Atmos. Chem. Phys. Discuss., 8, S8593–S8598, 2008
www.atmos-chem-phys-discuss.net/8/S8593/2008/

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.

Anonymous Referee #4

Received and published: 27 October 2008

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.

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 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.

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).

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?

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.

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.

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?

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?

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

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.

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?

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.

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

ACPD

8, S8593–S8598, 2008

Interactive Comment

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.

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

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

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

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?

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

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?

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 threshold is used instead?

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.

ACPD

8, S8593–S8598, 2008

Interactive Comment

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.

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 potential causes.

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.

Technical corrections

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

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

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

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?

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

ACPD

8, S8593–S8598, 2008

Interactive Comment

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

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

p.16736, line 9 and p.16739, line 16: What does the distribution of tropospheric NO_2 mean? Is it the vertical distribution?

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

ACPD

8, S8593–S8598, 2008

Interactive Comment