5 line 11: For a focus on stratospheric patterns, this would probably be crucial.

We agree with the reviewer but as shown above a stratospheric correction is also difficult without the introduced offset. We will add an additional section about the stratospheric NO_2.

Page 5 line 12: So daily Earth is the alternative, but what is the default?

Yes, it is an alternative. For NO_2 the daily solar reference is default. Daily Earth spectra are often used in the UV and for weak absorbers as CHOCHO and HCHO.

Page 5 line 20: Details and references for O4 (vis) and H2O are missing (might also be added to Table 1).

Done — see Table 1.

Page 6 line 21: What does "upper atmospheric" mean?

"upper atmospheric" is removed.

Page 6 line 30: What is meant by "this correction method"? The RSM? Then write it. Or any correction of the RSM close to the polar vortex? Then provide further details.

RSM is meant — we changed the sentence as follows:
For the reference sector method, the same cloud screening as for the data selection is used (see Sect. 2.7).

Page 7 line 2: "This correction" –> RSM?

Changed as suggested.

Page 7 line 5: "no negative values are expected": if the model is correct!

Done — we changed the sentence as follows:
Therefore, no significantly negative values are expected for the VCDs assuming the model is correct.

Page 7 line 9: "... using a linear approach" –> "the NO2 VCDs are scaled by a correction factor linear in T in order to correct for the temperature dependency of the NO2 cross section, as suggested in Boersma..."

Changed as suggested.

Page 12 line 24: avoid "believe"; you have provided several arguments for this conclusion.

Done.

Additionally as suggested by Referee #2, we will change four main points in the revised manuscript:

1. We will discuss errors in more detail. Therefore, a table with error sources is added to the revised manuscript.
2. We will include a discussion about the temperature dependency of the NO_2 SCDs which affects the UV and vis NO_2 retrievals different.
3. The figure with the absolute differences will be replaced by figures with relative differences which makes the differences between the SCDs and the VCDs for the two spectral ranges more clear.
4. We will discuss in more detail how CTM profiles should be changed to reconcile VCDs of the different spectral ranges as well as the model VCDs. Here, our observations suggest that compared to the real NO_2 profiles, in the TM5 model the NO_2 is higher in the atmosphere with lower surface concentrations.

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