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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Tropospheric NO_2 column densities deduced from zenith-sky DOAS measurements in Shanghai, China, and their application to satellite validation" *by* D. Chen et al.

D. Chen et al.

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First we want to thank this reviewer very much for the positive and constructive review. Before we address the comments in detail point by point, we first give a short overview on the major changes of the manuscript.

a) We inserted a much more detailed error discussion taking into account the effects of different contributing error sources, especially their dependence on SZA and the tropospheric NO2 VCD. The errors are expressed as absolute and relative errors and presented in the new Fig. 5.

b) We included additional sensitivity studies for the determination of the tropospheric AMF taking into account the effects of varying asymmetry parameter and surface

albedo. The results are summarized in Fig. 6 (old Fig. 10).

c) We now use tropospheric AMF for a single scattering albedo of 0.95 for the determination of the tropospheric NO2 VCD from the zenith-sky observations. While reliable information on this parameter is difficult to obtain, we think that a value of 0.95 might be more realistic than a value of 1.0 (purely scattering aerosols). The application of the new value leads to an increase of the tropospheric NO2 VCD by about 2-5% depending on SZA.

d) As also suggested by the other reviewers, we include a new figure (Fig. 15) showing the correlation analysis and time series comparison of the SCIAMACHY data with the surface NO2 concentration.

General comments
This paper presents a new method to extract the tropospheric vertical column density (VCD) of NO2 from zenith-sky DOAS measurements under highly-polluted conditions in Shanghai, China. Considering that the extracted tropospheric NO2 VCD would be important for validating the emission inventory and satellite data, the subject of this paper is appropriate for ACP. However, the total error estimates, which are an important part of the present work, seem too simplistic or misleading, although the authors have done several sensitivity tests for each error source. In particular, I am unconvincing that the total error can be summarized by a single value, as done in Section 3.1.4. However, I recommend this paper will be a ACP publication after adequately addressing my concerns described in detail below.

Reply: Many tanks for this positive assessment. We addressed all the points raised by the reviewer as indicated by our detailed response (see below). We updated our error discussion in a comprehensive way (see also point a) above).

Specific comments
p.16714, line 15-19: It is unclear what supports the authors' argument that zenith-sky DOAS measurements provide more realistic information about total tropospheric NO2

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than the long-path DOAS. This is not necessarily supported by a better comparison with SCIAMACHY data, while SCIAMACHY data have not well been validated, as the present study has been motivated.

Reply: We agree that it is not straight forward to make this conclusion from the correlation analysis, especially if only relatively little data points are available. Nevertheless, we are confident that the systematically higher correlation coefficients for the zenith observations compared to the surface observations for ideal conditions (CF $<$ 0.2, CTH $>$ 1 km) give an important hint in this direction. Since both, zenith scattered and satellite observations observe the total column, it is reasonable that they show higher correlation coefficients (at least under ideal conditions). In contrast, the surface observations are in any case sensitive only to a part of the total NO2 column.

The strongest evidence that zenith sky observations are more suitable for satellite validation arises from the findings of the comparison between zenith sky observations and surface concentrations as well as from the different influence of the boundary layer height on the tropospheric NO2 VCD.

First, it is found that the effect of boundary layer height is much stronger for the tropospheric NO2 VCD derived from the surface data. Since the information on the boundary layer height is limited, the corresponding uncertainties are much more important for the surface data compared to the zenith observations.

Finally, the correlation analyse between the two data sets strongly confirms these expectations.

In conclusion, especially for situations with large uncertainties of the boundary layer height, zenith sky observations are clearly better suited for satellite observation. Only for situations with rather stable and(or) known boundary layer heights, validation by surface concentration data will yield results of similar quality. This might e.g. be the case for satellite instruments with overpass times during the afternoon. We added this information at the end of Sect. 4.2.2.

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p.16714, line 22-23: I think that the sentence "Our comparison showed good agreement, ..." is unfair. A significant discrepancy has been left, as the spatial sampling effect explains only a portion of the systematic difference found in the comparisons (Sections 4.2.2 and 4.2.3).

Reply: Taking into account the results from similar validation experiments and in particular the fact that the location of our validation experiment experiences heavy pollution, we still think that the term 'good agreement' is appropriate. However, we agree that it should be also pointed out that still systematic differences exists, which are most probably related to errors of the satellite data caused by uncertainties of the aerosol absorbing properties and the profile heights of the aerosol and NO2 layer. We added this information to the abstract.

p.16718, line 8-9: Why did the authors choose the fitting window 434-462 nm? The range of 425-450 nm is generally used for DOAS analysis, including that of SCIAMACHY data used here (p.16733, line 5). In the case that the authors still think that the fitting window is best, should CHOCHO be included in the DOAS analysis?

Reply: The choice of the fitting window is not critical for the ground based observations because of the very strong NO2 absorptions at this polluted site. Thus the different fitting windows between ground based and satellite data are not important for this comparison. CHOCHO was not included into the fitting procedure, because the main focus was on NO2 and the CHOCHO absorptions are much smaller than those of NO2. We are thankful for this comment of the reviewer and will also analyse the CHOCHO absorptions in our data sets in the future.

p.16718, line 23-34: It may help if some descriptions of how to measure the Fraunhofer reference spectrum are added here. Otherwise, no information about the reference spectrum is given before Section 3, where the term "reference" is often used.

Reply: We added more information on the measurement of the Fraunhofer reference spectrum in Sect. 2.1.2 and more information on the determination of the NO2 absorp-

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tion in Sect. 3.1.3. We use now the term Fraunhofer reference spectrum consistently throughout the whole text.

p.16721, line 15-17: It would be better to show and discuss the NO2 DSCD for three days, not the single day of 17 December 2006.

Reply: Actually, as described in the manuscript, the NO2 DSCD for the three days we chose all display the same U-shape variation. And those three days are all characterized by ideal meteorological condition and low surface NO2 concentration (as demonstrated by long-path DOAS measurement). So it may be repetitive to show NO2 DSCD for three days here.

p.16721, line 18-21: I suggest the authors modifying this sentence to be more quantitative one. Did winds blow from sea throughout the day? What does a trajectory analysis tell us?

Reply: Many thanks for the suggestion. Yes, the winds blow from sea nearly throughout the day. We now add the word 'all-day' in the corresponding sentence. But due to the limited experimental equipment and condition, we did not apply a trajectory analysis here. We'll take it into account in the future.

p.16721, line 21- p.16722, line 4: I was confused many times here. Is "SCD(ref)" in equation 4 the same as that of equation 1 (p.16720)? Would it be better to replace "mea" and "ref" by "twilight" and "noon", respectively?

Reply: Yes, the 'SCDref' in Eq. (4) is the same as that of Eq. (1). In order to avoid confusion we now also use the term SCDmeas in Eq. (1) (instead of SCDtotal) and state now explicitly that the term SCDmeas in Eq. (4) corresponds to measurements during twilight. In addition we added the information that Eq. (4) followed from Eq. (1).

p.16722, line 2-4: The authors need to do more to justify ignoring the diurnal variation of stratospheric NO2 VCD. At least, the authors need to add more quantitative descriptions. How small is the error due to ignoring the diurnal variation of stratospheric

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NO2? If a 10%-diurnal variation is ignored, how large does it impact on the estimate of VCD(strato)?

Reply: There seems to be a misunderstanding here: the diurnal variation of the stratospheric NO2 VCD is only ignored for the determination of the VCDstrato during twilight. For this determination the respective error can be neglected because the ratio of the stratospheric AMF during twilight and noon is about 20. Thus a variation of the stratospheric VCD by a factor of two will translate into an error of the twilight NO2 VCD of only 2.5%. For the determination of the VCDstrato during the day, the diurnal variation is well taken into account by linearly interpolating the VCD between sunrise and sunset, as explained in Sect. 3.1.1. We added more information to the text to avoid this misunderstanding.

p.16722, line 13-25: As written in the manuscript, it is assumed that the stratospheric NO2 column is invariant in time and space. How much uncertainty does this assumption propagate into the estimate of SCD(trop) and VCD(trop)? In addition, I am unconvincing the statement "However, for polluted areas, the uncertainty caused by the stratospheric part should be rather small (especially for small SZA)." This uncertainly would be more important in summer, when the tropospheric concentration is smaller. Moreover, I do not understand why the additional two pairs of a.m. and p.m. stratospheric values reduce the error. More description and justification are necessary. Section 3.1.2: The authors should mention the wavelength of AMF calculations.

Reply: We agree and added much more detailed information on the respective errors and their effect on the tropospheric NO2 VCD in the completely modified section on the error estimation. It is true that even if different seasonal values for VCDstrato are used, still an error remains due to the temporal variability of the stratospheric NO2 VCD. However, these errors are smaller compared to the use of only one pair of stratospheric VCDs during the whole year. We estimated the remaining uncertainties using SCIAMACHY limb observations. We added the relevant information to the text. The AMF are calculated for 448nm. We added this information to the text.

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p.16723, line 7-14: While the authors realize that the NO2 vertical profile is a key parameter affecting the results, is the stratospheric NO2 column for the assumed McLinden climatology consistent with that deduced from zenith-sky DOAS measurements? For the tropospheric parts, what is the assumption of NO2 concentration in PBL (20 ppb) based on? Is it too high, especially in summer? Would it be more reasonable to assume that volume mixing ratio is constant in PBL, not number density?

Reply: Only for rather high SZA (and low tropospheric VCD), the uncertainties caused by the stratospheric VCD are the dominant error source for the tropospheric NO2 VCD (see new Fig. 5). In addition, even if the absolute values of the stratospheric VCD between the McLinden and our observations deviate, the relative profile shape might still be appropriate.

Similar arguments apply to the choice of the tropospheric NO2 mixing ratio. The most important effect on AMFtropo arises from the relative profile shape and not for the absolute value of the mixing ratio (as long as the optical depth is $<<1$). The reviewer is right that the assumption of a constant mixing ratio would have been the most appropriate choice. However, the differences between both choices are small and we chose a constant concentration for practical reasons.

p.16723, line 16-17: I strongly suggest assuming SSA=0.95 to avoid readers' confusion, while the authors state that this value is the most realistic value on p.16737. It would be helpful to add a reference for the SSA used.

Reply: We agree and recalculated the VCDtropo_zenith under the assumption of a SSA of 0.95 (see also point c) above). Also the sensitivity studies (Fig. 6) were redone using this assumption.

p.16724, line 23-26: How was this particular case selected? What about the results for summer?

Reply: This case was arbitrarily chosen, which shows the dominant influence of tro-

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pospheric VCD on total SCD. The case for summer can also demonstrate the similar influence considering the heavy NO2 pollution at the experimental site.

Section 3.1.4: As mentioned earlier, error estimates made here are too simplistic or misleading. What is the representativeness of all error estimates discussed here? Would it be better to mention both the relative and absolute values of the errors? I strongly suggest the authors summarizing their error estimates with respect to different atmospheric conditions and seasons, etc. It seems to me that the error estimates for different pollution levels (e.g., highly-polluted, moderate, and clean conditions) are necessary, especially for the tropospheric NO2 VCD.

Reply: We agree and added a more detailed error determination. In particular we add a new figure showing the dependence of the absolute and relative error on the SZA and the tropospheric VCD (Fig. 5).

p.16726, line 21-23: Would it be more reasonable to assume that volume mixing ratio is constant in PBL, not number density?

Reply: The reviewer is right that the assumption of a constant mixing ratio would have been the most appropriate choice. However, the differences between both choices are small and we chose a constant concentration for practical reasons.

p.16729, line 7-9: Why does it indicate an overestimate of the PBL height? By the way, what does the overestimate mean here?

Reply: The VCDtropo from the surface measurements is proportional to the BL. In contrast, the dependence of VCDtropo from the zenith observations on the BL is very small. If, as observed, VCDtropo from the surface measurements is typically larger in the morning, this can be explained if the true BL height is smaller than that assumed in the retrieval of VCDtropo_surface.

Section 4.1.1: Can the assumption of the asymmetry parameter be an additional source of errors in AMF?

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Reply: We agree and added another sensitivity study on the asymmetry parameter (see also Fig. 6). The effect can be especially important for small SZA. We added this information to Sect. 3.1.5. We now also include a sensitivity study for the influence of the surface albedo.

p.16730, line 19-21: I do not understand the sentence "Since the dominant fraction ...". How large errors can arise due to the assumption of the relative location of NO2 and aerosol layers?

Reply: Most observations are performed while the sun is not rather high (e.g. SZA $< 85°$). Especially the measurements contributing to the satellite observations were measured around noon. For low SZA, influence of the profile assumptions becomes rather small and thus most of the observations are only weakly affected by this potential error.

p.16731, line 5: Please quantify the agreement of AMFs.

Reply: We completely rewrote the whole section on the error determination and included quantitative statements.

p.16733, line 27-p.16734, line 6: I think that it is too strong to say that the tropospheric AMF simulation for ground-based measurements takes the seasonal variation into account, especially because of the omission of seasonal variation of NO2 profile. Why does the choice of NO2 profile shape have a stronger impact on satellite AMF?

Reply: Of course our treatment of the seasonal variation can only be a rough approximation. However, as can be seen in Fig. 3, the different settings have only very small effect on the tropospheric AMF for satellite observations. In contrast, since the sensitivity of satellite observations changes strongly with height, the tropospheric NO2 VCD depends strongly on the assumed PBL height.

Section 4.2.2: Most of the results are based on the single threshold (cloud fraction = 0.2) distinguishing cloudy and clear-sky conditions. What happens if the different

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threshold is used instead?

Reply: Many thanks for the suggestion. Actually, we selected CF=0.2 as the threshold of cloudy and clear-sky conditions by referring to the criteria stated in other papers (e.g. Ordóñez et al., 2006). In this study, by applying the threshold, we can get enough data points under both cloudy and clear-sky conditions for regression anaysis. But we think it's also valuable to analyse different threshold (e.g 0.1, 0.3) as the reviewer pointed out, and will do it in future analysis.

p.16735, line 10-11: It seems to me that the number of data is too small to say that the correlation has been improved.

Reply: We added the following statement to the text: "Note that because of the small number of data points, the correlation results should be treated with care and should be confirmed by additional studies in the future. "

p.16735, line 17-24: I strongly suggest that the authors add a plot showing correlations between the tropospheric NO2 VCD from SCIAMACHY and long-path DOAS observations. I think it logically wrong that a better comparison with SCIAMACHY data demonstrates the advantage against satellite validation, while SCIAMACHY data might be incorrect occasionally.

Reply: We added the graphs for the correlation analysis and time series comparison between the surface and satellite data (see Fig. 15). As stated at the beginning (see reply to the first of the specific comments) we disagree here. While we agree that also SCIA data have large errors, it is obvious that the correlation of the zenith data is especially better than those of the surface data, if there are ideal conditions for the satellite measurements (low cloud fraction, CTH $>$ 1 km).

p.16738, line 6-10: The spatial averaging effect (1.30-1.46) explains only a portion of the systematic difference (1.73, as mentioned on p.16735), but a significant difference still remains. I think that the authors should mention this difference and discuss its

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potential causes.

Reply: We agree and added additional discussion of the most probable reason for the remaining discrepancy at the end of Sect. 4.2.3.

p.16739, line 7-8: As mentioned above, a better comparison with SCIAMACHY data does not necessarily support that zenith-sky DOAS measurements provide more reliable and suitable data for satellite data validation, while SCIAMACHY data have not well been validated.

Reply: Again, while we agree that also SCIA data have large errors, we disagree on the overall statement. The fact is that the correlation of the zenith data is especially better than those of the surface data, if there are ideal conditions for the satellite measurements (low cloud fraction, CTH $>$ 1 km).

Technical corrections
The unit of column concentration should be "molecules cm-2", not "molecule cm-2", throughout the manuscript.

Reply: corrected

p.16714, line 25: "Nitrogen dioxide ..." should be "Nitrogen dioxide (NO2) ..."

Reply: corrected

p.16719, line 9-11: At the end of the sentence "Spectra in 372-444 nm ...", "C" as the unit of temperature is missing.

Reply: corrected

p.16720, line 15-17: I was a little confused about this sentence. This can be read as the whole extraction procedure relies on the long-path DOAS measurements. Is the long-path DOAS measurement used only for estimating the tropospheric VCD in the reference spectrum, as mentioned on p. 16724?

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Reply: To avoid confusion we added that long-path DOAS observations are used “for the selection of rather unpolluted days and for the determination of the NO2 absorption in the Fraunhofer reference spectrum. ”

p.16721, line 9-11: Information about the measurement location for Fig. 1 should be provided.

Reply: We’ve described in Sect. 2.1.1 that all the measurement carried out since 22 December 2006 are made on our urban site (Fudan University). So it may be not necessary to add the measurement location here.

p.16730, line 19: "were" should be "was".

Reply: corrected

p.16733, line 14-15: It may help if information on the wavelength for these aerosol optical properties is added.

Reply: All aerosol optical parameters are for 440 nm. We’ve added it.

p.16736, line 9 and p.16739, line 16: What does the distribution of tropospheric NO2 mean? Is it the vertical distribution?

Reply: Both, vertical and horizontal distribution is meant. We clarified this.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16713, 2008.