

## ***Interactive comment on “Validation of NO<sub>2</sub> and NO from the Atmospheric Chemistry Experiment (ACE)” by T. Kerzenmacher et al.***

**T. Kerzenmacher et al.**

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Thank you for the thorough and detailed list of comments for improvements to our paper. We were able to address all points made by anonymous referee #1 and believe that with his/her aid we were able to improve the paper. In the following we present the original comments in italics and our responses below with exception of the answers to the General Comments, which are given under the corresponding numbers.

### **Response to the General Comments**

1) In this validation effort we wanted to give a comprehensive overview of comparison measurements rather than a selection of those available. This will enable users of most other available NO and NO<sub>2</sub> data sets to see how the ACE data products compare, which may be useful for modellers and those who wish to combine NO and NO<sub>2</sub> data

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from a variety of instruments. This means that the paper is long, however, we have already excluded plots that we summarised as tables to reduce the length of the paper. Given the number of contributors to this validation effort, we think that the present length of the paper can be justified. However, we are grateful for the idea to better motivate the comparison, which we have done at the beginning of Section 3.

2) In Section 4.1 and the caption of Figure 6 (now 7) we give an explanation of the results shown in the figures. We don't call the standard deviation "fitting errors". Only in Figures 1 to 3 (now 2 to 4) has "fitting error" been used and these plots show uncertainties (for MAESTRO) and statistical fitting errors (for ACE-FTS). We have clarified this in Figures 1 to 3 (now 2 to 4).

In the third paragraph of Section 2.1 we have added:

"The retrieval program propagates estimated uncertainty through the spectral retrieval process. This is a good process for the linear inversion algorithm but does not work well for the Chahine method. For the version 1.2 retrievals, the Chahine method is used, and the uncertainties are propagated with a simplified algorithm. These uncertainties are, therefore, not very accurate but they provide some relative estimate and serve as a rough guide to the relative uncertainties of the MAESTRO measurements."

In the last paragraph of Section 2.2 we write now:

"These errors are calculated as the square root of the diagonal elements of the covariance matrix used in the least squares fitting procedure. If the measurement errors are normally distributed and one ignores correlations between the parameters, this represents the 1-sigma statistical fitting errors."

The standard deviation of the mean profiles provides a measure of natural variability. We can therefore compare random errors and differences to it to determine whether the ACE data quality is sufficient to detect natural variability.

3) Because ACE is a solar occultation instrument, there are only 30 profiles/day. When

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coincidence criteria are applied, the number of co-located profiles becomes small, particularly if subdivided into season and latitude bins. Splitting ACE profiles into season and latitude bands has been done for the OSIRIS comparisons and there was only one bin with more than 100 coincidences. We are currently working on an ACE NO<sub>y</sub> budget paper which addresses this issue further and gives more information about the data as a function of latitude and season.

For the SCIAMACHY nadir comparisons, no real conclusion could be drawn analysing for latitude other than saying that the mean differences were larger at mid and high latitudes. These differences are affected by the very small columns in winter which lead to large relative errors.

The range of latitudes used for the different comparisons is listed in Table 2.

4) The disagreement mentioned stems from the use of the term “typical” that we introduced to mean an average difference (indicated in the Abstract now and Section 7). We now state the maximum differences everywhere where we use “typical”, also.

5) We added the following two paragraphs to Section 2.2:

“For NO<sub>2</sub>, the wavenumber ranges for the microwindows remained the same between versions 1.0 and 2.2, but the altitude limits changed. The lower altitude limit was raised from 10 km in version 1.0 to 13 km in version 2.2 to avoid saturation of the spectral region that occurred at low altitudes in tropical occultations. The upper altitude limit was raised from 45 km in version 1.0 to 58 km in version 2.2 to capture enhancements in NO<sub>2</sub> at high altitudes during polar spring.

For NO, the upper altitude limit for retrievals was lowered from 115 km in version 1.0 to 110 km in version 2.2, and the lower altitude limit was raised from 12 to 15 km. Two NO microwindows from version 1.0, in the wavenumber range 1820 to 1830 cm<sup>-1</sup>, were in the overlap region between the MCT and InSb detectors. As a result, these two microwindows suffered from elevated noise and were therefore removed from version 2.2

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processing. Five new microwindows were added for version 2.2 NO retrievals. For version 1.0, there were four interfering species for NO retrievals ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_3$  and  $\text{N}_2\text{O}$ ). For version 2.2, the microwindow altitude ranges were selected such that there was only one interfering species ( $\text{O}_3$ ).

Previous ACE validation papers that included NO and  $\text{NO}_2$  are listed in Section 2 (second paragraph). There was never a comprehensive validation paper of ACE-FTS version 1 NO or  $\text{NO}_2$ . This paper is the first comprehensive validation of the ACE-FTS NO and  $\text{NO}_2$  data products.

6) This has been addressed following the specific suggestions below (we now use “good” instead).

7) We respond to specific suggestions below.

*Specific Comments:*

*Abstract:*

*“The ACE-FTS NO VMRs agree with the Satellite data sets to within about 20% between 25 and 40 km.” In Fig. 38, the MIPAS and the SAGE II sunrise observations differ by more than 20% in the considered altitude range.*

This sentence was changed to the following:

“The ACE-FTS and MAESTRO  $\text{NO}_2$  volume mixing ratio (VMR) profiles agree with the profiles from other satellite data sets to within about 20% between 25 and 40 km, with the exception of MIPAS ESA (for ACE-FTS) and SAGE II (for ACE-FTS (sunrise) and MAESTRO) and suggest a negative bias between 23 and 40 km of about -10%.”

*“In comparisons with HALOE, ACE-FTS NO VMRs typically agree to +8% from 22 to 64 km and to +10% from 93 to 105 km.”*

*For both altitude ranges, the difference to HALOE is larger than stated (see Figs. 35 and 36). This is not changed simply by adding the word “typically”. Also, for 93 to 105*

km, the typical difference would be around 30% (see Fig. 36).

We added “on average” to explain the term “typical” in the abstract. We now include the maximum differences in %: “In comparisons with HALOE, ACE-FTS NO VMRs typically (on average) agree to  $\pm 8\%$  from 22 to 64 km and to  $+10\%$  from 93 to 105 km, with maxima of 21% and 36%, respectively”

### *Introduction*

*P3031, L14 “Secondary occultation” - better: “... occultation (which is its secondary measurement mode)...”;*

This was changed as suggested.

*P3031, L20 “From nadir-viewing” - add: “total columns” (Also, for O3 and NO2 also limited profile information can be obtained from nadir measurements).*

“total columns” has been added, as suggested.

*P3031, L24 “in limb mode, which is its primary measurement” : Most of SCIAMACHY measurements are performed in nadir mode.*

“which is its primary measurement.” has been deleted.

### *Chapter 2 : ACE*

*P3032, L23 “coverage of the tropics,...” - I recommend including a map with the frequency of the observations (how many % of the observations are performed for which areas/latitudes).*

A new figure (Fig. 1 in the new document) has been added showing the dependence of the ACE sampling frequency on latitude.

*P3033, L2 The passage after “To date ...” might be skipped*

We think that it is important to mention the other validation efforts and studies using NO and NO<sub>2</sub> here. So we prefer to keep this paragraph.

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*P3033, L17 Are really only O3 and NO2 cross-sections for only one temperature used?*

Yes. There is very little temperature dependence in the Chappuis band so only a single temperature is used for O<sub>3</sub>.

Much of the historical NO<sub>2</sub> data has been retrieved assuming constant temperature and that has been done with the MAESTRO data to date. The sensitivity of the column retrieval to temperature has been investigated by using different cross-sections and has been determined to be 0.5% per K. The use of this correction in the profile retrievals is being investigated.

*P3033, L22 I suggest adding a typical reference for DOAS like e.g. Platt (1994) or Platt and Stutz (2008).*

These references have been added.

*P3033, L22 The passage from “The NO2 cross section ...” until “... other absorbers.” (P3034, L7) can be skipped.*

This text has been deleted, as suggested.

*P3034, L12 and Fig. 1 “...simple summary statistics” this term is more confusing than explaining. I suggest simply: “summary statistics” and - very important - to explain the plotted data in detail. Comparing with Fig. 6, I assume the plotted value is  $\sigma/\sqrt{N}$ , with  $N$  being the number of occultation measurements and  $\sigma$  the standard deviation of the vmr at the respective altitude. This would then also be in accord with the term “summary statistics”. If this is correct, then the formula for calculating this value should be given, and in the text and in the legends of the plots it should be called statistical error. Otherwise the reader gets the idea that the plot shows the error of the retrieval. Also in this case, the plots show the same value that is later called uncertainty of the mean (Fig. 6). If it is really a fitting error - meaning a value that is determined from the retrieval process and not from the results - then the formula for its calculation should be given. It can not be the estimated uncertainty by Kar et al. (2007), because*

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*this would be 5% for altitudes between 20 and 40 km, while the relative error shown in the article is (much) less than 1%. Moreover, if the plot shows the retrieval error (derived from an approach that should be described in the text), then it is strongly underestimated (by at least one order of magnitude) when comparing to the validation results presented in the following. Therefore, I have doubts if these plots are really of any importance to the reader. They certainly give a wrong impression on the quality of the data (at 20 km the presented absolute fitting error is less than 0.01 ppbv). If you like to keep these figures in the article you should 1) describe how you calculated the plotted data, 2) avoid the term fitting error if it is a statistical error and 3) explain what the plots say about the quality of the ACE data.*

The data in Figures 1–3 (now 2–4), are median profiles of errors reported in the data files for ACE-FTS and MAESTRO. A description of these errors has been added (see response to the General Comment 2). We now call these errors, uncertainties for MAESTRO and statistical fitting errors for ACE-FTS as this is what they are. These errors represent the precision (random error) of the ACE profiles, but say nothing about the systematic errors.

Unfortunately, a complete error budget for the ACE retrievals is not yet available. The only errors available are the statistical fitting errors (ACE-FTS) and the uncertainties (MAESTRO) as described in Section 2. No systematic error budget exists for the v2.2 data product. However, work is underway to produce an error budget for the next ACE-FTS version to be released (v3.0).

*P3034, L18 Since the temperature effects in the O<sub>3</sub> cross-section are also not accounted for, this should also result in an uncertainty?*

Yes, it is of the order of less than 1%. This is mentioned in the paper now: “The uncertainty for temperature effects in the O<sub>3</sub> cross sections is smaller than 1%.”

*P3034, L26 “... appears to be in the range 1 to 2 km ...” - Please state from where you conclude this.*

We added the following to the paper: “The altitude resolution of MAESTRO profiles appears to be in the range 1 to 2 km. This was concluded by Kar et al. (2007) based on comparisons of MAESTRO observations with coincident ozonesonde profiles.”

The conclusion was that the observations were consistent with the preflight estimate of 1.2 km as the vertical resolution based on the instrument characterization tests.

*Figs. 2 and 3 : see comment to Fig. 1 above*

The figures have been relabeled (see reply to comment to Fig. 1 above).

*Chapter 3 : Validation Instruments*

*P3037, L5 “...ten satellite products from eight instruments.” I suggest adding “for comparison”. Also, I think you forgot OMI and GOME which both are also measuring NO<sub>2</sub> columns.*

We added “for comparison” as suggested. We focussed on comparisons with limb-viewing instruments (with the exception of SCIAMACHY nadir) to validate ACE profiles at comparable vertical resolutions.

*Chapter 4 : Validation Approach*

*P3047, L23 “... determined on a species to species basis ...” - what do you want to say with this?*

This was a sentence used in a previous version of the paper when all NO<sub>y</sub> species were considered. This is redundant now and has therefore been removed.

*P3047, L26 Why is it checked if the ground-based and balloon measurements are coincident with each other? Are there comparisons of these measurements in the article?*

The sentence has been clarified. It refers to coincidence with the ACE instruments and not the ground-based and balloon-based measurements with respect to each other.

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P3050, L19 *“The ACE instruments only produce fitting errors” - Regarding the term fitting error : You are using it here and above in the sense of statistical error. I find this very misleading. Better write statistical error and say how it is calculated. It may be that in certain branches the word fitting error has the meaning of statistical error. From the meaning of the word itself however, one thinks it is the (total) error of the retrieval. If you want to use the word fitting error (which would be misleading) I think it is necessary to explain what you want the reader to understand with it.*

It is indeed the statistical fitting error, please see comment to P3034 L12 Fig.1. We rewrote the sentence as:

*“The ACE-FTS data products include only statistical fitting errors while MAESTRO provides an estimate of relative uncertainties (as described in Section 2). No systematic errors are available, therefore the error bars for the single profile comparisons are very small.”*

#### *Section 4.2*

*I suggest to restructure this section. You start with the term diurnal effect, then turn to the local time issue and the scaling factors, and then explain again the diurnal effect. This confuses the reader because one might think that are three effects to be considered. Also it makes the text unnecessarily long because many things are repeated.*

This section has been restructured as suggested.

#### *Chapter 5 : Results for the NO<sub>2</sub> comparison*

P3053, L17 *“They agree to within 10% ...” - The differences agree? This would mean that the differences (FTS-Maestro) agree to the differences found in Kar et al. Probably you want to say that the FTS and Maestro measurements agree?*

That is right and this is now corrected in the paper.

P3053, L19 *“... reaching values of 50% at 45 km.” - The mean value of Maestro for 45*

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km, shown in Fig. 6 a, is not 50% lower than FTS. Also, in this plot for higher altitudes, FTS is below Maestro and not vice versa.

The results shown are correct, and are largely caused by the fact that the MAESTRO VMRs are so variable at high altitudes.

We added the following text to section 5.1.1:

“There are some altitudes (38 to 41 km and 47 to 50 km) where the absolute differences are negative but the relative differences are positive. This is most obvious near 47 to 50 km, where the mean absolute differences are around -0.2 ppbv, but mean % differences are greater than 40%. The absolute differences at 50 km have a mean difference of -0.2 ppbv, but most of the points lie above 0 ppbv. So the large negative differences are skewing the result. The median does give +0.2 ppbv. Relative differences at 50 km have a mean of 41.2% and a median of 41.3%, so the mean % difference is probably more meaningful than the mean absolute difference. But this carries with it the caveat that the mixing ratios at this altitude are very small, so even large percent differences are not very significant in terms of the actual measurements. Examination of the ACE-FTS and MAESTRO data at 50 km shows that the negative absolute differences come from the many large MAESTRO VMRs caused by scatter in the data.”

*P3055, L12-18 You write that ACE-FTS and ACE-Maestro both show differences to HALOE within +/-15% from 22 to 42 km. This is quite surprising because in section 5.1.1 you find that FTS is around 10% lower than Maestro. If this is due to the fact that HALOE observations are performed for northern high latitudes mainly, I think this should be pointed out here.*

In the HALOE comparison we only use 36 coincidences whereas in Section 5.1.1 we were using 7850.

*P3056, L8 “... 25 to 40 km.” - add the reference to Fig 8a of Kar et al. already here.*

The position of the reference was changed as suggested.

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*P3056, L12 "... below 25 km." - add the reference to Fig 14 already here (not one line later which refers to Fig. 9a of Kar et al.)*

The position of the reference was changed as suggested.

*P3056, L22 Please say why there are fewer coincidences for FTS than for Maestro.*

We mention now in the paper that we are filtering for ACE profiles that have data in the 16 to 39 km height range. This reduces the number for ACE-FTS more than for the MAESTRO.

*P3058, L23 and Fig. 17 I suggest to add ticks at the upper axis and the 0% line. Also the yellow shading for the 20% region would be nice.*

The figure (now Fig. 18) was changed to include grid lines and yellow shading.

*P3060, L16 Why is this polar vortex criterion only applied for the OSIRIS comparisons?*

The Chalmers University group already had processing in place for this analysis, and provided the data, therefore we included this only for the OSIRIS comparison.

*P3060, L21 and Fig . 19 Why is the altitude grid of FTS and OSIRIS 2 km for this comparison?*

Figure 19 (now 20) was revised to have the same plotting grid as the other comparisons.

*P3061, L11 Again, FTS and Maestro show a similar (about 1ppbv) difference to OSIRIS at the peak, although FTS was found to be lower than Maestro in section 5.1.1. Please explain why this is so.*

The text has been modified to quantify the differences at the peak:

“OSIRIS VMRs are higher at the NO<sub>2</sub> peak by about 0.9 ppbv or 17% for ACE-FTS and by about 0.7 ppbv or 14% for MAESTRO. The results for MAESTRO and ACE-FTS are similar here due to sampling biases in the OSIRIS comparisons due to Odin/OSIRIS

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viewing constraints.”

*P3062, L12 Please explain why the total columns are expected to be larger than the partial columns, i.e. mention tropospheric part (above or here).*

We now mention the tropospheric part, as suggested.

*P3062, L20 How do you conclude that are no seasonal or latitudinal biases?*

We have examined the differences as function of latitude and SZA, by looking at the data separately and no clear systematic dependencies could be found. The photochemical correction on the SCIAMACHY data is relatively large in many cases and introduces a significant uncertainty in the comparison.

*P3064, L12 Is there an explanation why FTS and Maestro do not observe this gradient above 24 km?*

That ACE-FTS and MAESTRO do not observe this gradient possibly results from the NO<sub>2</sub> inhomogeneities (see text page 3063 lines 18–29 and page 3064 lines 1–10) also affecting the vertical profile retrieval at altitudes above 24 km. As shown by Berthet et al. (2007), variations of NO<sub>2</sub> amounts in the stratospheric layers (that are not homogeneous in this case) crossed by the SALOMON balloon instrument line-of-sight generates spurious NO<sub>2</sub> concentration values and artificial gradients, not only in the lower stratosphere levels but all along the retrieved NO<sub>2</sub> vertical profile. Homogeneity of stratospheric layers is however necessary (homogeneity hypothesis) to ensure a consistent vertical profile retrieval from remote-sensing instruments. We strongly suspect that the ACE-FTS and MAESTRO remote observations are similarly affected. Note that the differences between the NO<sub>2</sub> concentration values/gradients measured by ACE and SPIRALE give an idea of the bias induced when the hypothesis of homogeneity is not valid.

*P3064, L15 In Fig. 23c the difference of FTS to SAOZ is larger than 5% at 24.5 km.*

We changed the altitude to 22.5 km and the difference to 8%

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*P3066, L25 Here it would be nice to discuss the differences with respect to the location of the stations, i.e. why is the correlation worst for Kiruna? Also, the possible effect of clouds might be discussed here.*

We rewrote the last part of Section 5.3 as follows:

“For Kiruna, 8 out of 12 days of available measurements are during the strong vortex winter of 2005, but these data do not show more scatter than Ny Ålesund, which has only two available measurement days during the same period. There also do not appear to be significant gradients in NO and NO<sub>2</sub> across the vortex edge for the corresponding ACE-FTS measurements. Therefore we do not think that the larger scatter at the northern high latitude stations is due to the polar vortex.”

The FTIR measurements are made during clear sky conditions.

*P3067, L10 Did you check if the differences for the high-latitude stations can be explained by gradients due to denoxification?*

We cannot really tell from the ACE data itself if this is due to denoxification and we don't have the measurements and the method to assess denoxification at the FTIR sites. We therefore removed this statement.

*P3068, L9 Since the plotted profile is the mean profile of observations in May and September (or March and July), the variability of the profiles is (mainly) determined by seasonal effects. Therefore I do not think it makes sense to argue that the observed differences are within this variability. That is similar to: The mean value of all profiles measured by FTS in March and July differs to those measured from GB by 25%, but it agrees with the profiles measured in March.*

The reviewer is right, this argument has been removed.

*P3068, L29 Again, please point out that the errors shown in Figs. 1-3 are statistical errors and no systematical error is available.*

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The lack of systematic errors has been clarified. Figures 1 to 3 (now 2 to 4) have been relabeled as discussed above (see comment to P3034, L12 and Fig. 1)

*P3069, L3 In how far are these comparison results consistent with each other?*

This sentence has been rewritten as:

“The partial column comparison results from the DOAS system at Harestua (60.2° N), (14 to 15% for ACE-FTS and 26 to 30% for MAESTRO), show similar magnitudes to those from the FTIR at Kiruna (67.8° N) (11% for ACE-FTS and 22% for MAESTRO for the smaller columns).”

*Chapter 6 : Results for the NO and NO<sub>x</sub> comparisons*

*P3071, L3 The considerable increase of the difference starts already below the peak at 45 km.*

As suggested, changed to “...between 40 and 50 km”.

*P3071, L9 The difference is (much) larger than 20% also for altitudes above 50 km.*

Changed as suggested to: “...above 52 km, where the maximum difference is 30% up to 60 km.”

*P3072, L21-24 I think this argumentation is not possible. If the precision of both instruments is larger than the atmospheric variability, they can also be similar.*

This has been removed, because it is not necessary for the discussion.

*Chapter 7 : Summary and conclusions*

*P3075, L22 Since the differences to MIPAS are up to 70% or larger than 1.5 ppbv, I think “slightly more negative” is not the correct term.*

The sentence has been revised: “slightly” has been removed.

*P3075, L22-24 Yes ! Since this is the correct description of the agreement, it should be*

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*given also in the abstract !*

This is also mentioned in the Abstract now, as suggested.

*P3075, L26 - P3076, L11 The conclusion is not the right place for this. The reader would need this information, when the profiles are compared (section 5).*

This paragraph has been moved to Section 5 as suggested.

*P3076, L13 For altitudes close to the NO<sub>2</sub> peak a difference of 20% or 1 ppbv can not be called “very good”.*

The wording has been changed from “very good” to “good”.

*P3078, L22 Again, for altitudes around the NO<sub>2</sub> peak, a bias of 10% is not “slightly”.*

The sentence has been modified: “slightly” has been removed.

*P3078, L22 Again: the difference to MIPAS and SAGE data is larger.*

We rewrote the sentence as:

“The ACE-FTS and MAESTRO NO<sub>2</sub> VMRs agree with the other satellite data sets (with the exception of MIPAS ESA (for ACE-FTS) and SAGE II (for ACE- FTS (sunrise) and MAESTRO)) to within about 20%”

*P3079, L23 See comment to abstract.*

This has been revised as requested.

### *Technical Corrections*

All the technical corrections were implemented.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 3027, 2008.

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