Atmos. Chem. Phys. Discuss., 7, S6577–S6584, 2007
www.atmos-chem-phys-discuss.net/7/S6577/2007/

Atmospheric Chemistry and Physics Discussions

ACPD

7, S6577–S6584, 2007

Interactive Comment

Interactive comment on "SCIAMACHY tropospheric NO_2 over the Alpine region andimportance of pixel surface pressure for the column retrieval" *by* D. Schaub et al.

D. Schaub et al.

Received and published: 5 November 2007

We would like to thank the referee for the constructive and detailed comments. The referee has identified some inconsistencies which we have hopefully resolved to the referee's contentment.

The main modifications to the paper in response to this referee's comments are:

1. NO2 : NO column ratios needed for the computation of the NOx lifetimes are now taken from the TM4 model as suggested by the referee. The TM4 model ratios are largely consistent with our previous assumptions which were based on in situ observations at a single station on Mount Rigi (see details below). 2. Accordingly, former Figures 5 and 6 (new Figures 6 and 7) have been reproduced using these new NO2:NO

EGU

ratios. The uncertainty ranges in the new Fig. 7 now include the error introduced by the uncertainty in the NO2:NO ratios (see details below). 3. Instead of using a cloud fraction threshold of 0.2 for the lifetime estimates we are now using a threshold of 0.1 consistently throughout the paper. Other thresholds are only added when the sensitivity of a result to this parameter is of interest (e.g. in new Fig. 7). 4. An important change is a complete revision of the method of lifetime estimation. In the first version the emission rates derived from the Swiss emission inventory had been averaged over a fixed time interval (e.g. 9-10 UTC or 6-10 UTC) to obtain a rate representative for the time of the satellite overpass. However if the lifetime of NOx is long then also the emissions of the previous night (which are close to zero) or even the previous day will be important and therefore an emission rate based on a 6-10 UTC average will not be representative anymore. In the new version, we are therefore calculating an "effective emission rate" depending on the lifetime of NOx and valid for the specific time of the satellite overpass. This new approach is described in detail in Section 3.1 which includes a new Figure (Fig. 2) illustrating the problem. With this new approach the wintertime estimates get much closer to other values found in literature but remains on the low side. 5. A new panel (b) has been added to Figure 9 (former Fig. 8) showing the seasonal cycle of GOME and SCIAMACHY data for a cloud fraction limit of 0.2. Only 7 GOME pixels were left over the specified region of interest in winter for a cloud fraction of 0.1 (still shown in panel a). This is indeed a too low number to make a strong statement on wintertime differences (see response below). The amplitude of the seasonal cycle (max-min) is still about 25% lower in the SCIAMACHY data as compared to GOME, but this difference is less pronounced than it was for the limit of 0.1. 6. The referee has identified a problem in our argumentation regarding the differences of the effect of inadequate representation of topography on the SCIAMACHY and GOME retrievals. This has lead to changes in section 4.3 dealing with this issue as well as on the conclusions and abstract section. Further changes were motivated by the comments of the second referee (see corresponding answers to that referee).

Individual points

P431 19: A one-day lifetime is definitely too large for the planetary boundary layer (as also shown in this study). We have replaced the inappropriate reference to Warneck (2000) by a reference to Seinfeld and Pandis' book (1998) where a typical lifetime of 4-20 hours is suggested (page 72 in their book), in agreement with the present study.

P432 9: OMI pixel resolution of 13x24 km2 only valid at nadir. This is of course true and important. We changed the text as suggested.

P434 1: The referee is right. Sentence changed to ".. features of NO2, O3, O2-O2, H2O, and the filling-in of Fraunhofer lines by Raman scattering (Ring effect)"

P437 1: We have reviewed our assumptions concerning the seasonal dependence of NO2/NO ratios. Following the suggestions of this referee we analyzed the ratios in the TM4 model, by integrating over the NO and NO2 profiles from the surface to 8 km sampled over Switzerland on clear-sky days and as close in time to the SCIAMACHY overpasses as possible. Unfortunately, the NO2 and NO model profiles are not stored in the TEMIS product for each individual satellite pixel. Therefore, we had to apply seasonal mean ratios derived from 12 UTC output of the TM4 model generated within the EU project QUANTIFY for the year 2003. The new ratios are surprisingly close to our previous assumptions, except for winter. New (old) values for the four seasons are: MAM: 3.0(3), JJA: 4.0(4), SON: 2.8(3), DJF: 1.5(2). In addition, we now also provide uncertainty estimates for these values based on the variability of the ratios between individual TM4 profiles. The uncertainty in these ratios add to the uncertainty in the NOx columns calculated from the NO2 columns. Since NOx = R * NO2 (with R being the NOx:NO2 column ratio), the overall 1-sigma uncertainty of a NOx column is now calculated as sigma(NOx) = sqrt ((sigma(R)*NO2)ˆ2 + (R*sigma(NO2))ˆ2). This increased uncertainty leads to a somewhat larger uncertainty in the slopes (and hence lifetimes) determined in Figure 6 (previous Fig.5) because the orthogonal regression takes the uncertainties of the individual data points into account. However, the effect is small because sigma(NOx) is dominated by the uncertainty in NO2. The largest difference from our previous estimate is found for winter where we overěstimated

ACPD
7, S6577–S6584, 2007

Interactive Comment

the NO2:NO ratio. The value of 1.5 is actually close to the ratio of 1.6 measured at Mount Rigi. In the paper, we argued that because NO2:NO ratios are generally decreasing with height and because Rigi is an elevated site (approx. 500 m above the Swiss plateau) a ratio of 2 would be more appropriate for the columns. However, probably due to frequent temperature inversions (temperature affects the reaction rate of NO+O3) and due to generally very low O3 concentrations near the surface due to titration by NO, the NO2:NO ratios in the TM4 model in winter are actually somewhat lower at the surface than at the altitude of Rigi, in contrast to our assumptions. As a result of the change from a ratio of 2 to a new value of 1.5, our NOx lifetime estimate for winter increases from 11.2 hours to 12.3 hours. Using a new cloud fraction threshold of 0.1 instead of 0.2, however, reduces the value to about 10 hours. This values are still assuming a fixed emission time interval of 9-10 UTC. As noted above, this method has been completely revised by calculating a NOx lifetime dependent effective emission rate as described in Sect. 3.1. With this new method the wintertime estimate increases again to 13.1 hours for a cloud fraction of 0.1 and to 16 hours for a CF of 0.2.

P438 16: The Swiss "Alpenwetterstatistik" used for the classification of "anticyclonic days" distinguishes between advective and convective situations. Anticyclonic is a subclass of the convective class. The convective class is characterized by small pressure gradients in surface charts ($<$ 5 hPa per 444 km distance) and thus low winds (mostly 1 to 2 Bf, thus mostly $<$15 km/hr) near the surface. This is why we assume that "significant transport over large distances is considered to be unimportant for the anticyclonic days." Anticyclonic conditions are now described already in the methods section (Sect. 3.1).

P439 4: Multiplication character changed.

P439 25: Point (i): Our intention here was to state that in contrast to Schaub et al. (2006) we did not use any in-situ vertical profile information for the comparison. In that previous study this had allowed us to eliminate the influence of the a-priori NO2 profiles by making use of the averaging kernels. This point was not made clear here

ACPD

7, S6577–S6584, 2007

Interactive Comment

and the statement has been removed altogether. (ii) Averaging the emissions over the resolution of a SCIMACHY pixel accounts only partly for the smearing effect of transport. Transport of NOx into or out of the column becomes increasingly important for the column budget in comparison with emissions with decreasing pixel size. For columns over isolated sources like cities the net effect of transport is expected to be negative while it will be positive for the surrounding area. This may potentially lead to a smearing not accounted for even if we average the emissions over the pixel size. The whole sentence has been reformulated to clarify this point.

P440 23: This is a good point. We should have been using a consistent value for the cloud fraction threshold. Figures 5 and 6 have been replaced and are now presenting the data for a threshold of 0.1 consistent with Figure 4. Using a lower threshold of 0.1 decreases the number of data points available per season (as noted in the paper) which in turn increases the uncertainty in the lifetime estimates to some extent. On the other hand, the correlation between the observed columns and the pixel averaged emissions becomes significantly better which justifies the use of this lower threshold. The lifetime estimates for a threshold of 0.2 has been added to Table 1 and as a separate line in Figure 6 in order to illustrate the sensitivity to this parameter. Interestingly, the lifetimes become smaller for a smaller cloud fraction threshold which is most probably due to faster conversion of NOx to HNO3 with increasing sunlight.

P441 13: Fig. 6 indeed presents lifetime estimates from literature not only for summer but also for spring and winter. The sentence was probably misleading and has been changed.

P443 1-16: Fig. 6 has been regenerated (now Fig. 7) with the new TM4 model based NO2:NO column ratios and the uncertainty ranges now include the additional uncertainty introduced by the uncertainty in these ratios (which is much smaller than the uncertainty in the determination of the slopes shown in Fig. 5). It is true that our estimates are biased towards cloud-free, high pressure scenarios. However, most of the cited lifetime estimates and our own estimates based on assumed [OH] concentrations

ACPD

7, S6577–S6584, 2007

Interactive Comment

also hold for these situations. We have added a discussion of this point at the end of Sect. 4.1.2.

P444 9-10: The referee is right that the small number of 7 GOME points in winter is critical, in particular because the variance between the individual points is quite large and the uncertainty in the mean value correspondingly large. The small number of points is most probably due to the fact that anticyclonic conditions in winter (and autumn) are very often associated with fog such that there are only rare cases where the cloud fraction is below 0.1. Snow is certainly also an issue but the Swiss Plateau is covered by snow only during a small part of winter. We have therefore checked whether the picture changes assuming a cloud fraction limit of 0.2 and added a new panel in Figure 9 (former Fig. 8). With this threshold we obtain a reasonable sample size in winter of 32 points for GOME (instead of 7) and 141 pixels for SCIAMACHY (instead of 76). The statistics for other seasons is significantly improved as well. The differences between GOME and SCIAMACHY become smaller but still the amplitude of the seasonal cycle is considerably smaller in the SCIAMACHY data in particular for the median values. The text of Section 4.2 has been completely revised to accommodate these findings.

Section 4.3.2: The referee has identified a problem of our analysis challenging our reasoning for the observed differences between SCIAMACHY and GOME in winter. The referee is right that systematic errors due to the coarse model topography are also expected for the GOME pixels even if there is an exact match between pixel-averaged true altitude and the ECMWF/TM4 altitude assumed in the retrieval. The problem would not exist if NO2 would be evenly distributed within the pixel. But the referee points out correctly that the NO2 signal measured for a GOME pixel partly covering the Swiss Alps and the Plateau will predominately originate from the polluted part over the Swiss Plateau. For this part of the pixel the altitude assumed in the retrieval is still in error. In absolute terms the error will be smaller as for a SCIAMACHY pixel located entirely over the Swiss Plateau as it is diluted over a large pixel size.

In relative terms, however, the difference would remain the same if the NO_2 column over the elevated (Alpine) part of the GOME pixel would be zero. It is likely though that there will be some compensation from the mountainous parts including the Jura Mountains and pre-Alpine region where the columns are not zero (see Fig. 8b) but this is difficult to quantify. It is even more difficult to judge what the overall effect will be on a ROI_SP regional mean value and how much smaller it would be for GOME than for SCIAMACHY. In view of these uncertainties we refrain in the revised version from arguing that the differences in the wintertime values between SCIAMACHY and GOME are most likely due to this problem. Nevertheless, the problem of topography identified and described in the paper is a real one and the sensitivity study is clearly demonstrating this. We therefore believe that it is worth including this analysis in the paper. In order to quantify the overall effect (e.g. on ROI_SP mean values) it will be necessary to reprocess all the data with a correction for the topography as suggested e.g. by referee #2. This has not been possible in the framework of the present study but it will be one of the tasks of a new PhD study which is just starting. Section 4.3.2 has been rewritten, a section on the possible impact on GOME retrievals has been added, and the conclusions have been adjusted. Unfortunately, the a-priori NO_2 profiles used in the retrieval have not been available to us. We therefore used two distinctly different profiles representing winter and summer conditions and applied these to all November-March and Mai-August profiles, respectively. This is now stated more clearly in Section 3.2 and also in the caption of table 2.

Summary: A statement on the possible impact of the topography problem on the life-time estimates has been added. Since the topography effect has only been studied with a coarse sensitivity analysis we don't think it is justified to adjust the lifetime estimates in Table 2 for this effect.

Gerneral remark: Snow is not an issue in our analysis since the selected cloud fraction threshold of 0.1 efficiently excludes snowy conditions. The Swiss Plateau is covered by snow only during a small fraction of the winter season. An analysis of OMI data

ACPD
7, S6577–S6584, 2007
Interactive Comment

over Switzerland has shown that on clear sky days with snow the FRESCO algorithm identifies a low lying cloud leading to a high cloud fraction. This erroneous identification of snow as cloud only leads to a reduction of clear sky pixels available in winter.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 429, 2007.

ACPD

7, S6577–S6584, 2007

Interactive Comment