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Atmospheric Measurement Techniques Discussions

Interactive comment on "Potential and limitations of the MAX-DOAS method to retrieve the vertical distribution of tropospheric nitrogen dioxide" *by* T. Vlemmix et al.

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article

Authors response to reviews AMTD 2011-85

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First of all, the authors would like to sincerely thank four anonymous reviewers. Their valuable comments have lead to important improvements of this manuscript.

This document contains the authors response to the comments by all reviewers of AMTD manuscript 2011-85. Each reviewers remark is repeated here in italics and has been given a specific code used for cross-referencing, e.g. R1C1 refers to reviewer 1, comment 1.

1 Response to review 1

R1C1 *General comment:It is not clear for me what are the advantages/benefits of the approach used by the authors compared to the well established method of optimal estimation. I think the authors should discuss this point more extensively in the Introduction (end of Page 4017/beginning of page 4018) and/or in the Conclusions. It will be also interesting to show a comparison between both methods using CINDI campaign observations.*

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The authors agree with reviewer 1 that this point should be discussed in more detail. This point discussed in a new subsection (Sect. 4.4). This section also answers to the general comment R2C2 by reviewer 2. The point is mentioned again in the conclusions. This is the new section 4.4:

4.4 Limitations of MAX-DOAS profiling potential and dependence on the retrieval approach

In this section we discuss to which extent the conclusions drawn after the sensitivity studies depend specifically on the retrieval approach followed in this work, and which conclusions have a wider scope.

Retrieval approaches to derive NO_2 profile information from MAX-DOAS observations can roughly be separated in those using the 'optimal estimation method' (OE-method) Rodgers, 2000 and those using a 'parametrized profile method' (PP-method). In the following, we refer to the OE-method specifically as those implementations of OE which use a profile parametrization for aerosols and NO_2 that is defined for a relatively high number of independent layers, each with a vertical extent of typically 200 meters (see e.g. Frieß et al., 2006 and Clémer et al., 2010).With the PP-method, we here refer to retrieval approaches where the vertical profile (of aerosols and/or NO_2) is parametrized by a low number of well-selected parameters, which may have different dimensions, such as a column amount and a scale height (see this paper, Sinreich et al., 2005, Li et al., 2010 and Wagner et al., 2011). The number of selected parameters is usually approximately equal to a realistic estimate of the number of independent pieces of information contained in the MAX-DOAS measurements, and may vary between 1 (over-determined) and no more than 5 (under-determined). The solution is found by a least-squares minimization of differences between the measurements and forward simulations.

A major advantage of OE-method is the flexibility to retrieve a wide range of different profile shapes. In the here presented sensitivity study it has been shown that the MAX-

DOAS measurements are sensitive to the profile shapes (of aerosol extinction and NO_2) especially for the lowest part of the boundary layer. In this part of the troposphere, such shapes can be retrieved using the OE-method without assuming them in the a-priori. A disadvantage of the OE-method is that under some conditions the retrievals tend to be unstable and consequently yield profiles showing unrealistic oscillations. This effect is highest in that part of the troposphere (typically above 1-2 km) where the MAX-DOAS sensitivity functions (Fig. 1) are parallel, and therefore do not contribute with independent pieces of information. This height significantly decreases for higher AOT.

In this study, where the PP-method is used, it has been shown that a too much simplified description of the boundary layer profile shape, e.g. assuming homogeneous distribution of aerosols and NO_2, may lead to errors in the retrieval of both boundary layer and free tropospheric NO_2. For PP-approaches this problem may be solved by adding a third free parameter to describe the NO_2 and aerosol boundary layer profiles, such as the parametrization as used in the sensitivity studies, using the shape factor S. A similar approach is taken by Wagner et al., 2011. The need for non-homogeneous boundary layer profile descriptions is also supported by Morgan et al., 2010 where aerosol extinction profiles are reported that typically show an increase with altitude in the boundary layer.

An advantage of the PP-method, when compared to the OE-method, is that frequently occurring profile shapes, such as those showing a sharp decrease at the top of the boundary layer, can be retrieved for many different boundary layer heights. Because the MAX-DOAS sensitivity functions are so broad (Fig. 1), it is almost impossible to realize this with OE-methods, except when such a sharp decrease (for one particular height) would be defined in the a-priori and a-priori error estimates of the vertical profile.

With respect to the free troposphere both approaches are equally limited by fact that the vertical sensitivity functions of all elevation viewing angles are flat, and in addition decrease to zero towards the top of the free troposphere. This implies that for both

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approaches a-priori assumptions are critical in this part of the atmosphere. When the NO_2 radiosonde (Sluis et al., 2010) will be further developed, a long-term data set of profiles NO_2 can be used to make a realistic, well-founded a-priori assumption for free tropospheric NO_2. Such an assumption would probably have to take seasonal variations into account.'

The following conclusions have been rephrased, and also contain statements about the optimal estimation method, made because of reviewers comments R1C1 and R2C2:

- 'When using the two NO_2 layer retrieval model, elevated NO_2 layers are frequently found for the wrong reason, i.e. not because there is an elevated NO_2 layer in the real atmosphere, but due to a low signal to noise ratio, or due to a BL profile parametrization for aerosols or NO_2 that does not correspond to the real situation. This effect may lead to an error in the tropospheric NO_2 column up to 10%. Probably an optimal estimation approach would be more accurate for a wider range of aerosol and NO_2 BL profile shapes.'
- 'Accurate MAX-DOAS retrieval of NO_2 in the free troposphere is possible only when (i) there are no clouds, (ii) the AOT is sufficiently low, (iii) the aerosol extinction and NO_2 profiles are sufficiently constant in time, (iv) the signal to noise ratio of the MAX-DOAS measurements is sufficiently high, (v) the BL profile parametrizations for aerosols and NO_2 adequately describe the real profile shapes, and (vi) the vertical temperature and pressure profiles correspond to those in the retrieval model. Only when these conditions are fulfilled, then it may be possible to retrieve the height and concentration of a free tropospheric NO_2 layer. The accuracy and precision for retrieval of NO_2 in the free troposphere therefore strongly depend on a-priori assumptions. This conclusion is not limited to the retrieval approach chosen in this work, but equally applies to retrieval methods based on optimal estimation.'

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R1C2 *Page 4016, line 18: Please also refer to Hendrick et al. (2004) for stratospheric* NO_2 *retrieval from zenith-sky measurements.*

Done.

R1C3

Page 4017, line 11: You refer to Figure 1 for sensitivity functions. Please mention in the legend of this figure that these are actually altitude-dependent air-mass factors. Otherwise the reader has to wait till page 4022 to find a description of these sensitivity functions.

Done.

R1C4 *Page 4017, lines 14-17: 5 degrees of freedom for signal (DOFS) from MAX-DOAS observations is very optimistic and is only obtained in theoretical studies (e.g., Friess et al., 2006). Using real observational data, the DOFS is generally not larger than 2-2.5.*

We agree, see the additional remark in Sect. 1.2: 'Under realistic conditions, values above three are rarely encountered (see Clémer et al., 2010, and Sect. 4 and 5 below).'

R1C5 *2-2.5. Page 4024, line 8-10: What is the geometry used for the radiative transfer calculations ? Spherical ? Pseudo-spherical ? Please mention it.*

The plane-parallel version of DAK was used. This has been mentioned at the beginning of Sect. 3.2.

R1C6 *Page 4025, line 21 and page 4039, lines 16-19: Fixed values based on AERONET observations in Cabauw are used for single scattering albedo and asymmetry parameter. What is the natural variability of these parameters at the Cabauw site*

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? What is the impact of using fixed values for these parameters on the agreement with independent data (see Fig 11) ?

The following lines have been added to Sect. 3.2.1: ‘For the entire period of three years (not only blue sky days) the AERONET level 1.5 product for $\lambda = 440$ nm shows an average of 0.72 ± 0.03 for the asymmetry parameter and 0.92 ± 0.06 for the single scattering albedo. The impact on the MAX-DOAS retrievals of errors in these parameters (see e.g. Vlemmix et al., 2010) is relatively small compared to other sources of uncertainty, see Sect. 4.’

R1C7 *Page 4029, line 17: 200 inversion runs are used to create an ensemble of retrieval outcome. Why do you choose 200 and not 50, 500 or 1000 ?*

The following has been added to the manuscript, also partly to answer the next comment [R1C8]: ‘The number of 200 repetitions is selected to have a reasonable description of the ensemble properties and at the same time to have a reasonable computing time. Without special efforts to optimize for speed, a performance was realized of 16 seconds for 200 runs. For a typical day with 12 hours of observation, with an analysis for each half hour, the total analysis time would be 6 minutes. Although more runs would lead to a more accurate distribution for each retrieval parameter, tests have shown that the average and extremes of the distribution are almost unaffected by increasing the number of repetitions to 2000. For fewer runs (e.g. 20), these values become unstable.’

R1C8 *Page 4038, line 14: five should be six. Which criteria do you use for selection of days from the CINDI campaign ? Cloud-free days ? What is the computing time for one day of MAX-DOAS retrievals ?*

Five has been changed to six, and the criteria have been described, see the beginning of the new Sect. 5.1 and comment R4C15 below. The computing time is added in the same section as R1C7.

R1C9 *Page 4038, lines 19-21: For the application to the CINDI campaign data, models with one and two* NO_2 *layers are used. Do you assume* NO_2 *uniformly mixed in the layers ? If yes, what is the impact on the comparison results of varying the* NO_2 *proïňĄle shape ?*

The answer to the first question is yes, it is described in Sect. 3 that for the retrieval models all layers are assumed uniformly mixed. The impact of a profile shape that is different in reality, is studied in the sensitivity studies C and D. The tropospheric NO_2 column may be overestimated up to about 10%. The volume mixing ratio may be overestimated even much more for low values of S, which essentially describe elevated layers (Fig. 8, column 4) within the boundary layer. For the two NO_2 layer retrieval model, NO_2 may be retrieved for the second layer as a consequence of the wrong assumption for the aerosol and NO_2 profile shapes in the boundary layer. In addition, the wrongly assumed profile shape in the boundary layer may lead to non-zero values in the free troposphere, even when, in reality, there is no NO_2 in the free troposphere. This point is mentioned at the beginning of the last paragraph of Sect. 5.1 ('The sensitivity study in the previous section ... aerosol extinction retrieval).'), and in the new version of the manuscript also in the conclusions.

R1C10 *Page 4040, lines 1-9: The uncertainties on the retrieved parameters are larger in the afternoon, maybe due to the occurrence of clouds. Why do you apply your algorithm in cloudy or partly cloudy conditions since it is valid only for clear-sky conditions ?*

The following has been added to the beginning of Sect. 5.1: 'The algorithm is applied also under cloudy conditions to illustrate the effect of such conditions on the accuracy of the retrieval (which decreases significantly, especially for the two layer retrieval model).'

R1C11 *Page 4041, lines 1-4: what is the error bars on the NO_2 sonde data points ?* No error bar is reported, because, as written in Sluis et al., 2010 'A proper estimate of the uncertainty in flight can only be given if the sonde measurements are compared to an independent source of NO_2 proïňĄle information.'

R1C12 *Page 4044, lines 15-21 and Fig 15 page 4072: Could you estimate the error bars on the data points in Fig 15 in order to better discuss the significance of the differences between MAX-DOAS and in-situ measurements ?*

See the new version of the figure. A part of section 5.2.2 has been rephrased to make a clearer distinction between the results shown in Figure 15 (based on averages, for each hour, over five days), and the results shown in (the original) Tab. 3 (based on all data, treated as independent observations). For this reason, Tab. 3 is also enlarged with three rows which give a quantitative description of the results shown in Figure 15.

The rephrased part of section 5.2.2 now reads:

'The comparison is performed in two ways: (i) by comparing the two data sets without averaging, in order to quantify the agreement between the two data sets for individual observations, see the upper half of Tab. 3, and (ii) by considering the average diurnal evolution of the two data sets. In that case all observations (within the five days) of the two measurement techniques are averaged per hour of the day. This is shown in Fig. 15 and the bottom half of Tab. 3.

With respect to the averaged diurnal evolution, a good agreement is found between the in-situ observations and the MAX-DOAS derived NO_2 volume mixing ratios. The general pattern of the diurnal evolution – showing a dilution caused by thermal convection –is captured best by the two NO_2 layer retrieval model and the combined product of the two models (where for each observation the model selection is based on $\chi^2_{\mathrm{NO_2}}$). Those two retrieval products agree with the in-situ observations within their uncertainty range. The one layer model tends to underestimate the volume mixing ratios a little: the MAX-

DOAS values are 18% lower than the in-situ values. For the two NO_2 layer model a correlation is found of 0.94 and an average difference of 0.10 ppb. The combined product has the same correlation, and an even smaller average difference: 0.04 ppb. The slope of the linear fit, obtained with the same fitting method as used in the comparison between MAX-DOAS and lidar (Sect. 5.2.1), is 1.10 for the two layer model.

The comparison based on individual observations shows larger differences, see Tab. 3. The morning hours sometimes show an over- or underestimation relative to the in-situ monitor (Fig.11). This effect in the morning is not always due to clouds or measurement noise in combination with low NO_2 layers, see the discussion above, but may also be due to errors in the assumed profile shapes for aerosols and NO_2. For compact NO_2 layers close to the surface (which are typical for the morning), volume mixing ratios can only be retrieved accurately from the MAX-DOAS measurements if there is an almost exact agreement between the real profile shape and the profile shape assumed in the retrieval model (see Sect.4).'

R1C13 *Page 4020, line 9: Hermans should be between brackets.*

Done.

R1C14 *Page 4040, line 15: 'at the 24th' should be replaced by 'at June 24th'.*

Done.

R1C15 *Page 4068, Fig 11: Plots of Fig 11 are too small, making the discussion related to this figure very difficult to follow.*

The figure is made in portrait style. For the AMTD document it appears small, since it is printed on a page which itself is in landscape style. In AMT the same figure will cover a full A4 page, and therefore automatically be larger.

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2 Response to review 2

R2C1 *1. The authors investigate the effects of the choices for several free parameters on the inversion. In practice, however, the first choice when performing MAX-DOAS measurements is on the number and values of elevation angles. Within this study, they are fixed (2,4,8,16,30,90) without any discussion and without the announced reference (4020/12). Please add a motivation for this particular choice and discuss, how far a different choice (additional angles?) might improve the inversion performance. Also comment on the required accuracy of elevation angles.*

This has been done. The following lines have been added to Sect. 2.:

'This selection of viewing elevations is chosen to find a balance between on the one hand a sufficiently small total integration time needed for the scan of one vertical profile, which is important to prevent errors due to changing atmospheric conditions, and on the other hand to make optimal use of the differences in vertical sensitivity of the various elevations (Fig. 1). This difference is largest for the smallest viewing elevations. The set of elevations is comparable to the set used in Clémer, et al. (2010), but with only one instead of three elevations between 8° and 30°, since it is shown in Fig. 1 that these elevations have a quite similar (flat) vertical sensitivity. The highest elevation is needed to put a constraint on the tropospheric NO_2 column (this elevation is almost insensitive to the vertical profile shape), the lowest elevations contain most information with respect to the the aerosol and NO_2 profile shapes. Although an observation for $\alpha = 1^\circ$ could improve the profiling potential even more (see Fig. 5 in Wagner, 2011) it was decided not to use this elevation, firstly because it cannot be used at many sites where the horizon cannot be seen, and secondly because this elevation is, for conditions with a high visibility, extremely sensitive to small errors in the instrument alignment. This affects both the aerosol and NO_2 retrieval step of the algorithm. For the set of elevations used in this study, the elevation viewing angle accuracy needs to

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be highest for the 2° elevation: 0.3° or better.'

R2C2 *2. The inversion approach is simple and transparent; however, several groups use OE for the retrieval of proïňĄles. Please discuss the differences in approach and results of both methods; how far could groups using OE still learn something from your study?*

A similar question was asked by reviewer 1, and changes have been made accordingly. See [R1C1] in this document.

R2C3 *3. In the introduction, you point out the importance of profile information for the validation of satellite retrievals. Please refer to this aspect in the conclusions: How far are MAX-DOAS measurements and the presented inversion algorithm suited to validate/improve satellite retrievals?*

Done. The authors agree with the reviewer that this point should be addressed. This is included in a new section (Sect. 4.4.1). in the new version of the manuscript. This section reads:

'**4.4.1 Consequences for satellite validation**

MAX-DOAS observations of tropospheric NO_2 can be used for validation of satellite observations. A comparison of individual tropospheric column measurements of satellite and MAX-DOAS should take into account the differences in assumed profile shapes and the difference in vertical sensitivities, as described by Rodgers, et al., 2003. For example, the profile shape assumed for the OMI tropospheric NO_2 product (DOMINO) is taken from the TM4 chemistry transport model (Boersma et al., 2011). For MAX-DOAS a basic profile shape can be retrieved from the observations themselves, but, as noted above, the retrieval strongly depends on a-priori assumptions. Space-borne observations are more sensitive to NO_2 in the free troposphere than to NO_2 in the

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boundary layer (see Fig. 1 in Boersma et al., 2003), whereas the opposite is the case for ground based MAX-DOAS observations (Fig. 1 shown above). Flexible a-priori assumptions are the only way to accurately retrieve free tropospheric NO_2 if it is present. However, for most of the time this will not be the case: the boundary layer partial NO_2 column is usually much higher than the free tropospheric partial column. As a consequence, flexible a-priori assumptions for the free troposphere will for the majority of cases lead to less accurate and less precise retrievals.

Long term data sets of MAX-DOAS profile observations can be used to validate the profile description generated by chemistry transport models, which are used as an input for the satellite retrieval. For this application it is especially important that the MAX-DOAS profile retrievals produce realistic first order profile descriptions for NO_2 in the boundary layer. '

R2C4 *4014/6: Replace "in which MAX-DOAS retrievals play a role" by "of satellite observations".*

Done.

R2C5 *4014/11: What are "retrieved model uncertainties"?*

This line is removed after comment R4C1 of reviewer 4.

R2C6 *4014/15: "The height of the elevated NO_2 layer can only be retrieved": This sounds as if the height of the elevated layer is a free parameter, but it is fixed within this study.*

This line is removed after comment R4C1 of reviewer 4.

R2C7 *4018: Add a reference to Wagner et al., AMTD, 2011, http://www.atmos-meas-tech- discuss.net/4/3891/2011/amtd-4-3891-2011-discussion.html.*

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Done.

R2C8 *4019/7: Replace "successfulness and limitations" by "performance".*

This line is removed after comment R3C1 of reviewer 3.

R2C9 *4023/20: Due to the different lifetimes of aerosols and NO_2, the elevated layer heights could be different for both, which would probably affect the inversion. Please comment on that.*

The authors agree with this point. However, no (long term) data sets are available, e.g. for the Netherlands, that can be used to make a realistic estimate of heights for free tropospheric NO_2 and aerosols. Aerosol and NO_2 amounts in the free troposphere are generally expected to be low, but occasionally moderately high in comparison to boundary layer amounts.

It is the purpose of this section to give a description of the settings of the retrieval model. This point made by the reviewer, about the reason to choose a height of 3-3.5 km for aerosols, would be more in place in a discussion of results. However, since the sensitivity studies (sensitivity study E) already show that it is disadvantageous to use an elevated aerosol layer at a fixed altitude, and the results in the rest of the paper are obtained for a single aerosol layer parametrization, it is decided not to add this point to the discussion.

R2C10 *4025/10: Please discuss how far additional measurements in the UV might provide additional information and improve the inversion.*

This discussion has been added to Sect. 3.2.1: 'Note that it is demonstrated in Frieß et al., 2006 that combination of four wavelength bands (360, 477, 577, 630 nm) leads for aerosol extinction retrievals to one additional piece of information compared to a single

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wavelength approach. It depends on the wavelength range of the instrument used if this can be realized.'

R2C11 *4029-4030: The procedure is somewhat tenuous: First you vary the input to learn something on uncertainties, but then you skip those results you don't like. For a measurement, where the truth is not known, extreme values can not be identified and skipped that easily!*

The challenge is to characterize the distribution of retrieved values for a certain parameter by an average solution and an uncertainty estimate. The approach chosen is more conservative (and results in larger uncertainties) than a more common approach, e.g. to make a Gaussian fit to the distribution and report the one sigma width as an uncertainty estimate. In that case the uncertainty estimate would be based on the middle 68% of the distribution: the uncertainty range would be smaller and therefore more 'optimistic'.

The remark by the reviewer has lead to reconsider the special approach that was followed for the volume mixing ratio, as described in the original manuscript in Sect. 3.3, and which was illustrated in Fig. 5. It was decided to change the procedure, in order to be more in line with the other parameters: the uncertainty is now also for the volume mixing ratio defined by the middle 90% of the distribution. However, the only change with respect to other parameters (needed because the distribution of volume mixing ratios is highly asymmetric) is that not the ensemble average is used as the solution, but instead the ensemble median of the volume mixing ratio. This change is described in the new version of the manuscript (Sect. 3.3)

This has lead to changes in Figures 5, 7, 8, 9, 11, 15 (since the results shown in Fig. 7 and 8 were performed for zero noise, no changes are visible for those Figures) and Table 3.

R2C12 *4035/2: molec cm-2*

Done.

R2C13 *4035/5: The effect is relatively small for AOT=0.2; for polluted regions (China), however, it can probably be much higher!?*

The authors agree with this remark. It is answered by the change made for comment R4C14 by reviewer 4, see below.

R2C14 *4040/4: "suspect": Be more specific! Have there been clouds, e.g. in the BSRN?*

The following line has been added to Sect. 5.1: 'As noted above, discontinuities in the AERONET data (first column of Fig.11) indicate the presence of clouds. These discontinuities sometimes coincide with high uncertainties in the tropospheric NO_2 column. For periods in which the frequency of AERONET observations is high (continuous cloud free periods), the uncertainty estimates for N_{Tr} are relatively low.'

R2C15 *Table 1: Maximum AOD is 1, which might be exceeded over China!*

The following line has been added to Sect. 3.2.1: 'The range for the AOT is chosen to be realistic for the Netherlands. Depending on the measurement site, it may be needed to extend this range.'

R2C16 *4071/5: molec cm-2*

Done.

R2C17 *Figure 14: Linear regression assumes an independent and a dependent variable; this is not the case here, and both lidar and MAX-DOAS have errors. Please apply an appropriate method (see Cantrell et al., 2008, ACP, http://www.atmos-chem-phys.net/8/5477/2008/acp-8-5477-2008.pdf).*

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This point made by the reviewer reveals a mistake in the manuscript: although the slope and intercept of the linear fit were actually determined with what in Cantrell et al., 2008 is referred to as a 'bi-variate method', the method used is in the manuscript erroneously referred to as a 'linear regression'. The following has been added in Sect. 5.2.1: 'A bi-variate fitting method was used, where the squared orthogonal distance of each x-y point to the fitted line was minimized. Errors were taken into account by varying each x and each y within its uncertainty estimate (using random Gaussian noise) and repeating the fit procedure a thousand times (the fit results did not change significantly when this number would either be ten times lower or ten times higher). The resulting fit parameters were found to change as expected after the x- and y-axis were interchanged. It is remarkable that the slope found in this comparison is comparable to the slope reported in Roscoe et al.,2010 (their Fig. 6), where differential slant column measurements from the KNMI instrument used in this study are compared to an average of other MAX-DOAS instruments used at the CINDI campaign. If the MAX-DOAS measurements used in this study would be artificially corrected using those results, then a slope would have been found of almost one, and a small intercept.'

3 Response to review 3

R3C1 *Each section start with "In this section ... ". In addition there is a separate subsec- tion 1.3 which outlines the manuscript. I do not see that these lines are necessary since a (short) paper can be structured using section headers along with the argument. Therefore, I suggest to delete 1.3 and the "In this section ..." sentences.*

Section 1.3 has been deleted, as well as most of the 'In this section' parts.

R3C2 *The concept of the elevated layer is not fully motivated and justified. It is a good point in the sensitivity study. The selection of the retrieval (with or without elevated*

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layer) for the comparison with the LIDAR measurements should be justified by more than the value of the reduced χ^2 . Is there any indication for the additional layer? From meteorology, satellite observations, or trajectory models?

First of all, the authors would like to point out the following, which was written in the original manuscript on p.4023 l.14-16: 'The retrieval for the second NO_2 layer should be interpreted as *the partial NO_2 column above approximately 1 km, with unknown altitude*.' This remark implies that, although the retrieval model contains an elevated layer, the retrievals should not be interpreted in a strict sense as a clear indication for NO_2 around this altitude in the free tropsophere. The above sentence, describing how the outcome of the two layer retrieval model should be interpreted, is based on Fig. 1 and Fig 10. They both indicate that the MAX-DOAS measurements can almost not determine the height of NO_2 at higher altitudes. Since this sentence/remark is crucial for the interpretation of the retrievals of the two-layer model, it is in the new version of the manuscript repeated in the caption of Figure 12, where the elevated NO_2 layers plotted in blue may raise questions by readers who may not have read the remark on p. 4023. In addition a similar remark is added to the conclusions.

A choice for the two layer model, based on a comparison of the value of the reduced χ^2, implies that the two-layer model more adequately reproduces the measurements than the one layer model. It does not imply that the two layer model gives an accurate description of the real profile, especially when taking the above remark into account. If the median χ^2 would be well above 1, then the selected retrieval model does probably not correspond to the real one.

Prediction of elevated layers with external data sources is very challenging. Meteorological models can in principle be used to explain transport from the boundary layer to the free troposphere, but real explanations can only be given if emission sources and life time estimates are very well described. Although a relevant point, it is considered to be beyond the scope of this work.

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R3C3 *Figure 14: I support the point made by Referee 2 on the appropriate regression method. However, the Press et al. routine directly provides the error estimates of of slope and intercept.*

See R2C17.

R3C4 *Section "Conclusion and outlook" should be renamed to "Summary and conclusion"or "Conclusions" since it contains mainly the findings and discussion of this study. In my opinion, the "outlook" is a minor issue here.*

This has been changed.

R3C5 *Technical points of the other 2 reviewer are not repe page 4029, line 23: "anew" should read "a new"*

This line has been changed.

R3C6 *Figures suffer from grayish low-res lines at the axis and error bars. Please revise.* This has been done for figures where this effect was most striking. Error bars were not changed, they were plotted in grey to be visible, but not dominant to the eye.

4 Response to review 4

R4C1 *In my opinion, the title of the paper does not reïňĆect the study presented. The authors do not investigate the MAX- DOAS method potential and limitations for profile retrieval in general but rather the 2 and 1 layer profile parameterized inversion technique.*

The authors agree with the reviewer that the title of the manuscript could be misleading due to the fact that the 'potential and limitations ...' have been investigated only for two

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parametrizations and only for a look-up table based least-squares approach. We think however, that the conclusions drawn have a wider scope, especially the limited ability to accurately retrieve free tropospheric amounts of NO_2 using MAX-DOAS observations. This is explained in the new section which was added after the comments of reviewers 1 and R1C1 and R2C2.

We propose to change the title of the paper to: '**Ability of the MAX-DOAS method to derive profile information for NO_2: can the boundary layer and free troposphere be separated?**'. This change has also lead to a changed paragraph in the abstract, which gives a more direct answer to the question in the title, than the original paragraph.

R4C2 *p. 4018 / 16: not clear what "extended model version" is.*

This section has been removed because of remark R3C1 by reviewer 3.

R4C3 *p. 4020 / 1: polynomial orders used 2-5.* This has been changed in the manuscript.

R4C4 *p. 4020 / 5: please specify instrument spectral resolution and sampling.*

The following has been included in Sect. 2: 'This instrument is equipped with an Ocean Optics USB2000+ spectrometer which has a linear CCD detector with 2048 pixels and covers a wavelength range from 400 to 600 nm. The spectral resolution is approximately 0.9 nm.'

R4C5 *p. 4020 / 6: replace the reference to QDOAS manual with the updated manual info: http://uv-vis.aeronomie.be/software/QDOAS/.*

Done.

R4C6 *p. 4020 / 9: please specify which version and temperature of Hermans abs. cross section you used.*

The temperature of the cross section used was 296 K this has been included in the manuscript. The cross section is not published in a peer-reviewed paper. The website with the data is given in the references.

R4C7 *p. 4020 / 26: I agree with the authors that the DOAS ïňĄt error does not represent the true measurement accuracy. However, I do not think that RMS of the measurements relative to one hour average is appropriate either. As authors point out NO_2 volume mixing ratios (vmr) can change on a small time scale (minutes) depending on the emission rates, transport etc. In case of changing NO_2 vmr the main source of this variability is not DOAS measurement accuracy. I would recommend, in addition to DOAS fit errors, to account for abs. cross section accuracy and uncertainty due temperature dependence of the NO_2 cross section used in DOAS fit.*

The authors agree that, if the purpose of the error estimate would be to define the best estimate for an *individual* differential slant column measurement, this procedure would give a better error estimate.

However, in the case of the MAX-DOAS profile retrieval problem for NO_2, the accuracy of individual observations may be quite high, and at the same time show significant changes within a few minutes due to changing atmospheric conditions. Sequential observations at six elevations (acquired within approximately 5-10 minutes) are used to retrieve one aerosol extinction and NO_2 profile, despite the fact that in between each individual observation the sampled air mass is changing. In addition, the viewing elevations used are sensitive to a different spatial domain, which, for conditions with high visibility, varies significantly between the viewing directions. The authors therefore think that the proposed estimate for the measurement uncertainty is more appropriate because it will generally be much larger than the measurement uncertainty estimate proposed by the reviewer. The approach described in the paper will better reflect the uncertainties needed in the light of the aerosol and NO_2 profile retrieval problem. For the use in Eq. 11 and 12 the most important aspect of the uncertainty estimate is

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to express the precision of the measurement (whereas the unknown error in the NO_2 absorption cross section affects the accuracy).

A large DOAS fit error will also increase the error estimate as described in the manuscript (Eq. 3), namely because a large uncertainty in the DOAS fit will produce a signal that varies significantly with time.

The (unknown error) in the cross section may be considered of secondary importance in the light of the study to the potential of MAX-DOAS to retrieve NO_2 profile shapes. Although the error in the cross section leads to a systematic error in the total column, it will not strongly affect the retrieval of the profile shape.

In answer to this point, the last paragraph of Sect. 2 has been changed to: 'This procedure yields a measure for uncertainty that is generally larger than if the uncertainty estimate would be based on the residual of the DOAS fit and combined with the uncertainty estimates of the NO_2 cross section and the vertical temperature profile, although the latter approach would give a more accurate uncertainty estimate for individual differential slant column observations. From the perspective of NO_2 and aerosol profile retrieval, this alternative uncertainty estimate is however not representative since it applies to an observation at one moment in time, whereas the measurements at other viewing angles are taken at another moment in time, several minutes earlier or later, thus for changed atmospheric conditions. The uncertainty estimate defined in Eq. 3 and used in Eq. 11 and 12 focuses on the precision of measurements given the variations in time.'.

R4C8 *p. 4022 / 12: please specify the initial guess values for each parameter retrieved by the inversion.*

The following is added to Sect. 3.3 : 'The initial value used for NO_2 in the first step of the algorithm (aerosol retrieval) is: N_{N1}=15×10^{15} molec cm^{-2}, H_{N1}=0.4 km. The initial aerosol extinction state is: τ_{A1}=0.5 and H_{A1}=0.4 km. In the subsequent NO_2 retrieval,

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the first guess for NO_2 is: N_{N1}=30×10^{15} molec cm^{-2} and H_{N1}=0.4 km.'

R4C9;10 combined *p. 4022 / 9, 10: choice of the upper layer height (3.5 km) and extent (0.5 km) seems rather random and unrealistic. p. 4023 /3: this paragraph states that there is no height sensitivity above 2 km (for low AOD), logically it is not clear why you proceed with the inversion algorithm that considers the second layer above 2 km. I would recommend re-parameterizing your inversion model to include 2 layers, where height, extent and abundance of both layers are retrieved (or derived from the retrieval) to make the model more realistic.*

The authors would like to emphasize that any choice made will be rather random, since little information is available about NO_2 in the free troposphere. The authors do not agree with the reviewer that it is (according to the reviewer) from a logical point of view not clear why an inversion algorithm is used that considers a second layer above 2 km, whereas it is stated that there is no height sensitivity above 2km. This reason for this is that the lack of height sensitivity does not mean a lack of sensitivity to the presence of NO_2, see Fig. 10. The lack of height sensitivity above 2 km (for cases with realistic noise levels) was the reason not to add the height of the elevated layer as a fourth free parameter. In addition, it is mentioned in the new version of the conclusions that re-parametrizing of the inversion model should focus first on the boundary layer, which should be described with three parameters. This would mean that the height of an elevated NO_2 layer would be a fifth free parameter. This parameter will, for most of the cases, be highly uncertain due to the low information content of the MAX-DOAS measurements.

In response to this comment, Sect. 3.1 has been rephrased (see below), and changes have been made in the conclusions. In addition, it is emphasized at several places in the new version of the manuscript (e.g. in the caption of Fig. 12, and in the conclusions) that NO_2 retrieved in the second layer of the two layer retrieval model should be interpreted as: NO_2 above approximately 1 km, with unknown altitude. See also the last lines in the new section 4.4, written in answer to comment R1C1.

The following has been added to Sect. 3.1: ‘This interpretation will be consistent with other retrievals based on alternative parametrizations for the free troposphere. If, for example, another vertical extent would have been chosen for the elevated layer, e.g. 2.5 instead of 0.5 km, but with the same average height (3.25 km), then retrievals will appear different in plots (see e.g. Fig. 12), but the integrated amount of NO_2 in the second layer (N_{N2}) would be approximately the same. Thus whereas the visual impact of other parametrizations can be high, in essence the changes may be mostly cosmetic. In Sect. 4.3.2 it is discussed if it is feasible to add a fourth free parameter for the average height of the elevated layer.’

The following has been added to Sect. 4.3.2: ‘This implies that for realistic situations, a-priori assumptions about the free tropospheric part of the NO_2 profile are critical. Flexible a-priori assumptions allow more accurate retrievals, but frequently with low precision. Less flexible a-priori assumptions may have a higher precision, but only for specific cases where the a-priori assumption corresponds to the real situation at the time of measurement.’

R4C11 *p. 4024 / 8: Please give more details about DAK. Please specify what layer height grid is used in the forward model, which NO_2 and O3, aerosol stratospheric profiles are used. Do you consider NO_2 and O3 cross section temperature dependence (with altitude) in the forward model calculations?*

The following has been added to Sect. 3.2: ‘The layer height grid used in the DAK radiative transfer simulations is defined as follows: 25 layers of 1 km from 0-25 km altitude, followed by 10 layers of 2.5 km vertical extent between 25 and 50 km, and finally 10 layers of 5 km between 50 and 100 km. For forward simulations additional intermediate layers were defined. For example, the S-shape parametrization was realized using 7 sub-layers. Ozone was not included in the forward simulations since the ozone layer has almost no influence on the differential slant NO_2 columns determined with the (simultaneous) zenith observation as a reference, especially at 477 nm. For NO_2 a stratospheric profile was assumed as defined by the U.S. standard mid-latitude summer profile (Anderson et al., 1986). The forward simulations accounted for the absorption cross section temperature dependence of NO_2.'.

R4C12 *p. 4025 / 21 please include standard deviation for SSA and asymmetry parameter from AERONET (2007 - 2009). Is there a seasonal dependence of these properties?*

See the changes described in answer to comment R1C6 by reviewer 1. In addition it should be noted that the seasonal dependence is very small compared to the natural variability in these parameters.

R4C13 *p. 4026 / 1: Temperature correction coefficients derived in this section scientifically make sense, however, it is not clear if they are improving the retrieval or not. The effective temperature is calculated for the two layers only based on the "scaled" US standard atmosphere profile by the surface T measurements. The actual atmosphere might be "off" by a few degrees. In addition, the elevated (even erroneously retrieved) NO_2 layer will decrease Teff. Error in the AMF in aerosol retrieval step is also non-zero. Differential NO_2 abs cross section has temperature dependence as a function of wavelength. This will produce slightly different results depending on which (several) local minima and maxima are used for diff. cross section calculation.*

According to the authors, the temperature correction shows an improvement with respect to the alternative of not applying the correction (i.e. assuming one temperature for NO_2 throughout the atmosphere, namely the fixed temperatures of the cross sections used in the DOAS fit and the radiative transfer simulations), which is the only available alternative. Since both the real temperature and the NO_2 profile should be considered unknown (except for the case when it happens to be measured with a radio sonde) the authors see no other option than to assume temperature and NO_2 profiles as described in the manuscript. This leads to a temperature correction that is consistent within the retrieval model: if the actual situation corresponds to that of the retrieval model, then the temperature correction is appropriate.

The following is added to Sect. 3.2: 'Note that the most important aspect of the temperature correction is the use of the independent observations of the surface temperature. This allows a first order temperature correction, based on an assumed vertical profile shape. The temperature correction factors are most accurate for cases where the real NO_2 profile is adequately described by the NO_2 profile parametrization in the retrieval model, and where in addition the temperature profile is comparable to the U.S. standard profile scaled with the surface temperature. The effect of an error in the temperature profile has been tested (for the same settings as in sensitivity study F), and it was found that if the temperature of the NO_2 layer at 3-3.5 km is estimated wrong by 10°C, then the error on the partial NO_2 column retrieved for this layer (N_{N2}) is about 1%. This indicates that the errors due to the assumed temperature profile shape are small compared to the uncertainties in the NO_2 profile shape. However, errors in the profile retrieval due to a wrong temperature profile assumption are generally higher than that, due to the fact that the temperature correction factors C_α^{abs} and C_α^{diff} are frequently determined for the wrong NO_2 profile shape. This effect is included in the results reported in the sensitivity studies in Sect. 4.'

R4C14 *p. 4034 / 25: please explain why an elevated layer of 0.1 km extent and 0.2 AOD was chosen.*

The following has been added to Sect. 4.3.1: 'These choices for the elevated aerosol profile are considered to be realistic for the Netherlands, where the mean total aerosol extinction optical thickness observed by the AERONET sun photometer in Cabauw (2007-2009) is 0.26±0.20 ($\lambda = 440$ nm). The vertical extent of the elevated layer (0.1 km) was considered realistic for a residual aerosol layer and in addition much less relevant than the vertical extent of aerosol layers starting at the surface.'

R4C15 *p. 4038 / 10: please list the selected days and criteria used for selection.*

The first part of Sect. 5.1 has been changed to: 'Six days (18, 23, 24, 30 June, 2 and 4 July 2009) from the CINDI campaign to illustrate the outcome of the retrieval algorithm for three parameters: aerosol optical thickness, tropospheric NO_2 columns, and average NO_2 volume mixing ratio (see Fig. 11). The last five days are 'category A' days according to Piters et al. 2011, and for this reason are most optimal for the retrieval approach which assumes cloud free conditions. In practice, such conditions occurred mostly in the mornings. It should be noted that the algorithm is applied also under cloudy conditions to illustrate the effect of such conditions on the accuracy of the retrieval (which decreases significantly, especially for the two layer retrieval model). The in-situ observations show that the five category A days have quite the same behavior in terms of the temporal evolution of the volume mixing ratio measured at the surface. June 18 is shown in addition as an example of a day with an a-typical behavior in this respect.'

R4C16 *p. 4039 / 8: why AERONET level 1.5 instead of 2 is used? Cloud screening is important for both AERONET and MAX-DOAS measurements.*

For the selected days, the level 1.5 and level 2.0 AOT data are the same. This has been changed in the manuscript.

R4C17 *p. 4039 / 19: In addition to uncertainties due to aerosol forward scattering, external stray light at small relative azimuth angles might contribute to large differences between the AERONET and MAX-DOAS AODs.*

This has been added to the manuscript.

R4C18 *p. 4040 / 7: please rephrase. The effect of clouds on radiance depends on the* *cloud optical depth.*

This section was changed.

R4C19 *p. 4040 / 29: please rephrase "strong confirmation". NO_2 radiosonde method presented in Sluis et al. (2010) is not an established technique.*

Done.

R4C20 *Figures 8, 9 11 and 12 are too small.*

Since the size of the figure partly is related to the orientation of the paper on which it is printed (which is in 'landscape' for AMTD and 'portrait' for AMT), it is decided not to change figures 11 and 12: those will automatically appear larger when printed in AMT. Since this is not the case for Fig. 8 and 9, these were changed to be less broad such that the plots themselves (and not the legend) take more space relative to the width of the page.

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