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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Odin stratospheric proxy NO_y measurements and climatology" *by* S. Brohede et al.

S. Brohede et al.

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1 General comments

- *What role plays the adjustment of SMR HNO3 to ACE-FTS HNO3 observations, given the a posteriori validation of the ODIN proxy NOy with ACE-FTS measurements?*

  The Odin NOy proxy measurements have the provision of global (near-global) coverage on a daily basis which cannot be achieved by any solar occultation instrument, such as ACE-FTS. We clearly state that our method is dependent on ACE-FTS measurements, through the adjustment of HNO_3. Also, since HNO_3 ACE-FTS seems to agree well with both MIPAS and MLS we're confident that the

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tuning to ACE-FTS is justified. See specific comments below.

- *The authors claim that the NOy partitioning is rather independent of the absolute total NOy, and this an important baseline (maybe the most important) of their analysis, but I am not convinced that the full atmospheric variability (in altitude, season and latitude) really has been covered when elaborating towards this statement.*

  We have made further studies and adjustments in order to convince the reader that this is truly the case. At least for the latitudes/seasons covered by the Odin proxy NOy (i.e excluding polar night conditions). See specific comments below.

- *The treatment of heterogeneous chemistry in the photochemical box model is not clear; this has implications for the interpretation of observations under PSC occurrence.*

  We agree that the paper was not totally clear on this point. The text has been updated to clearly say that PSCs are not included in the box model and that affected regions could have additional errors due to increased uncertainty in the partitioning. See answers to specific comments below.

- *The paper is hard to read and at several places (as detailed in the specific comments below) specific information should be provided earlier for better understanding.*

  Changes have been made in order to increase the logic and readability of the paper.

- *Finally, I would appreciate if the restriction to daytime (or, at least, the exclusion of polar night) conditions could be considered in the title of the paper, since, as*

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stated at many places throughout the paper, the proxy NOy is not provided for polar night conditions. I recommend publication after these and the following specific comments have been considered.

We do not see the need for the title to be that specific. The daytime restriction of the Odin data set is noted already in the second sentence of the Abstract, which we think is sufficient. Also, adding ”daytime” to the title would be somewhat misleading since it could be interpreted as is having a diurnal variation (which is not the case) and that only the daytime portion is captured. Also we think there is no good way of adding the ”polar night exclusion” to the title without getting a very awkward title. A better way to include this in the title would be to add something like ”near global measurements” since the daytime restriction reduces the latitude coverage in the winter hemisphere. However, we think that this is redundant as well since, as the reviewer points out, the daytime restriction is ”stated at many places”..

2 Specific comments

- *p5849,l8: More recently, Funke et al. (2005) have found that the mesospheric source of NOx transported into the stratosphere during Antarctic polar winter may represent up to 9% of total stratospheric NOy in the Southern hemisphere. Further, Funke et al. (2008) have found that up to 6 ppbv mesospheric N_2O can be produced by the reaction NO_2+ N(4S)$\rightarrow$ N_2O + O which is subsequently transported into the stratosphere. This amount will be missing in the NOy budget; does the photo-chemical box model include this reaction?*

We’ve added the Funke et al. (2005) reference in this section. And yes, the box model does include this reaction but it is not really relevant as only the partitioning in the stratosphere is considered based on climatological N_2O. Any NO_2 or HNO_3

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created from this reaction will be accounted for in NOy, but if the primary form is another NOy species (such as N_2O_5 or $ClONO_2$) then it will not. Since N_2O forms NOx via NO, and NO is closely coupled to NO_2, we are indirectly accounting for this in the Odin proxy NOy through the OSIRIS NO_2 observations.

- *p5851, l11: Orsolini et al. (2005) and Stiller et al. (2005) found HNO_3 volume mixing ratios of up to 14 ppbv in the upper stratosphere, during episodes of strong downward transport in the polar vortex.*

  Yes, it's true that episodes of high concentrations of HNO_3 sporadically occur during the polar night. But since the polar night is not covered by the Odin proxy NOy, our statement (that HNO_3 can be ignored in the upper stratosphere) still make sense. However, since this is only a general statement in the introduction and that the construction of the NOy proxy does not depend on it, we've decided to remove it from the text.

- *p5851, l21: Other and possibly better suited references for MIPAS NOy measurements would be: Mengistu Tsidu et al., 2004; Mengistu Tsidu et al., 2005; Wang et al.,2007a,b; Fischer et al., 2008. Further, the MIPAS instrument is still operational (after a disruption from March 2004 to January 2005). However, it has to be admitted that data provision is delayed, and only very few level-2 data (trace gas distributions) have been made operationally available by ESA for the period after January 2005. Full data provision for this period is announced for this summer (2008) by ESA.*

  At least the Mengistu Tsidu et al (2005) and Fischer et al (2008) seem to be more appropriate references here. We've replaced the Brühl et al (2007) by those two, as suggested.

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We've changed the text regarding the MIPAS data to say: " ...,but with complete data available only between July 2002 and March 2004 and sporadic thereafter". This describes the present situation without going into depth about the future MIPAS data provision.

- *p5854, l3-7: Please quantify "good agreement with various solar occultation instruments". What does it mean that "OSIRIS climatological NO2 is found to be consistent with the Chemical Transport Model (CTM) simulations except in the polar vortex region"? Should we trust in the measurements or the model? Could you give a reference for the model? Is it validated?*

  We agree that our formulation is too vague here and we've made changes to be more specific. We've also added a reference for the CTM (REPROBUS). The deviation between REPROBUS and OSIRIS measurement in the polar vortex region is most likely attributed to limitation in the model (probably too strong downward transport) as discussed in Brohede 2007c.

- *p5855, l2: What is the conclusion on the ACE-FTS NOy validation regarding accuracy and precision?*

  The validation studies on ACE-FTS NOy by Wolff et al. (HNO_3, $ClONO_2$ and N_2O_5) and Kerzenmacher et al. (NO and NO_2) are now completed and published in ACPD. A summary of the results from these studies are now included in section 2.2. However the specific accuracy and precision of the total NOy are not provided.

- *p5855, l9ff: Does the photochemical box model include heterogeneous chemistry on PSC particles? If so, this must be stated here. Discussion on p5867, l11-21 is dependent on this information.*

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Good point. The model contains heterogeneous chemistry but no PSCs, so effectively no. Text has been added to clarify this.

- *p5855, l20: You use monthly global means of NOy from elsewhere for the photochemical model; does this mean that the NOy partitioning is independent of total available NOy? The discussion of this point comes too late (in section 3.1).*

  Yes, the partitioning is largely independent on the total as discussed in section 3.1. We have repeated the statement from this section in 2.3 as suggested. We don't want to move the entire discussion of this topic here since this section is supposed to describe the general features of the box model, rather than our implementation of it which goes into Sect. 3.1.

- *p5857, l17-19: This is a central part for understanding of the method, and discussion is much too short. Please elaborate further and extend description of Fig.4: What does a +0.4 and a -0.4 perturbation mean, variation of NOy between 60% and 140% of the reference value? If this interpretation is correct, is this variation sufficient to cover all situations in the stratosphere? I don't believe so. For which altitude are the curves given? Is a change of 0.08 to 0.04 (i.e. a factor of 2) as in case of $ClONO_2$ really negligible? I don't understand at all the lower of the figure.*

  Since the method always uses the sum of $ClONO_2$ + $2\times N_2O_5$, regardless of whether it is scaled by OSIRIS or SMR, the most relevant quantity is how their sum changes with NOy. Note that their changes are opposite in sign so there is some cancellation. We have added this onto the plot. Also, in this worst case where the fraction of $ClONO_2$ changes from 0.08 to 0.04 it is not the relative change that matters but the absolute, and in the absolute sense this would lead

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to a 4% error on NOy.

- *p5858, l11-16: I understand that SMR HNO_3 is adjusted to ACE-FTS HNO_3, and HNO_3 makes up about 80% of NOy in the lower stratosphere (around 20 km, see Fig.1); under these conditions, is it surprising that the ODIN proxy NOy and ACE-FTS NOy agree within 20% (see Fig. 6)? Secondly, why has an altitude shift of 1 km applied if the shift identified in the Wang et al. (2007) paper is 1.5 km (1-2 km as stated on p5853,l18)?*

  Due to the SMR HNO_3 tuning toward ACE-FTS, it's NOT surprising that the Odin proxy NOy and ACE-FTS agrees well at 20 km where HNO_3 is totally dominating. The agreement is moreover good up to 34 km, even better for higher altitudes. We don't get the reviewers comment, does he/she mean that they should agree to to BETTER than 20% at low altitudes? We assume that this is the point.

  The correction is based on the average situation of all coincidences 2002-2006 while fig 6 is split up into two different regions. Note that the the difference have opposite signs in upper and lower panel (c) which would cancel out to some degree when averaged together. Hence, the correction does not work perfectly for all regions and latitudes but is a compromise. It would be too arbitrary to apply different correction functions for each latitude/season without any physical explanation.

  The answer to the second comment is simply that a 1 km shift gives a better agreement with ACE-FTS in combination with the magnitude correction in equation 1. Note that Wang et al. do not apply such a correction.

- *p5859, section 3.1.1: Why does N_2O_5 and $ClONO_2$ always scale with HNO_3 (in case of SMR) and NO_2 (in case of OSIRIS)? Compare comment on p5857,*

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l17-19 regarding this point, in particular the comment on $ClONO_2$. Please discuss critically possible conversion reactions.

N_2O_5 can be converted to HNO_3 via heterogeneous chemistry. $ClONO_2$ is more closely related to NO_2 via chemistry, of course, but its longer lifetime means it could more closely reflect HNO_3 due to transport effects. It is kind of a moot point since to a first approximation NO_2 defines N_2O_5 and $ClONO_2$ due to its smaller measurement errors. We do not fully understand the point the reviewer is making but it seems related to the choice of merging method. Arguments can made for different methods but in the end we chose one that (1) made sense and (2) performed well.

- *p5863, l15-17: How meaningful is the comparison to ACE-FTS given the fact that HNO_3 from SMR has been adjusted to ACE-FTS observations, and HNO_3 can make up to 80% of the NOy budget? Please discuss this point in more detail.*

  The main purpose of the comparison is to evaluate the different merging techniques to find the most appropriate. At low altitudes the adjusted HNO_3 is dominating which, as the reviewer points out, naturally gives good agreement. At higher altitudes this is, however, not the case for which an ACE comparison is more meaningful. We have added text to say this more clearly in section 3.2.

  Note also that ACE-FTS, in turn, agrees very well with MIPAS and MLS (within 10% between 10-36 km) as found by [Wolff et al. 2008]. This justifies the idea of correcting SMR profiles rather than ACE-FTS and suggests that a similar adjustment to SMR-HNO_3 would be needed if using MIPAS or MLS data in the construction of the Odin proxy NOy. This text has been added to Sect. 3.3.1 for clarity.

- *p5865, l19 - p5866, l7: This discussion comes far too late and should be moved*

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into section 3.1. Regarding Appendix A, I would like to see a much more detailed discussion of the deviations between model and MkIV data regarding $ClONO_2$, N_2O_5 , and HNO_3 (e.g. julian day 75, year 2000; julian day 337, year 1999; julian day 350, year 2002).

We have added a line in Sect. 3.1 noting the NOy-sensivity study in the Sect. 3.4. In addition, a more detailed study has been performed to help understand the differences in these three cases - as initially suggested these seem to arise primarily from the steady-state nature of the box model. As mentioned in the text, the wintertime differences will not affect the climatology as OSIRIS is unable to measure at these times/latitudes.

- *p5867, l11-21: How reliable are the NOy proxys for situations including heterogeneous chemistry, i.e. is the NOy partitioning given correctly? This depends on the inclusion of heterogeneous chemistry into the photochemical box model used for constructing the proxy NOy . Please provide the respective information.*

  The box model prescribes only background heterogeneous chemistry on aerosols but no PSCs, so under perturbed conditions in the vortex the box model partitioning may have larger errors. A sentence has been added in section 2.3 to point this out more clearly. We have also provided a caveat in the result section that larger errors are expected in the presence of PSCs due to larger partitioning errors.

- *p5868, l1-3: I would expect much higher inter-annual variation of denitrification in the Northern winter polar vortex, given the high variability of the Northern polar vortex. Please comment why you expect/see higher inter-annual variation in the Southern Hemisphere.*

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The reason is that complete denitrification only occurs in the SH, but the sub-reasons are twofold: The magnitude of this denitrification varies substantially from year to year. Remember the sudden stratospheric warming and ozone hole split event in 2002 which significantly contributes to the large STD seen over the 5 years. However, the main reason for the higher STDs expressed in percent in the SH vortex region compared to the NH is simply the low concentrations (close to zero) found here. The difference in STDs are much less pronounced when viewed in absolute numbers (ppb). Relative numbers are deceptive sometimes, but are the most common way to present STDs and hence preferred in this study. A sentence has been added to say something about the STDs in absolute numbers on p5868.

- *p5871, l14-16: I believe there is still some discussion going on where and when the enhanced NOx vmrs were produced before being transported downwards; compare for example Seppälä et al., 2007.*

Yes, there is still this debate about a direct production of that cannot be ruled out. The precise mechanism of the enhancement is, however, not important for this study. We have explained that this is more a qualitative feature than quantitative since the box model does not include SPEs anyway. To avoid this discussion further, we've made the text more vague by removing "...transported down from the mesosphere".

- *p5851, l 22-25: The remark on the QBO signal seems highly speculative to me; it needs more elaboration if it is to be retained in the paper.*

We think it's appropriate to keep the QBO remark since it may be of interest for future studies, although it's somewhat speculative (maybe not HIGHLY speculative though). The text clearly says that this is not confirmed but possible due to

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the QBO signal in N_2O. A manuscript by Jin et al. has recently been submitted to ACPD describing the QBO-signal in the SMR N_2O data. We've changed the end of the QBO remark to say that: "An in-depth study of this is beyond the scope of this work"

- *p5873, l15: As shown by Funke et al. (2005) descent of air from the mesosphere leads to higher amounts of NOx (and, thus, NOy) in the polar stratosphere, not lower ones. NOy is removed from the stratosphere by sedimentation of PSC particles.*

  In general, downward transport from the mesosphere inside the polar vortex is expected to give low concentration, since mesospheric air is naturally low in . This is not the case during sporadic SPE events (e.g in 2003) which is what the Funke et al. reference discussed. The 2003 SPE exception is mentioned in the same paragraph so no further clarification is necessary here. It's correct that NOy is primary removed from the stratosphere by sedimentation of PSC particles, but the Odin only contains gas-phase , meaning that also sequestered onto PSC particles are invisible to us.

- *p5873, l19: Compare comment to p5871, l14-16.*

  Our formulation here: "...emanating from the solar storms from October 2003" is vague enough to cover also the direct production of in addition to the downward transport.

3 Technical corrections

- *5874, l4: I believe there is a typo in the web address.*

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Actually not. The OSIRIS web server is really OSIRUS with an ”U” due to some miscommunication several years ago when setting up the server.

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