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ACPD

5, S1736–S1750, 2005

Interactive Comment

Interactive comment on "Stratospheric and tropospheric NO_2 variability on the diurnal and annual scale: a combined retrieval from ENVISAT/SCIAMACHY and solar FTIR at the Permanent Ground-Truthing Facility Zugspitze/Garmisch" *by* R. Sussmann et al.

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Final Response to Referee #1 (F. Boersma)

We like to thank F. Boersma for carefully reading this manuscript and making very helpful suggestions for improvements to this paper, and expressed this in the acknowledgment.

In final response, we thereafter provide positive point-to-point replies to all specific referee comments, and a list of all related manuscript changes we have performed.

"page 2378, line 8: remove 'selection'"

We did so.

"p2378, l11: what does 'uncorrected' mean here?"

We changed p2378, l11 to explain this (new): "The resulting difference between SCIAMACHY and FTIR columns (without correcting for the different sensitivities of the instruments) varies between 0.59–0.95E+15 cm^{-2} with an average of 0.74E+15 cm^{-2}."

"p2379, l5: remove 'respectively'"

We did so.

"p2379, l13-15: from surface measurements and trajectory calculations it was well known that pollution events could last long and also be tranported. I would like to see a justification for the statement that 'Such pollution events had been underestimated...'"

We do not know which "surface measurements and trajectory calculations" the referee is referring to. Our statement originates from the fact that the papers we are making reference to, i.e., the ones by Leue et al. (2001), Stohl et al. (2003), and Schaub et al. (2005) are presenting their findings (long duration, large extension, long-range transport) as new ones, together with the fact that the short life time of NO_2 in the boundary layer makes long-range transport rather unlikely. We made this clear by changing p2379, l12-13 (new): "Such pollution events had been underestimated in duration and horizontal extension in the past due to the short lifetime of NO_2 in the boundary layer:"

"p2379, l19: I only see one approximation, the TEM by Richter and Burrows. However there are more: the Richter et al. method to scale a CTM stratosphere, and data assimilation of NO2 slant columns into a CTM (Boersma et al., JGR, 2004) deserve to be mentioned. And there are methods to account for stratospheric variability by

ACPD
5, S1736–S1750, 2005

Interactive Comment

employing filtering techniques on the data alone (Leue et al., 2001)."

We have reworded p2379, l18-25 according to the suggestion: "Satellite based retrievals of tropospheric NO_2 have to account for the stratospheric contribution which has been done by different approaches. The reference sector method makes use of unpolluted columns above the ocean as a reference (e.g., Richter and Burrows, 2002) and thus assumes negligible tropospheric NO_2 over the Pacific between 180° and 190° longitude, as well as longitudinal homogeneity of the stratospheric NO_2 layer. However, close to the Polar Vortex or during major changes in stratospheric dynamics, this approximation is introducing some artifacts at high latitudes in winter and spring. Further approaches like image processing techniques (e.g., Leue et al., 2001), or assimilation into a chemistry transport model (Boersma et al., 2004) have been applied. However, the best method would be to use independent data such as the SCIAMACHY limb measurements (Bovensmann et al., 1999) or, as explored in this paper, simultaneous ground-based measurements."

"p2380, l1: On the other hand, work by Heland et al. (GRL, 2002) and Martin et al. (JGR, 2004) has given clues that NO2 satellite is not so bad. Please also mention this."

We did so by changing at p2379, l26-28 (new): "First comparisons of satellite derived tropospheric NO_2 with air borne profile and column measurements (Heland et al., 2002; Martin et al., 2004; Heue et al., 2004) showed good agreement for homogeneous situations, but in the presence of spatial gradients, differences to ground-based measurements can be large (Petritoli et al., 2004). Error estimates for the satellite data are about 50% for polluted regions and larger in clean regions (Richter and Burrows, 2002; Boersma et al., 2004)."

"p2380, l6: 'in general terms', what does this mean?"

We clarified p2380, l6 (new): "For this purpose in general terms (dealing with a variety of further trace species, satellite missions, and ground-based instrumentation), ..."

"p2385, l14-16: I think an error propagation study is in order here. Later on, the results of such an analysis could be compared with the results in section 2.9."

We agree, and added a new Figure (3b) showing the increasing rates retrieved from FTIR measurements plotted for the different months of the year together with their error bars (retrieved from Fig. 3a), and changed the text accordingly, p2385, l5-9 (new):

"Figure 3a shows all individual FTIR columns of the data set, but now plotted as function of the hour of the day, and separated for the 12 different months by colors. For each month a linear fit is performed to all the individual columns of this month.

Fig. 3b gives evidence, that there is no significant seasonal change of the daytime increasing rate of stratospheric NO_2 within the FTIR error bars."

The caption for the new Fig. 3b added is (page 2416): "(b) The 12 different diurnal increasing rates obtained from the fits performed to the monthly FTIR data sets in (a). The plotted slope error bars (2 sigma) are obtained from the linear fits in (a), and the red line gives the average increasing rate, i.e., 1.02(6)E+14 cm^{-2}/h."

We also added the statistical error to the retrieved average daytime increasing rate at p2385, l17: "The resulting daytime NO_2 increasing rate is 1.02(6)E+14 cm^{-2}/h."

section 2.7: Nice concept. However, more words should be spent on the error in the estimated FTIR column based on application of the daytime increasing rate."

We added to p2386, l3: "We give a conservative estimate of the propagation of the error of the daytime increasing rate (0.06E+14 cm^{-2}, see above) into the virtual coincidence column as follows. Assuming that there is only one late-evening FTIR measurement at 19:00 UT, i.e., 9 hours after the 10:00 UT satellite overpass, the error of the daytime increasing rate would then result in an error of the virtual coincidence column of 9 h $\times$ 0.06E+14 cm^{-2}/h = 0.54E+14 cm^{-2}, which would be $\approx$1 % for a typical summer column level of 4.5E+15 cm^{-2}. In analogy, we estimate for a winter-evening FTIR measurement at 15:00 UT a 5 h $\times$ 0.06E+14 cm^{-2}/h = 0.3E+14 cm^{-2} error which would be $\approx$1.5 %

for a typical winter column level of 2E+15 cm^{-2}.

p2386, l5: why is Fig.7 introduced before Figs. 5 and 6?

We re-ordered the figures accordingly.

"p2386, l8-9: (i) in terms of validation, this is a bad idea. Comparing FTIR and SCIA on days that SCIA did not measure will result in checking the functional fit to the SCIA data and this is only an indirect way of validation."

We do not perform "validation" of absolute differences between FTIR and SCIAMACHY in this paper. Rather, our approach makes synergistic use of the differences in the time series of the two different instruments and aims at thereby retrieving the principle characteristics of the time series of free tropospheric NO_2. Restricting to "coincidences" would be less favorable for this purpose than the use of the functional fit.

"p2386, l9-12: (ii) here a similar reasoning holds. I agree that an idea can be obtained on the day-to-day scatter, but then the precision and accuracy of the functional fit should be very high."

Precision and accuracy of the functional are sufficiently high for this purpose indeed. This can be directly seen from inspection of Fig. 5 of the revised paper: The functional-fit line is well centered within the scatter bandwidth of the daily data throughout the time series of both FTIR and SCIAMACHY.

"p2387, l19: why are there brackets around the pixel size?"

We removed the brackets.

"p2388, l8: 'no cloud clearing'. This is a fundamental weakness of the manuscript. First of all, cloud information may help the authors: the pollution clearing scheme might well be simplified when cloud information is used. Second, not taking into account the effects of clouds introduces problems in interpreting the results: cloudy pixels generally screen the NO2 pollution underneath and strongly influence the sensitivity of any NO2

ACPD

5, S1736–S1750, 2005

Interactive Comment

above (or within) the cloud. Even in the stratosphere, the sensitivity to NO2 is significantly enhanced when clouds are present. This effect should be accounted for in the AMF. It may well explain part of the bias of SCIA relative to FTIR."

The reviewer is correct that clouds can have a large impact on the results, although the effect for the background situations studied here is much smaller than for the typical applications where boundary layer NO_2 is studied. Ideally, each pixel should be treated independently with cloud fraction and cloud top height, but this is problematic over mountains over which cloud retrieval algorithms do not work as accurate as over flat terrain. Also, proper treatment necessitates the knowledge of the vertical NO_2 profile which would have to come from a model introducing a priori assumptions in the retrieval.

As a compromise, we have taken up the reviewers suggestion to apply cloud screening, and by doing this, the results become more consistent as one would expect. As now all the analysis is performed on the cloud screened data set, all relevant parts of the manuscript have been changed accordingly. In particular, the title of Section 3.4 has been changed, a paragraph describing the cloud clearing scheme been introduced to this section, and the cloud-cleared data set has been added to Figure 5, i.e., p2389, l10-21 (new):

"3.4 Scientific SCIAMACHY UB1.5 columns: full data set and cloud clearing

The SCIAMACHY NO_2 columns data set retrieved by the UB1.5 algorithm at the University of Bremen for a 200-km radius around the Zugspitze is shown in Fig. 6. Plotted are columns retrieved from all individual measurements (grey), as well as a reduced data set (orange) which resulted from application of a cloud clearing scheme. We applied a simple intensity threshold which leads to an effective clearing of both cloud and snow covered pixels. This data set will be exclusively utilized throughout this paper thereafter.

The figure displays a clear annual cycle for the daily minimum values whereas the

ACPD

5, S1736–S1750, 2005

daily maxima are spiking to very high values frequently. Note from Fig. 6 that by the cloud clearing the highest spikes of the full data set have been eliminated. This can be understood in terms of the strongly enhanced sensitivity to tropospheric pollution above snow or clouds.

Obviously, quite often strong regional boundary layer pollution events occur within the 200-km selection radius around Zugspitze. The retrieved SCIAMACHY columns are a reasonable measure of both the stratospheric and total column for clean conditions, and are significantly impacted by boundary layer pollution events, although they strongly underestimate boundary pollution enhancements in quantitative terms. This behavior will be characterized in more detail in the sensitivity study given in Sect. 5.2."

"p2388, l13-14: This line is nonsense. The result of DOAS is NOT that slant column densities are integrated along the effective light path, but rather that slant column densities should be interpreted as the column of molecules along the effective light path."

The sentence has been clarified, p2388, l13-14 (new): "The results of the DOAS retrievals are slant column densities (SCD) that correspond to the column of molecules integrated along the effective light path through the atmosphere."

"p2388, l21: it is new to me that the AMF is dependent on pressure profiles or do the authors mean surface pressure? Moreover, it is a bit odd not to mention the most important forward model parameter for AMF calculations here, i.e. clouds."

The AMF is sensitive to pressure if we think in NO_2 mixing ratios. However, the formulation was misleading and has been changed. We have also included clouds as important parameters. The manuscript has been changed at p2388, l18 (new): "The UV-DOAS AMF are a function of solar zenith angle, the instrument line of sight, the relative azimuth between viewing direction and the sun, but also depends on the vertical profile of NO_2 and parameters such as surface albedo, aerosol loading or clouds."

"p2389, l2: what is the motivation or justification for assuming stratospheric background

ACPD

5, S1736–S1750, 2005

Interactive Comment

EGU

aerosols?"

It is not clear to us why the reviewer raises this question. There certainly are aerosols present in the stratosphere (although currently at low concentrations) and they have an impact on radiative transfer in the stratosphere. It therefore is common practice to account for these aerosols in the radiative transfer calculations. In contrast to aerosols in the troposphere, the variability of stratospheric aerosols in space and time is small and the impact on the results small.

"p2390, l17: I fail to see why days with > 12 measurements would avoid including polluted data."

We inserted an explanation for this into the revised manuscript, see below. Note that our approach is a statistical elbow-type test which delivers no sharp threshold, and allows for some degree of freedom for the exact threshold used. For the revised manuscript we are using a reduced threshold of 6 instead of 12. This is to keep a sufficient number of data since we are now dealing already with a reduced number of data due to the cloud clearing that has now additionally been applied to the data. We added the following explanation at p2390, l17: "This fit is restricted to days with $>$6 column measurements within the 200-km selection radius around the Zugspitze, in order to avoid including polluted data to the series of minimum values. Using only days with several measurements increases the probability that the smallest of these measurements is not affected by boundary layer pollution. The threshold minimum number of 6 pixels available per day was retrieved from a statistical (elbow type) distribution plot of the difference between the average column and minimum column for each day against the number of measurements available for that day. For high numbers the difference shows a small scatter around a stable value of $\approx$1E+15 cm^{-2}, while for smaller numbers it is collapsing towards zero. The minimum number of 6 used for our subsequent analysis was read out via eye from the elbow corner of this scatter plot."

"p2392, l1: I understand the point, but there are subtle issues here. Over the Pacific, a 'reduced US standard NO2 profile' is likely a much better assumption for AMF calculations than over the Zugspitze area. Assuming the 'reduced' profile will result in higher AMF values and therefore reduced scatter. If a non-reduced profile would be used in the AMF, the scatter might well exceed 10%, and hence corrupt the validity of the pollution-clearing approach."

This is an interesting point. If we use a constant AMF for each day, then of course no change in scatter would result as a common factor will only affect the mean, not the relative deviation. However, if we use an individual AMF for each measurement (which would necessitate model input at high spatial resolution) then the reviewer is right and the scatter could be increased if the model predicts larger surface concentrations in some but not all of the pixels. The same would also happen if one would apply this variable AMF to the measurements over the Pacific which is not justified but demonstrates that the information is coming from the assumptions, not the measurements. It therefore seems more appropriate to use the 0-hypothesis here instead of introducing substantial a priori information.

"p2393, l17-18: I don't agree. See general comments.The assumption of identical sampling characteristics is just wrong, as the authors are well aware of. Therefore, an effort should be made to separate the different sensitivities from retrieval errors, as suggested above."

While our study introduces new concepts that can be applied to validation studies (virtual coincidence column, pollution clearing), our focus is on synergistic use of FTIR and SCIAMACHY data to retrieve troposheric NO_2. For this purpose we make the simplifying assumption that retrieval errors are negligible relative to the differences which result from the different sensitivities. Clearly, "to separate the different sensitivities from retrieval errors" is beyond the scope of our present paper and could well be the focus of an upcoming study.

To make this clear we made the following changes to the manuscript:

ACPD

5, S1736–S1750, 2005

p2392, l14 (new): "4 Intercomparison of SCIAMACHY versus FTIR column retrievals"

paragraph 4.2. (new):

"4.2 Intercomparison of absolute column levels

The difference of the time series of SCIAMACHY and FTIR is displayed in Fig. 5 (red curve). The SCIAMACHY columns are showing significantly higher values throughout the full validation period. The difference (col_{SCIA}–col_{FTIR}) is 0.83E+15 cm^{-2} on average, with a minimum of 0.60E+15 cm^{-2} and a maximum of 1.24E+15 cm^{-2}.

This kind of intercomparison of the direct-output NO_2 column levels from two different remote sounding systems (satellite versus ground) has been performed in many previous papers, and the differences been interpreted in terms of errors of the satellite instrument. However, we would like to point out that this approach is only the first possibility out of two limiting (theoretical) cases: i) The observed differences are due to intrinsic errors in either of the two remote sounding data sets under the simplifying assumption that the two measurement systems have identical sampling characteristics or, ii) the observed difference can be attributed to the different sampling characteristics of the two instruments (differing averaging kernels) under the assumption that they are both working in principle without intrinsic errors. Reality will be in between these limiting cases. A theoretical framework to deal with this problem for the purpose of satellite validation has been given by Rodgers and Connor (2003).

We decided to thereafter follow the assumption ii) as a basis for our subsequent synergistic use of SCIAMACHY and FTIR data aiming at the retrieval of tropospheric NO_2. I.e., we assume the difference shown in Fig. 5 is dominated by the differing sensitivities of SCIAMACHY versus FTIR and not by intrinsic errors of SCIAMACHY (or FTIR) measurements. Clearly, this is a simplifying assumption for the purpose of this study, and future validation studies have to be performed in order to explore to which degree this assumption holds. Our concepts of "virtual coincidence" and "pollution clearing" can contribute to the required refined validation studies."

p2401, l1 (new): "5.5 Discussion of the retrieved tropospheric columns series in terms of validity"

p2401, l12-14 (new): "This is only a qualitative statement and it means that from our findings we can neither exclude nor find any evidence for an intrinsic principle error in the SCIAMACHY data set."

p2401, l19, we added: "A more quantitative validation of our new method could be performed in an upcoming study using collocated SCIAMACHY tropospheric columns retrieved with the Richter and Burrows (2002) method. In fact the two methods are independent (because now the stratospheric background to be removed is that of FTIR and not that retrieved by SCIAMACHY over the Pacific Ocean) so that useful indications on selfconsistency and/or validation of the new approach (or limitations of the old one) can be pointed out." (We also added this idea to the conclusions in a shortened version).

"p2394, l21: it might be instructive for readers to learn why the FTIR retrieval is not zenith-angle dependent."

We did not claim that in this generalized form. In fact the FTIR is more zenith angle dependent above 30 km than SCIAMACHY. The issue is that FTIR has nearly no sensitivity in the troposphere at all, where SCIAMACHY shows its strongest zenith angle dependency. While we agree that a thorough quantitative investigation of the causes for the differing kernel shapes observed would be interesting from an academic point of view, we believe this could only be seriously performed by an extended sensitivity study (investigating the differences in spectroscopy and radiative transfer between the IR and visible spectral domains in detail). We think that this effort would be beyond the scope of this paper.

"p2397, l7: I think the numbers mentioned here and in Table 3 should be discussed in terms of validity. They are true given assumptions on albedo, clouds, etc."

ACPD

5, S1736–S1750, 2005

Interactive Comment

We have included a cloud clearing into the revised mauscript, see above. Furtherore, we had dedicated a full Section (3.2.) to a detailed description of all assumptions that have been used for the UB1.5 column retrieval. We do not see the necessity to again and again repeat our assumptions. This would make the paper less readable.

"p2398, l23, Fig. 12b is introduced before Fig 11 and 12(a)."

We re-ordered the figures accordingly.

"p2399, l2, why is the vector $\vec{x}_{trop}$ defined following equation (5)? I see the need to translate mixing ratios to subcolumns, but multiplying VMR with the FTIR AMF's is introducing sensitivities in a profile that is supposed to serve as an a priori profile, subject to the kernels. Therefore, applying AMF's seems incorrect to me here or am I missing something?"

The "infrared air mass factors" are in fact nothing else than the partial air columns of the different layers (which do not contain any effects from light path enhancements as they do in the UV/vis). We clarified this by adding at p2399, l5: "... are the infrared airmass factors (i.e., the partial air columns of the different layers) which ..."

"p2399, l2: what is the sensitivity of the results for different assumptions on the vector $\vec{x}_{trop}$? See general issues."

We added an explanation why we defined $\vec{x}_{trop}$ the way we did, see below. Since we do not know which other assumptions would be reasonable, a sensitivity study on "different assumptions on $\vec{x}_{trop}$ would end up in complete arbitrarity. We added the following text at p2399, l6: "Our retrieval constraint is set up from two parameters, i.e., it allows for retrieval of two independent degrees of freedom, because this is what can be expected from using two complementary input parameters, namely col_{FTIR} and col_{SCIA}. The constraint for the stratospheric part is a simple scaling of the US standard profile as used also for the FTIR retrieval. For the lower part we use a scaling of a VMR profile that is constant with altitude. This is because only one degree of

ACPD

5, S1736–S1750, 2005

freedom is left for this lower part, and it is the zero-order approach in our case where no better a priori information on the vertical distribution of free tropospheric background NO_2 is available. Our approach of linking the two parts of the profile together just at the point where the tropospheric VMR matches the US standard profile is the simplest solution that avoids (unphysical) negative VMR gradients at the transition between the lower and upper part of the profile."

"p2399, l12: add Eq. (2)."

We did so.

"p2401, l8-9: were these column values observed by ground-based instruments or by GOME, as suggested on p2404, l10-11. If GOME, than the 'evidence' comes down to reasoning that both SCIA and GOME observe NO2 in the same range -in completely different areas- and that therefore SCIA is in a 'reasonable' range. The statement in l10-11 would then be meaningless since we don't know if we can trust GOME over the Po Valley."

We corrected p2404, l10-11 accordingly (new): "Similar column levels have been found from ground-based UV/vis measurements of the background (free) tropospheric column in the Po valley."

"p2401, l1: lifetime also plays a role here as NOx has more loss pathways in summer than in winter. It is not just the emissions."

We understand p2402, l1 is addressed here. We thank for this hint and add it to our explanation in p2402, l1 (new): "... and a broader symmetric summer minimum which is due to the smaller emissions in combination with a reduced NO_2 lifetime in summer."

"p2402, l25-27: I am lost here. I don't see the fact that the SCIA-true difference is smaller than the FTIR-true difference gives the proof. Hopefully the authors can explain it more clearly."

We understand this had not been explained in a clear way. However, after we have introduced a cloud clearing now within the revised version of the manuscript, the problem of a bypassing of our pollution clearing scheme by extraordinarily high pollution enhancements has disappeared. This is because the highest pollution enhancements (due to pollution above snow or clouds, see our discussion above) are already filtered out by the cloud clearing. As a consequence for the revised manuscript, we removed Fig. 12b, as well as the second and third paragraph of Section 5.6.

"p2403,l20: what does 'uncorrected' mean here?"

We reworded p2403, l19-20 (new): "From a direct intercomparison (i.e., without correcting for the different sensitivities) we derived the difference between SCIAMACHY and FTIR columns."

"p2403, l28: 'true to a best approximation': isn't this the same as stating that you think -for some reason- that this IS the best approximation. And if so, why?"

We reworded p2403, l27-29: "This is achieved by using measurements from a mountain station which is located above the possibly polluted boundary layer and an a priori profile with the tropospheric part set to zero."

"p2404,l14-15: this line is illustrative of what is missing from the manuscript. It is a simple statement without any proof from the results shown in the manuscript. It is certain that there are SCIA errors, and the whole idea of a validation study is to quantify these errors, and to provide at least a guess of where these errors come from, and how they could be eliminated. None of this is dealt with in the manuscript. Even the statement that the errors will not exceed the clean tropospheric column values may be false. The clean tropospheric column may well be underestimated due to kernel and profile shape issues mentioned above, and if this were the case, the errors in SCIA would exceed the reported 'clean tropospheric columns'."

1. See our reply to the referee comment "p2393, l17-18: I don't agree." above: We have clarified by a couple of manuscript changes, that our focus is not on validation

of SCIAMACHY absolute bias (although we are developing new concepts that can be used for upcoming validation studies dealing with this issue), and we are using the simplifying assumption that both SCIAMACHY and FTIR are working without intrinsic errors to follow our goal of synergistically using FTIR and SCIAMCHY to retrieve tropospheric NO_2.

2. We did not state that "the errors will not exceed the clean tropospheric column values". We stated that "these errors will be at maximum in the order of the expected differences resulting from the clean tropospheric column." The statement "expected differences" was meant to include the kernel effect and is therefore correct if interpreted as meant. To make this unambiguously clear to the reader we added to p2404, l14-15: "... in the order of the expected differences between SCIAMACHY and FTIR (applying the averaging kernels) resulting from the free tropospheric column."

"p2404, l19: in principle yes, but it is not sufficient to use one SCIA kernel and one 'retrieval constraint' as is done in the manuscript. Every single SCIA observation then needs to take into account the best estimate of the forward model parameters. This should be mentioned."

We added the following sentence to p2404, l19: "For this, the averaging kernels have to be determined for each measurement independently using the best estimates for albedo, aerosols, clouds and NO_2 profile available (Eskes and Boersma, 2003)."

"p2404, last section. The manuscript would benefit from a rough sketch on the feasibility of an 'integrated observing system'. How many appropriate sites are available at the moment? Is their geographical distribution good enough?"

We agree that the question of feasibility of our outlooking proposal, i.e., an integrated observing system based upon a series of ground stations is interesting. However, we prefer to perform a quantitative feasibility study in a separate, subsequent paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 2377, 2005.