# Author's Response to Anonymous Review #2 (AMTD, 3, 2317-2366, 2010)

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## Introduction

First of all, the authors greatly acknowledge the anonymous reviewer for carefully reading the manuscript and for giving constructive comments and suggestions that have led to clear improvements.

This document contains the author's response to the comments of anonymous reviewer #2. Each comment by the reviewer is discussed separately with the following typesetting: The exact reviewer's comments are in italics (numbered C1, C2, etc.), the author's response is in roman (numbered R1, R2, etc.), and the changes in the manuscript are typesetted in bold.

## Review Comments and Authors Response

[C1] *p. 2320, l. 11: "... is about 5 to 10 km" Please point out that this number is wavelength dependent and might only be true for the wavelengths used in this paper.*

[R1] This is done in the new version of the manuscript.

- (P. 2320, L. 11) **Radiative transfer simulations at 428 nm show that the horizontal representative range is about 5 to 10 km, whereas the vertical range is about 1 to 4 km. Both ranges are wavelength dependent.**

[C2] *p 2323, l. 14: I could not find any description of the Mini MAX-DOAS instrument in Sinreich et al. (2005).*

[R2] The reference should have been Bobrowski, N., Ph.D. thesis (2005). This is corrected in the manuscript.

[C3] *p. 2327 section 2.4: Are the intensities corrected for dark current and electronic offset before the ratio is taken? Are you applying the ratio also to the zenith spectrum which is closest in time? Please describe this in the manuscript.*

[R3] The correction of spectra as described in section 2.3.1 is applied to all spectra, in preparation of both the DOAS analysis and the calculation of relative intensities. Also the zenith spectum closest in time is used as a reference in the DOAS analysis and in the ratio with the non-zenith spectra. The authors agree with the reviewer that this should be described in the manuscript. The first paragraph of section 2.4 now becomes:

- **The observation of relative intensity of skylight is another method to derive information on atmospheric constituents from the MAX-DOAS instrument. Intensity of skylight, $I$, is measured here as the MAX-DOAS detector signal, corrected for electronic-offset (see Section 2.3.1), averaged over a certain spectral interval in one viewing direction. Only relative values of intensity can be compared to their simulated counterparts, since the instrument is not radiometrically calibrated. In this work relative intensity, $I_\alpha^{\mathrm{rel}}$, refers to the ratio of the intensity in direction $\alpha$ to the intensity in the zenith direction, where the nearest (in time) zenith spectrum is used:**

[C4] *p. 2330, l. 22-24: Why a simulation excluding* $NO_2$ *is needed? The differential air mass factor can be derived by simulations at the elevation angle and at zenith direction, both including* $NO_2$*, taking their difference.*

[R4] It is not clear to the authors if the anonymous reviewer here refers to (1) the 'conventional' method – which is discussed in the line to which the reviewer refers (P.2330, L.22-24) – or (2) the method applied in this work, described in section 3.1.3 from line 25 onwards – since the reviewer's comment seems to be aimed at the method applied in this work. We have chosen to anticipate on both cases.

Case (1): In this case it must be assumed that the reviewer does not agree that in the 'conventional method' simulations including and excluding $NO_2$ are combined.

To make a clearer distinction between other methods and our method, it was decided to re-write the second paragraph of section 3.1.3, to add references, and to replace the word 'conventional' by 'traditional', in agreement with the reference (Platt and Stutz, 2008, p. 348).

- **The differential air mass factor was calculated in a way that is somewhat different from (A) the traditional method (see Platt and Stutz, 2008, p. 348), and (B) the box-AMF method (see e.g.**

**Hönninger et al., 2004 and Wagner et al., 2007), two methods that can be applied to simulations at a single wavelength. In the case of the traditional method, the AMF is derived from two radiative transfer simulations: one for an atmosphere excluding $NO_2$, and another one for an atmosphere including $NO_2$, assuming a specific vertical distribution of $NO_2$. Also in the case of the box-AMF method (B), $NO_2$ is added and removed to the simulated atmosphere, but here only in thin vertical layers, one at a time. For both (A) and (B) the differential AMF ($\Delta M_\alpha$) for an elevation is found by subtracting from its AMF ($M_\alpha$) the zenith-AMF ($M_{90^\circ}$).**

Case (2): It should be noted that the authors fully agree with the reviewer that this method is possible (only including $NO_2$), provided that more than one wavelength is used. In fact, this is precisely what is done in this work, described in section 3.1.3. There may be some ambiguity here, which may have led to the reviewer's comment, since the derivation of equation (15), but not equation (15) itself, requires reference to an atmosphere excluding $NO_2$ (the subscript $^{(0)}$ in the equations 6-12). This is described in the manuscript. For clarity the following line is added after equation (15):

- (P. 2332 L.17 ) **Note from this equation that the differential AMF is calculated only from radiative transfer simulations including $NO_2$, at three wavelengths, in contrast to the other methods mentioned at the beginning of this section, where simulations excluding $NO_2$ are needed as well but only at a single wavelength.**

[C5] *p. 2339, l. 23-25: Since the errors of the retrieval and the analysis of the 30° elevation angle values can easily explain a difference of 20% there is no significant difference. They rather agree within their errors. Also, the conclusion p. 2340, l. 1-3, is not proven in Fig. 13. Thus, the next conclusion of p. 2340, l. 4-5, is invalid, too.*

[R5] Although the authors do not agree with the reviewer that there is no significant difference, this question of the reviewer has made clear to the authors that the arguments put forward in the lines referred to by the reviewer are not written as clear-cut as intended, nor is Fig. 13 very clear at first sight.

The authors propose to rephrase section 4.2 after the first paragraph, and to replace Fig. 13 with a similar figure (Fig. 1 in this document).

Fig. 13 is changed in the following way: in order to show a plot that more clearly brings forward the main message, noise is suppressed in the new Fig. 13 by application of a one-hour running average on the differential slant column data. The red and grey lines of the original Fig. 13 are replaced by a grey band. Different colors are used.

The rephrased part of section 4.2 will is as follows:

- (p.2339 ,l. 5) **Using the geometric approximation is simple: it does not require an inversion based on radiative transfer modelling. The accuracy of this approximation has been discussed by e.g. Hönninger et al. (2004), Wittrock et al. (2004), and Pinardi et al. (2008), based on radiative transfer modelling results.**

  **Simulations with DAK show that, depending on the boundary layer aerosol load, large differences may occur between the geometrical and modelled differential air mass factors at low elevations $\alpha \leq 16^\circ$ (see Fig. 7, right plot). Therefore the GA should not be used for these elevations. For higher elevations, the difference becomes much smaller. It seems from Fig. 7 that the radiative transfer model and the GA have almost the same differential air mass factor for $30^\circ$ elevation. However, it can be seen from Fig. 12 that even for this high elevation, the difference between the GA and the model may become as large as 25%, depending on the relative position of the sun, and to a lesser extent on the AOT. At smaller relative azimuths this relative difference is even higher.**

  **The question remains whether the algorithm proposed here, using a combination of lower elevation angles, an aerosol correction and AMFs derived from radiative transfer model calculations, gives a more accurate value for the tropospheric $NO_2$ column than the GA used on the $30^\circ$ elevation measurement.**

  **Fig. 13 shows the tropospheric $NO_2$ column derived from the GA for $\alpha = 30^\circ$ (blue line), and the tropospheric $NO_2$ column and its estimated uncertainty derived with the two-step algorithm applied to $\alpha = 4^\circ$, $8^\circ$ and $16^\circ$ (grey band) for a clear-sky day. The systematic difference between the two methods for most of this day can be fully explained by the known systematic discrepancies of the GA which does not take multiple scattering, the relative azimuth and the solar zenith angle into account.**

  **This can be seen when looking at the difference between the results of the GA (blue line) and the two-step algorithm applied to $\alpha = 30^\circ$ (red line), which directly reflects the difference in AMFs (see also the red line in Fig. 12). The results of the two-step algorithm at $\alpha = 30^\circ$ is close to the results for lower elevation angles (grey band), within twice the estimated uncertainty. The larger uncertainty between 8:30 and 9:30 AM indicates an uncertain retrieval, which is probably caused by a relatively large difference between measurement conditions and one or several parameters that are assumed fixed in the model (e.g. the boundary layer height).**

**The estimated uncertainty in the tropospheric $NO_2$ column derived with the two-step algorithm is smaller than 15% for most of the day. In Section 3.3 it is shown that this uncertainty includes the effect of some major systematic and random error sources, because of the combination of the measurements at three different elevation angles.**

**It can be concluded that the uncertainty in the results of the two-step algorithm is often smaller than the known systematic discrepancies of the GA. The combination of multiple elevations enables an uncertainty estimate, based on the measurements conditions rather than on simulations, which is not possible with the GA: lower elevations than $30^\circ$ cannot be used as they have even larger systematic discrepancies, and higher elevations do not add new information since the vertical sensitivity functions (box-AMF) of those higher elevations are almost identical to $30^\circ$, i.e. they are parallel to the orange line in Fig. 8.**

[C6] *Is the difference between the retrieval of this paper and the GA dependent on the AOT? Can you please comment on that?*

[R6] The tropospheric $NO_2$ column retrieval of this paper differs from the GA in the differential air mass factors that are applied to the $NO_2$ differential slant column observations. The differential air mass factors $\Delta M_\alpha$ depend on the AOT, and therefore the difference with the GA depends on the AOT. However, this dependence on the AOT varies with the position of the sun. In Fig. 2 (in this document) the dependence of the difference in $\Delta M_\alpha$ on the AOT is shown explicitly for two positions of the sun. Since the position of the sun has a larger effect on the difference between the GA and the DAK differential air mass factors than the AOT, the authors have chosen to show the dependence on the solar position in Fig. 12 of the manuscript, for a fixed AOT. For illustration, Fig. 3 in this document shows the Fig. 12 of the manuscript for a different AOT (0.5). The following line has been changed in the manuscript:

- (P. 2339, L.15) **However, it can be seen from Fig. 12 that even for this high elevation, the difference between the GA and the model may become as large as 25%, depending on the relative position of the sun, and to a lesser extent on the AOT.**

[C7] *p. 2340, l. 16: The 1251 data points are out of how many points total?*

[R7] The total number of AERONET observations that fell within periods where the MAX-DOAS instrument was operational was 1415. This information has been added to section 4.3.

[C8] *capture Table 1: The calculation '[P(case2)-P(case1)]/P(case1) x 100%' instead of the given equation makes sense since only then you describe the deviation of case2 from case1 in %. Please change the table and the numbers in the text accordingly.*

[R8] Although this comment of the reviewer has made the authors realize that the original manuscript was not very clear at this point, they choose not to change the numbers in the table, but to improve the caption.

It is the intention of the authors that the table is read as follows: 'What is the error in the three parameters ($I_\alpha^{rel}$, $\Delta M_\alpha$ and $N_\alpha^{Tr}$) if measurement conditions for one parameter P would be as in case 2 (the others as in case 1), when a look-up table is used according to all settings as in case 1?' If the sensitivity study is interpreted in this way, then P(case 2) is the 'true' state and P(case 1) the falsely assumed state, causing the error. This interpretation is in agreement with the way the percentages are calculated in Table 1.

In order to be more precise in the text about the intention of the authors as described above, some changes have been made.

- The second paragraph of section 3.2 is removed.
- The caption of Table 1 has been written in more detail:

> **Sensitivity study of eight parameters affecting tropospheric $NO_2$ retrieval: AOT, boundary layer height for $NO_2$ and aerosols (BLH), boundary layer column of $NO_2$ (N), asymmetry parameter of aerosols (ASY), single scattering albedo of aerosols (SSA), surface albedo (ALB), and polarization (POL). Each parameter was changed in the DAK model from case 1 (reference value) to case 2, with all other parameters unchanged. For the elevations $4^\circ$, $8^\circ$ and $16^\circ$, the effect of this change is given in percent for the relative intensity ($I^{\mathrm{rel}}$), the differential air mass factor ($\Delta M$), and for the tropospheric $NO_2$ column retrieved by the two-step algorithm ($N^{Tr}$). The percentage was calculated as follows: $[P(\text{case 1})–P(\text{case 2})]/P(\text{case 2})\times100\%$, where, for each line, $P(\text{case 2})$ is the model simulation where only the quantity indicated by the first column of that line was changed to case 2, and where all other parameters were as in case 1. The values in the table therefore represent the error made when the 'true' atmosphere would be in a state with one specific parameter as in case 2, whereas this and all other parameters are assumed to be as in case 1 (which corresponds to the settings of the look-up tables described in Section 3.1.2.). Values were calculated for a solar zenith angle of $60^\circ$ and a relative azimuth of $180^\circ$.**

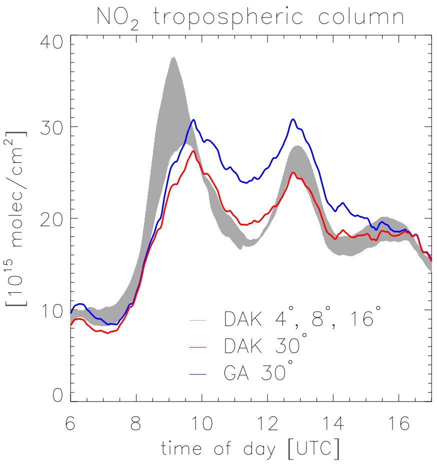

Figure 1: Alternative Fig 13. Retrieved tropospheric NO$_2$ column in De Bilt for 21 March 2009. The grey band indicates the tropospheric NO$_2$ column retrieval with the two-step algorithm, based on differential slant column measurements at $\alpha = 4°$, $8°$ and $16°$. The red line represents the two step-algorithm applied to 30°. The blue line is based on the geometrical approximation (GA), also for 30° elevation. A one-hour running average has been applied to the differential slant column data in order to suppress noise.

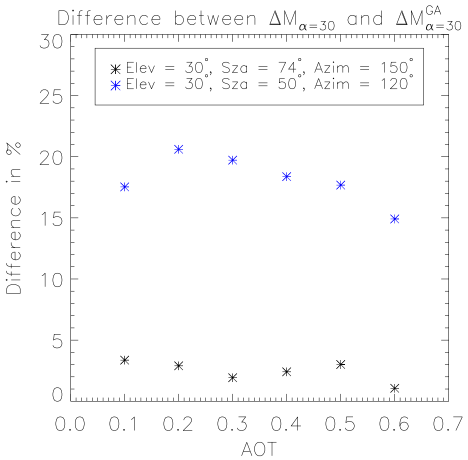

Figure 2: Difference in percent between the differential air mass factors $\Delta M_\alpha$ of the GA and the DAK model at 30° elevation as a function of the AOT for two different positions of the sun.

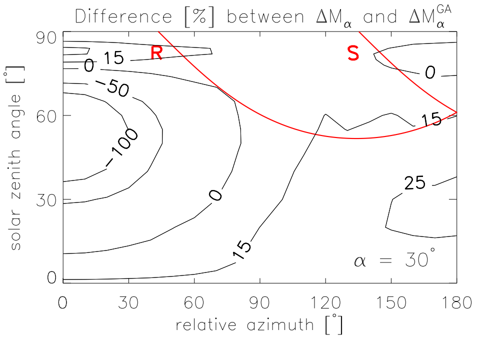

Figure 3: Same as Fig 12. in manuscript, but for AOT = 0.5.