

Abstract

Multiplexed Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) instruments can measure from the ground the absorption by nitrogen dioxide (NO₂) of scattered sunlight seen in multiple viewing directions. This paper studies the potential of this technique to derive the vertical distribution of NO₂ in the troposphere. Such profile information is essential in validation studies in which MAX-DOAS retrievals play a role.

The retrieval algorithm used is based on a pre-calculated look-up table and assumes homogeneous mixing of aerosols and NO₂ in layers extending from the surface to a variable height. Two retrieval models are compared: one including and one excluding an elevated NO₂ layer at a fixed altitude in the free troposphere. An ensemble technique is applied to derive retrieved model uncertainties.

Sensitivity studies demonstrate that MAX-DOAS based retrievals can make a distinction between an NO₂ layer that extends from the surface to a certain height (having a constant mixing ratio, or a mixing ratio that decreases with altitude) and an elevated NO₂ layer. The height of the elevated NO₂ layer can only be retrieved accurately when the aerosol extinction profile is known and the measurement noise is low. The uncertainty in this elevated NO₂ layer height provides the main source of uncertainty in the retrieval of the free tropospheric contribution to the tropospheric NO₂ column.

A comparison was performed with independent data, based on observations done at the CINDI campaign, held in the Netherlands in 2009. Comparison with lidar partial tropospheric NO₂ columns showed a correlation of 0.78, and an average difference of 0.1×10^{15} molec cm⁻². The diurnal evolution of the NO₂ volume mixing ratio measured by in-situ monitors at the surface and averaged over five days with cloud-free mornings, compares quite well to the MAX-DOAS retrieval: a correlation was found of 0.8, and an average difference of 0.2 ppb.

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1 Introduction

1.1 Background and motivation

Nitrogen dioxide (NO_2) is an atmospheric constituent worth monitoring for several reasons: it is an indicator for high temperature combustion processes (traffic, power plants), and therefore an indicator of air pollution caused by anthropogenic activities; it plays an important role in atmospheric chemistry, both in the stratosphere (ozone destruction), and in the troposphere (ozone formation), see Crutzen (1970); it is involved in aerosol formation (Chan et al., 2010), and therefore indirectly affects the global radiation budget (Shindell et al., 2009).

NO_2 is monitored worldwide in national observation networks of in-situ monitors (mostly $\text{NO}_x = \text{NO} + \text{NO}_2$), often both in urban and in rural regions. Since the last decade, NO_2 is also monitored from space (total, stratospheric and tropospheric NO_2 columns) by satellite instruments, namely GOME (Richter and Burrows, 2002), SCIAMACHY (Blond et al., 2007), OMI (Boersma et al., 2007) and GOME-2 (Richter et al., 2011). Whereas in-situ measurements have the advantage of being specific to the air that is inhaled by humans, space borne observations have the advantage of observing not only NO_2 at the surface, but the entire vertical NO_2 column. Although the first quantity is more directly related to the effect of NO_2 on human health, the second quantity is more relevant for studies of transport and trends in NO_2 abundances (Richter et al., 2005; van der A et al., 2008). Observations from space have the additional advantage of global coverage (depending on the satellite orbit) with only a single instrument, making studies of regional transport and trend studies of NO_2 abundances much less dependent on instrumental and calibration differences between national in-situ monitoring networks.

Validation of tropospheric NO_2 column observations from space is challenging as it demands a measurement technique that is sensitive to the same spatial domain (vertical and horizontal) as the satellite observation (Brinksma et al., 2008; Hains et al., 2010). This requirement makes a comparison with in-situ surface observations

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problematic: surface observations in principle apply solely to one location at the surface, and can only be extended into the vertical (e.g. a boundary layer column) if information on the boundary layer height is available from other measurement techniques and if an NO₂ profile shape is assumed within the boundary layer (e.g. homogeneous mixing), see Boersma et al. (2009). The NO₂ profile shape is not routinely monitored. A new development which would enable this in the future is the monitoring of NO₂ from radiosondes (Sluis et al., 2010). This technique is currently under development and is not as well established nor as widely used as that for e.g. ozone.

Another candidate for validation of tropospheric NO₂ columns derived from space borne observations is the MAX-DOAS technique which is based on spectral analysis of scattered sunlight (UV/VIS) measured from the surface at multiple angles in the vertical plane (elevations), see e.g. Hoenninger et al. (2004) and Wittrock et al. (2004). MAX-DOAS instruments can be used to retrieve many trace gases and aerosols (Irie et al., 2011), are relatively low-cost, can run autonomously and therefore are a suitable candidate for global monitoring networks. MAX-DOAS observations can be used to derive tropospheric NO₂ columns by using multiple elevations (e.g. Pikel'naya et al., 2007; Irie et al., 2008b and Vlemmix et al., 2010), and its zenith sky measurements can be used for stratospheric NO₂ retrieval (Pommereau and Goutail, 1988 and Vandaele et al., 2005).

This paper describes the development of a retrieval algorithm to derive the tropospheric NO₂ profile from MAX-DOAS measurements. This is not only relevant to enhance the accuracy of the MAX-DOAS tropospheric NO₂ column retrieval, but also to improve the comparison with satellite retrievals for which the unknown vertical distribution of NO₂ is one of the main sources of uncertainty (Boersma et al., 2004). Since it is well known that MAX-DOAS NO₂ measurements have a strong dependence on the aerosol extinction profile (Wagner et al., 2004; Friess et al., 2006), the retrieval algorithm is designed to simultaneously retrieve an aerosol extinction and an NO₂ profile.

1.2 Profile retrievals with MAX-DOAS

The retrieval of vertical profiles of aerosols and trace gases from ground based MAX-DOAS observations is a typical example of an ill-posed inversion problem: a problem where the information contained in the observations is too limited to identify a unique solution, which – in this application – would be a vertical profile defined at some vertical resolution. The profiling potential of MAX-DOAS observations comes from the differences in the vertical sensitivity of the different viewing elevations. The information content of the MAX-DOAS observations is however limited due to the fact that the vertical sensitivity functions for different elevations (i) all peak at the same altitude, namely the surface, (ii) are relatively broad, and (iii) decrease with altitude in a mutual similar manner (see Fig. 1 and Sect. 3.1). The sensitivity functions are thus by no means orthogonal with respect to one another, especially above 1–2 km (depending on the aerosol extinction in the boundary layer).

As a consequence, the potential of any profile retrieval algorithm based (solely) on MAX-DOAS observations is limited to only a few (2–5) degrees of freedom to describe the vertical distribution of aerosols or trace gases (see e.g. Friess et al., 2006 and Clemer et al., 2010). Despite this limitation, it is important to derive such “profiles”, since any additional profile information could improve both the retrieval accuracy of the tropospheric columns and the validity of inter-comparisons with other measurement techniques such as space-borne observations and lidar.

Until now, several approaches have been reported in the literature, describing retrieval algorithms to derive aerosol and/or NO₂ profile information from MAX-DOAS observations. Some of them have their strength in relative simplicity (e.g. Sinreich et al., 2005; Li et al., 2010). Others (e.g. Friess et al., 2006; Irie et al., 2008a; Clemer et al., 2010) are based on the more sophisticated optimal estimation formalism described in Rodgers (2000). Retrieval algorithms designed according to the optimal estimation method not only find solutions (e.g. vertical profiles), but distinguish themselves by the diagnostic information that accompanies this solution (averaging kernel,

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error estimates). Those diagnostics are important in many contexts: validation, assimilation, using the data to derive climatologies, and so on.

Here we use the following approach: a simple profile parameterization that gives a first order description of typical vertical distributions of aerosols and NO₂, namely well mixed layers starting at the surface, with possibly an additional elevated layer. Because of the low number of independent pieces of information contained in the MAX-DOAS measurements, such a conservative approach is expected to be less sensitive to unrealistic solutions, e.g. strong oscillations in the retrieved profile, than a retrieval based on many vertical layers.

Our approach builds on the method described in Li et al. (2010). Their MAX-DOAS retrieval of aerosol extinction profiles is based on simple aerosol block-profile parameterizations and a least-squares minimization strategy, and showed good agreement with surface aerosol extinction measurements performed in China. We propose to extend this approach to a combined aerosol and NO₂ retrieval (similar to e.g. Sinreich et al., 2005). We study the feasibility of retrieving aerosols and NO₂ at higher altitudes by testing an extended model version. Additional diagnostic information (error estimate, goodness of fit) is determined using an ensemble technique that is described in Sect. 3.3.

1.3 Content of this paper

This paper starts with a brief introduction to the MAX-DOAS measurement technique (Sect. 2). Subsequently, the development of the retrieval algorithm is described (Sect. 3): a motivation for the design of the conceptual retrieval model (selection of free parameters), a description of forward radiative transfer simulations, the inversion procedure, and finally the method used to determine retrieval uncertainties.

In Sect. 4, the retrieval algorithm is tested in six sensitivity studies. The first tests the accuracy and systematic biases of the NO₂ retrieval for different noise levels, if the profile shape is the same as assumed in the retrieval model. In the second study the same is done for the aerosol retrieval. The third and fourth sensitivity study examine

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the effect of aerosol and NO₂ distributions in the boundary layer that are different than assumed in the retrieval model. The last two sensitivity studies test how sensitive the retrieval is for elevated aerosols and elevated NO₂ layers up to the stratosphere.

Section 5 describes the application of the retrieval algorithm to observations done at the Cabauw Intercomparison of Nitrogen Dioxide measuring Instruments campaign (CINDI) held in the Netherlands in 2009. The simultaneously performed lidar observations provide a good opportunity to test the successfulness and limitations of the retrieval algorithm in practice.

2 MAX-DOAS measurements and uncertainties

The MAX-DOAS measurement technique has been described in detail in e.g. Hoeningner et al. (2004) and Wittrock et al. (2004) and will be described here only shortly.

Ground based MAX-DOAS observations consist of spectral UV and/or VIS observations of scattered sunlight at various elevations α within the vertical plane. The raw measurements of MAX-DOAS instruments have a relatively high spectral resolution (typically well below 1 nm). After the raw spectra are corrected for electronic effects (e.g. as described in Vlemmix et al., 2010), the DOAS method (Platt and Stutz, 2008) is applied to the corrected spectra $I(\lambda)$ in order to derive “differential slant columns” ΔN^S (S refers to “slant”) for the various absorbers present in the spectral window of interest.

The essence of the DOAS approach lies in the separation of fine scale spectral differential absorption structures $\Delta\sigma_i(\lambda)$ – that uniquely characterize absorbers – from broad band absorption and scattering effects (Rayleigh and Mie scattering, and broad band part of trace gas absorption cross sections). The differential slant column of each of the n trace gases in the selected spectral window is found using the DOAS equation:

$$\ln \left[\frac{I(\lambda)}{I_{\text{ref}}(\lambda)} \right] = - \sum_{i=1}^n \Delta\sigma_i(\lambda) \Delta N_i^S + P(\lambda), \quad (1)$$

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interpolation between the times of measurement. Subsequently a one-hour running average ($\Delta T = 1$ hr) is applied to the measurements, yielding $\Delta \bar{N}_\alpha^S(t)$. Variations of the raw measurements with respect to these averaged measurements are used to determine the RMS.

$$\epsilon_\alpha(t) = \sqrt{\frac{1}{\Delta T} \int_{t-\frac{\Delta T}{2}}^{t+\frac{\Delta T}{2}} \left[\Delta N_\alpha^S(t) - \Delta \bar{N}_\alpha^S(t) \right]^2 dt} \quad (3)$$

This procedure yields a measure for uncertainty that is generally larger than if uncertainties were based on the residual of the DOAS fit of the measurements, which is merely an estimate of the quality of the individual measurements. We think however, that these uncertainties based on the DOAS fit are an underestimation of the real uncertainties, which are also affected by e.g. temporal variations on a time scale of minutes to tens of minutes in the aerosol and NO_2 fields. Those changes are not measured simultaneously at the different elevations, due to the sequential observation method. As the retrieval model assumes one atmospheric state corresponding to the measurements at the different elevations, which will be a mixture of the – slightly changed – states observed sequentially at the different elevations, the effect of non-simultaneous observations is to be included in the uncertainty and therefore effectively captured in the above described procedure to determine the measurement uncertainty.

3 Retrieval algorithm

In this section a description will be given of the retrieval method that has been developed. First the conceptual atmospheric model used in the retrieval will be introduced and the choice of model parameters motivated. Then the simulation method of measurements with the forward model will be described. Subsequently the inversion method is outlined, followed by a description of the uncertainty estimates.

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3.1 Retrieval model

The retrieval algorithm is based on a conceptual atmospheric model (see Fig. 2) consisting of:

- Lower NO₂ layer, indicated by N1: from the surface to height H_{N1} with partial NO₂ column N_{N1} and constant volume mixing ratio in the layer,
- Lower aerosol layer, indicated by A1: a layer from the surface to height H_{A1} with partial aerosol optical thickness τ_{A1} and constant extinction coefficient in the layer,
- Upper NO₂ layer (optional), indicated by N2: from 3.0 to 3.5 km altitude containing partial NO₂ column N_{N2}
- Upper aerosol layer (optional), indicated by A2: from 3.0 to 3.5 km altitude with partial aerosol optical thickness τ_{A2} .

The two upper layers are optional: in Sect. 4 we will assess the use of the two optional upper layers by studying the behavior of the retrieval algorithm including and excluding each of the two layers. The retrieval algorithm thus has 2 or 3 free parameters describing the aerosol extinction profile, and 2 or 3 free parameters describing the NO₂ profile.

The choice for this parameterization, or conceptual model, is based on (1) the fact that tropospheric NO₂ is most often found in the boundary layer, especially in the vicinity of pollution sources, but may also be present higher up in the free troposphere, and (2) on the specific altitude dependent sensitivities to NO₂ of the MAX-DOAS technique, as shown in Fig. 1.

This figure shows the elevation- and altitude-dependent differential air mass factors of NO₂, which may be interpreted as the vertical sensitivity to NO₂ of the MAX-DOAS measurements at different elevations (see also Sect. 3.2.2). Our interpretation of this figure is that the potential of MAX-DOAS to discriminate between NO₂ at different altitudes is limited to roughly the lowest kilometer of the atmosphere (depending on the

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aerosol extinction profile), and for this reason we parameterized our profile with a lower NO_2 layer (N1) with variable height.

Above this altitude of approximately 1 km, the sensitivity functions of the different elevations are practically parallel and therefore contain almost no independent pieces of information from which to determine the altitude of a second NO_2 layer. We therefore decided to locate the second “free tropospheric” model layer, quite arbitrarily, at 3–3.5 km altitude, i.e. somewhere in the range where the sensitivity functions are parallel. It should be noted here that the sensitivity functions already indicate that it is very difficult to determine the actual height of an elevated NO_2 layer above a certain height (approximately 2 km for low AOT, and approximately 1 km for a high AOT, see Fig. 1). As a consequence, one should be careful to interpret NO_2 retrieved in the second layer as a free tropospheric NO_2 . If, for example, the true NO_2 layer would extend from 0 to 2 km, then it is conceivable, especially for high AOT, that the retrieval algorithm would put part of the NO_2 in N2, NO_2 that is in reality located in the highest part of N1. The second NO_2 layer could therefore also be described as “the partial NO_2 column above approximately 1 km, with unknown altitude”. See also Sect. 4.3.2.

Although the argumentation based on height-dependent sensitivity to NO_2 does not equally apply to aerosols – the altitude of which may be expected to have a more noticeable effect on O_4 measurements – it was chosen to put a second aerosol layer at the same fixed altitude, and to study the effect of this choice in the sensitivity study.

In order to separate the different versions of the retrieval model, we use the following names: M_{1a}^{1n} for the basic model with only the layers A1 and N1, M_{1a}^{2n} for the model including also the second NO_2 layer N2, and M_{2a}^{1n} for the model with one NO_2 layer and two aerosol layers. The latter model is only used in sensitivity study E (Sect. 4.3.1). Based on the conclusion of sensitivity study E, it was decided not to use the models M_{2a}^{1n} and M_{2a}^{2n} in the application to real measurements.

Apart from the six primary retrieval parameters, described above, there are four other ‘derived’ parameters that will frequently be referred to in this work:

- total tropospheric NO_2 column: $N_{Tr} = N_{N1} + N_{N2}$

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- total AOT: $\tau_{\text{tot}} = \tau_{A1} + \tau_{A2}$
- average aerosol extinction of A1: $k_{A1} = \tau_{A1}/H_{A1}$ [km^{-1}]
- average NO_2 volume mixing ratio within N1: X_{N1} [ppb], derived from N_{N1} and H_{N1}

The calculation of the average NO_2 volume mixing ratio depends on the temperature and pressure profile for which we use US standard profile shapes scaled with the surface temperature and pressure at the time of the measurement.

3.2 Forward modeling

The multiple scattering radiative transfer model DAK (Doubling-Adding KNMI, see De Haan et al., 1987, Stammes et al., 1989, and Stammes, 2001) was used to simulate measurements corresponding to model states. There are three types of simulated measurements contained in the look-up tables (see Sect. 3.2.1): differential slant NO_2 columns, differential slant O_4 columns, and relative intensities, for which we use the symbols $\Delta N^{S,\text{NO}_2}$, $\Delta N^{S,\text{O}_4}$, and I^{rel} respectively (S refers to slant). The slant columns of absorber a (either NO_2 or O_4) for elevation α are simulated for a single wavelength according to:

$$N_{\alpha}^{S,\text{abs}} = -\frac{\ln\left(\frac{I_{\alpha}^{\text{abs}}}{I_{\alpha}^0}\right)}{\sigma_{\text{abs}}}, \quad (4)$$

where I_{α}^0 is the simulated sky radiance without the absorber and I_{α}^{abs} is the simulated sky radiance with the absorber. σ_{abs} denotes the absorption cross section of the absorber of interest. The *differential* slant column is subsequently calculated according to:

$$\Delta N_{\alpha}^{S,\text{abs}} = N_{\alpha}^{S,\text{abs}} - N_{90^{\circ}}^{S,\text{abs}}. \quad (5)$$

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Relative intensities are defined as:

$$I_{\alpha}^{\text{rel}} = \frac{I_{\alpha}}{I_{90^{\circ}}}. \quad (6)$$

3.2.1 Look-up tables

Look-up tables of differential slant NO₂ columns, differential slant O₄ columns and relative intensities were generated for each value of the parameters in Table 1. The number of values of each parameter is limited, often because of practical limitations of disk storage and computation time. Given these limitations, it is essential to use a non-equidistant grid for several parameters, such as the height of the NO₂ and aerosol layers, the aerosol optical thickness, the elevation and solar zenith angle.

Simulations are performed for a single wavelength: 477 nm. This wavelength falls within the absorption spectrum of NO₂, but was primarily selected because it coincides with a local maximum of the absorption cross section of O₄.

The disadvantage of the choice for a single wavelength is that the wavelength dependence of the air mass factor, within the spectral window that is used for the DOAS analysis of the measurements, is not taken into account. However, since (a) the variation of the air mass factor within the fitting window (425–490 nm) is relatively small (<2%), and (b) the selected wavelength is not on one of the extremes of the fitting window, errors introduced by using single wavelength simulations are small compared to other sources of uncertainty.

The value of the single scattering albedo and asymmetry parameter of aerosols, namely 0.90 and 0.72 respectively, are also fixed. The choice for the values is based on an average of AERONET observations in Cabauw (the Netherlands) on blue sky days throughout the years 2007–2009.

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3.2.2 Temperature effects

Absorption of sunlight by NO₂ and O₄ is temperature dependent (see e.g. Vandaele et al., 1998 and Greenblatt et al., 1990). For NO₂ this is a consequence of the temperature dependency of the absorption cross section, for O₄ it is due to the relation between temperature (and pressure) and the number density of (oxygen) molecules, as described by the ideal gas law, and to the temperature dependence of the absorption cross section of O₄ itself. Since measurements and simulations of the differential slant column densities are combined in the cost function of the retrieval algorithm (see Sect. 3.3), it is important to have a consistent approach that accounts for temperature effects on both. The temperature correction applied in this work is different for NO₂ and O₄ as will be described below.

The correction for NO₂ consists of two parts: firstly to determine the effective NO₂ temperature, and secondly to derive two correction factors: one for the simulations and one for the measurements, see below. The effective NO₂ temperature is calculated as follows:

$$T_{\alpha}^{\text{eff}}(\Psi) = \sum_{i=1}^2 \frac{T^i \Delta m_{\alpha}^i(\Psi) N_{Ni}}{\Delta m_{\alpha}^i(\Psi) N_{Ni}}, \quad (7)$$

where $i = 1$ corresponds to the lowest NO₂ layer, and $i = 2$ to the second NO₂ layer. Ψ refers to the dependency on the model parameters H_{N1} , H_{A1} , τ_{A1} and τ_{A2} and to the position of the sun relative to the instrument viewing direction. N_{Ni} is the partial vertical NO₂ column, and T^i the (average) layer temperature. $\Delta m_{\alpha}^i(\Psi)$ denotes the elevation and height-dependent differential air mass factor (elevation dependent vertical sensitivity to NO₂) which was calculated according to:

$$\Delta m_{\alpha}^i(\Psi) = \frac{\Delta N_{\alpha}^{S, \text{NO}_2, i+}(\Psi) - \Delta N_{\alpha}^{S, \text{NO}_2, \text{ref}}(\Psi)}{N^{V, i+} - N^{V, \text{ref}}}, \quad (8)$$

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As noted above, the absorption due to O_4 is dependent on the temperature and pressure profiles. We accounted for this effect by using the observed surface temperature and pressure at the time and location of the MAX-DOAS observation as input in the retrieval algorithm. The look-up table simulations are performed for two surface temperatures and pressures with which a US standard mid-latitude summer temperature and pressure profile is scaled. Linear interpolation is applied between those surface temperatures and pressures to obtain the simulated O_4 measurements.

3.3 Inversion

The inversion step of the retrieval algorithm (Fig. 3) is based on two successive least-squares minimizations: first the aerosol parameters are retrieved and then the NO_2 parameters. As the aerosol retrieval is not completely independent of the NO_2 retrieval, due to the broad band absorption by NO_2 , which is more pronounced at small elevations, an iteration is performed after the first retrieval, where an improved guess of the NO_2 profile is used in the aerosol retrieval.

The cost functions that are minimized, are:

$$\chi_{\text{aero}}^2 = \sum_{i=1}^5 \left(\frac{f_{sc} \cdot \Delta N_{\alpha_i}^{S,O_4} - \widehat{\Delta N_{\alpha_i}^{S,O_4}}}{\epsilon_{\alpha_i}^{O_4}} \right)^2 + \left[\left(\frac{I_{\alpha_i}^{\text{rel}} - \widehat{I_{\alpha_i}^{\text{rel}}}}{\epsilon_{\alpha_i}^{\text{rel}}} \right)^2 \right]_{\text{optional}}, \quad (11)$$

and

$$\chi_{NO_2}^2 = \sum_{i=1}^5 \left(\frac{C_{\alpha_i}^{\text{diff}} \cdot \Delta N_{\alpha_i}^{S,NO_2} - C_{\alpha_i}^{\text{abs}} \cdot \widehat{\Delta N_{\alpha_i}^{S,NO_2}}}{\epsilon_{\alpha_i}^{NO_2}} \right)^2, \quad (12)$$

where ϵ denotes the measurement uncertainty, see Sect. 2. The index i is used to number the viewing elevations: $\alpha_i = \{2^\circ, 4^\circ, 8^\circ, 16^\circ, 30^\circ\}$. Simulated measurements are indicated with a hat. f_{sc} is an empirically determined scaling factor (see below).

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The added value of relative intensities, the second part of the aerosol cost function, is studied in Sect. 4.

The numerical minimization process of the two cost functions is performed with the Nelder-Mead method, also known as downhill simplex method (Nelder and Mead, 1965). This algorithm is fast and does not require derivatives. Each iteration of this algorithm requires a multidimensional linear interpolation within the domain of the look-up table in order to calculate simulated measurements corresponding to a certain model state.

The empirical scaling factor f_{sc} was first reported by Clemer et al. (2010), also used in Zieger et al. (2011), and found to have the approximate value of 0.8. Clemer et al. found that measured differential slant O_4 columns had such high values that they could not be simulated with their model. This difference could not be due to aerosols, since the measurements were done for conditions with low aerosol optical thickness (AOT < 0.1) whereas aerosols generally decrease the differential slant O_4 columns. We did a similar study as Clemer et al., using a different radiative transfer model and instrument, and found the same result. The origin of the discrepancy is still unknown.

An important aspect of our retrieval algorithm is the use of multiple runs (200) of the inversion to create an ensemble of retrieval outcomes. In each new run, we provide the inversion algorithm with a slightly different set of measurements (NO_2 and O_4 differential slant columns, each at five elevations) that are created from the original set of measurements but changed within their estimated uncertainty range using artificially generated Gaussian noise. For each elevation and for each parameter different noise perturbations are generated anew for every run. The final aerosol and NO_2 solutions, after 200 steps, are defined by the average aerosol and NO_2 model parameters within the ensemble of retrieval outcomes. The uncertainty range of each model parameter, and each derived parameter (e.g. a sum or ratio of model parameters) is determined from the lower and upper boundaries of the middle 90 % of the retrieval ensemble for that derived parameter, i.e. the extreme values on each side of the distribution are discarded.

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A slightly different procedure is followed for the NO₂ volume mixing ratio to prevent the retrieval from strong overestimation in the presence of high levels of noise. Such a correction is needed because the volume mixing ratio X_{N1} is proportional to the reciprocal of the layer height H_{N1} . Whereas high noise levels lead to potentially larger deviations among the 200 retrievals from the true value of H_{N1} , it does not strongly affect the ensemble average of H_{N1} retrievals. However, when converted to volume mixing ratio, the inverse relationship breaks up the symmetrical distribution: for an equal (but opposite) over- and underestimation in H_{N1} with respect to the true value, the corresponding under- and overestimation in X_{N1} will not be equally far from the true value (see Fig. 5). For high noise levels there are relatively many retrievals of H_{N1} that are far too low, leading to sometimes extreme overestimation of X_{N1} , which significantly increases the ensemble average.

In order to avoid this unwanted effect, we have adapted the procedure to calculate the ensemble average of X_{N1} . Instead of including the outcomes of the middle 90 % of the 200 runs within the ensemble, a selection criterion on H_{N1} is applied to exclude extremes: only retrievals where H_{N1} deviates less than 50 % from the the ensemble average of H_{N1} (based on 200 runs) are included in the ensemble for which the average and uncertainty of X_{N1} is determined. The first retrieval of H_{N1} in Fig. 5 is relatively accurate, with only a few deviations larger than 50 %, whereas the second retrieval is less accurate. Applying the same procedure to both ensembles results in a small change of the NO₂ volume mixing ratio in the first case (−5 %), and a relatively large change in the second case (−25 %), as indicated by shift from the black to the red horizontal lines. Note the logarithmic scale on the vertical axis of the NO₂ concentration plots.

An advantage of the ensemble based procedure is that it takes into account the propagation of the uncertainty in the aerosol retrieval to the uncertainty in the NO₂ retrieval in a natural manner, because each of the 200 individual NO₂ retrievals follows a different aerosol retrieval. Another benefit is that the same method to determine the uncertainty can be used for normal and derived parameters (Sect. 3.1). Each derived

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parameter is determined from two “normal” parameters. Because normal parameters are not fully independent, their uncertainties cannot simply be combined according to standard rules for error calculation applicable to independent parameters. For example: the two partial NO₂ columns in the double NO₂ layer retrieval model (N_{N1} and N_{N2}) may both have relatively large uncertainty, whereas their sum (N_{Tr}) is less uncertain.

A third advantage of the ensemble approach is that it yields a distribution of χ^2 values for both the aerosol and for NO₂ retrieval. Values of χ^2 obtained for individual runs cannot be used to judge the appropriateness of the retrieval model, because measurement uncertainty may lead to sometimes high χ^2 values, even for an appropriate model. However, the ensemble median of the reduced χ^2 ($\chi_{v,\text{median}}^2$), based on 200 runs, is a more reliable quantity from which to judge the appropriateness of the retrieval model. Note that “reduced”, denoted with v , here refers to a correction for the number of degrees of freedom, i.e. a division by the number of independent observations (differential slant columns at five elevations) minus the number of model parameters (two or three, depending on the model version).

If the value of $\chi_{v,\text{median}}^2$ within the ensemble is much larger than 1, then it is likely that the retrieval model is not appropriate. This would be the case, for example, if there was mostly free tropospheric NO₂ present when measurements were made, and retrieval model M_{1a}^{1n} without the second NO₂ layer would be used. The relation between the appropriateness of the model and the value of $\chi_{v,\text{median}}^2$ is illustrated in the next section. For simplicity we will use the notation $\chi_{\text{NO}_2}^2$ or χ_{aer}^2 in the remainder of this work, meaning $\chi_{v,\text{median},\text{NO}_2}^2$ and $\chi_{v,\text{median},\text{aerosol}}^2$, respectively.

4 Sensitivity study

In this section we test the behavior of the algorithm in six situations (indicated with the capitals A–F), see Fig. 6 and Table 2. Firstly, the algorithm is tested with simulated measurements that are calculated for atmospheric states that exactly match the model,

which would be large for the highest noise levels if the correction that is discussed in Sect. 3.3 would not have been applied.

The effect of noise (measurement uncertainty) is somewhat more complicated in the two NO₂ layer model (2nd row of Fig. 7). Higher noise levels not only lead to larger overestimation of the NO₂ volume mixing ratio than in the single layer model, but also to a false distribution of the NO₂ between the two layers: elevated NO₂ is retrieved in N2, although the true NO₂ profile in the sensitivity study does not include NO₂ above the BL. This leads to small overestimation of the tropospheric NO₂ column up to 15%. The effect of noise on the retrieval may explain the sometimes high values of N2 seen in the retrievals based on CINDI observations, as seen in e.g. Fig. 12 (Sect. 5.1).

A similar study was done to test the sensitivity of the aerosol layer height to noise (sensitivity study B). This effect is generally small (<5%). Only the highest noise level included in the study (15%) leads to potentially large overestimation of H_{A1} (>50%), especially for low aerosol layer heights (<0.5 km).

4.2 Inhomogeneous distribution in boundary layer

One of the assumptions of the retrieval model is that aerosols and NO₂ are homogeneously mixed in the two model layers A1 and N1. This may however not be the case in reality. We therefore test the effect of the assumption of homogeneity by simulating measurements for such cases where the aerosol or NO₂ distribution is not homogeneous. In order to simulate these measurements, we used the shape parameter S (see Fig. 6) to parameterize a set of boundary layer profile shapes for either aerosol extinction or NO₂ concentration. In each simulation of the sensitivity studies C and D, the total amount of NO₂ and aerosols is kept constant, a height of 0.5 km was used for both profiles, and the S -parameterization was only used for one of the two profiles (homogeneous mixing was used for the other).

Figure 8 shows the effect of the different profile shapes for aerosols (top row) and NO₂ (bottom row) on five selected retrieval parameters, H_{A1} , H_{N1} , k_{A1} , X_{N1} , N_{Tr} , and on $\chi_{NO_2}^2$. For both constituents, it can be seen that values of $S < 1$ lead to an

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overestimation, and $S > 1$ leads to an underestimation of the retrieved layer height. For $S > 1$, this leads to relatively small differences with the “surface” extinction in the aerosol study and “surface” X_{N_1} in the NO₂ study. For $S < 1$ the deviation is large, due to the inappropriateness of the retrieval model for such profile shapes: $S = 0$ describes a profile shape that could better be described by an elevated layer between approximately 0.25 and 0.5 km than by a layer extending from the surface.

Although values of $S < 1$ lead to unrealistic surface volume mixing ratios, the effect on the retrieval of the tropospheric NO₂ column is much smaller, and somewhat different for the single and double NO₂ layer models. In the case of low S -values for aerosols, the double NO₂ layer model retrieves part of the NO₂ in the second layer, leading to a small overestimation of the total tropospheric column, not only compared to the truth, but also with respect to the single layer model.

The last column of Fig. 8 shows the effect of the different S -values on $\chi_{NO_2}^2$. High values for $\chi_{NO_2}^2$ coincide with small inaccuracies in the retrieval of the tropospheric NO₂ column, and with large errors of the surface NO₂ volume mixing ratio.

4.3 Elevated layers

4.3.1 Elevated aerosols

The study for elevated aerosol layers (sensitivity study E) has three purposes: (i) to quantify inaccuracies in the NO₂ retrieval due to elevated aerosol layers, if the retrieval would be based on O₄ measurements and a single aerosol layer model, (ii) to see if the NO₂ retrieval improves if a second aerosol layer, at a fixed altitude, is included in the retrieval model, and (iii) to assess if the addition of relative intensity measurements to the aerosol cost function leads to further improvements.

The simulated atmosphere here consists of an elevated aerosol layer – with a vertical extent of 0.1 km and with partial AOT of 0.2 – placed at different heights. In addition there is a low aerosol layer: a block profile extending from the surface, with a height of

accurately be retrieved. Please note that this aerosol profile retrieval, is only possible under cloud free conditions. From the perspective of NO_2 profile retrieval it is therefore better not to include relative intensities in the cost function, and therefore not to use the second aerosol layer with a fixed altitude: there is no positive effect on the tropospheric NO_2 column retrieval, a decrease of accuracy in the average X_{N1} for high aerosol layers and under cloudy conditions, and only a small improvement in this retrieval parameter for low aerosol layers. For this reason, both retrieval model versions M_{2a}^{1n} and M_{2a}^{2n} will not be used in the application to real observations performed during the CINDI campaign (Sect. 5).

4.3.2 Elevated NO_2

In this section the effectiveness will be tested of the separation between high and low NO_2 in the double NO_2 layer retrieval model. Is NO_2 – that in the simulations is located in elevated layers – actually retrieved in the second model layer?

The simulated atmosphere here consists of an elevated NO_2 layer with a vertical extent of 0.1 km and with a partial NO_2 column of 1×10^{16} molec cm^{-2} placed at different heights. The aerosol profile is fixed in this study: a block profile with a height of 0.6 km and $\text{AOT} = 0.2$, see also Fig. 6. The results of this sensitivity study are shown in Fig. 10.

The one NO_2 layer model underestimates NO_2 already by more than 30% if it is located at 1 km, and this underestimation rapidly decreases with altitude. The two NO_2 layer model is clearly more sensitive to elevated NO_2 , underestimating the partial column only > 3 km and even overestimating if it is below < 3 km (due to the choice to locate the second NO_2 layer between 3 and 3.5 km in the model). Note that relatively high overestimation (up to 40% of the tropospheric NO_2 column) only applies to that part of the total tropospheric NO_2 column that is actually found in an elevated layer; in this study no NO_2 was located near the surface.

If the second NO_2 layer in the retrieval model would have been put at a higher fixed altitude, then there would be an overestimation up to that altitude, if it would have

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been put lower, then the underestimation would have started already from that altitude onwards. It could therefore be preferable to use the measurements to retrieve the height of the second NO₂ layer, instead of having it at a fixed altitude, and thus to add another degree of freedom to the retrieval model. The right hand side plot of Fig. 10 – showing the behaviour of $\chi_{\text{NO}_2}^2$ as a function of the height of the elevated NO₂ layer – indicates that this may be possible for measurements with a high measurement accuracy.

It is interesting to note that the retrieval of the partial and total NO₂ columns (left plot of Fig. 10) not strongly depends on noise, for both the retrieval models M_{1a}^{1n} and M_{1a}^{2n} . However, the $\chi_{\text{NO}_2}^2$ values show a much stronger dependence. The lower absolute values of $\chi_{\text{NO}_2}^2$ for higher noise are due to the fact that higher noise in our algorithm corresponds to higher values of the measurement uncertainty ϵ , which leads to lower values of $\chi_{\text{NO}_2}^2$, see Eq. (12).

Not only the absolute level of the $\chi_{\text{NO}_2}^2$ curves changes as a result from noise, but, more interestingly, also the shape. Especially for the two NO₂ layer model (M_{1a}^{2n}) it is clear that the minimum of $\chi_{\text{NO}_2}^2$ corresponds roughly to the height where the layer N2 is placed in the retrieval model. This indicates that in the absence of noise the NO₂ differential slant column measurements contain some information on the height of the elevated NO₂ layer. For higher noise the minimum has almost disappeared: at most a distinction can be made between NO₂ below and above approximately 15 km.

To decide which retrieval model is preferable, the one or the two NO₂ layer retrieval model, it is best to look at the model with the lowest value of $\chi_{\text{NO}_2}^2$. However, if both are about one, for example in a situation with high noise, then the measurements do not contain information to constrain more than two free parameters to describe the NO₂ profile, and it is advised to use the one layer retrieval model.

Another final that may be drawn from Fig. 10 is that both the single and double NO₂ layer retrieval have little, but still some, sensitivity to NO₂ in the low stratosphere (a

typical stratospheric NO₂ profile may start at approximately 10 km and peak at around 25 km, see Hendrick et al., 2004).

5 Application to measurements performed at the CINDI campaign

In this section, we describe the application of the above described single and double NO₂ layer retrieval algorithms to MAX-DOAS observations performed during the Cabauw Intercomparison campaign for Nitrogen Dioxide measuring Instruments (CINDI), held at the Cabauw Experimental Site for Atmospheric Research (CESAR) near Cabauw (51.970° N, 4.926° E), the Netherlands, in June and July 2009 (see Piters, 2011, to be submitted, and Roscoe et al., 2010). First we will show the results of the MAX-DOAS retrieval for six days. Subsequently we will discuss in detail the comparison of tropospheric NO₂ columns with the NO₂ lidar, and the comparison of the average NO₂ volume mixing ratio with in situ monitors.

5.1 Retrieval results for selected days

We have selected five days from the CINDI campaign to illustrate the outcome of the retrieval algorithm for three parameters: aerosol optical thickness, tropospheric NO₂ columns, and average NO₂ volume mixing ratio (see Fig. 11). The three parameters are compared to independent observations from an AERONET sun photometer, NO₂ lidar and in-situ monitors, respectively. Also shown are tropospheric NO₂ columns from the OMI instrument (Levelt et al., 2006) and from the NO₂ sonde, (Sluis et al., 2010). The MAX-DOAS retrieval algorithm was run with a single aerosol layer, not using relative intensity measurements in the cost function (see Sect. 4.3.1), and both for one and two NO₂ layers: the models M_{1a}^{1n} and M_{1a}^{2n} . Only results for the model with the lowest value of the reduced $\chi_{NO_2}^2$ are shown in the Fig. 11. Because only one aerosol layer was used, this choice only affects the NO₂ parameters. The fourth column of Fig. 11 shows the maximum height up to which the lidar measurements were performed – this

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height was determined by the quality of the lidar return signal, which is determined by atmospheric conditions, such as the presence of clouds – and the height below which 95 % of the NO₂ was present in the measured lidar profile. This information is taken into account in the comparison with MAX-DOAS retrievals, following the procedure described in Sect. 5.2.

The aerosol optical thickness retrievals shown in the first column of Fig. 11 show a reasonable agreement with AERONET, considering the differences in measurement technique (scattered versus direct sunlight observations). AERONET level 1.5 data were used and interpolated to 477 nm using the Angstrom relation and the AERONET measurements at 440 and 675 nm. Note that discontinuities in the AERONET data give an indication of the presence of clouds. Large uncertainties are seen for retrievals in the second half of some days. This may be due to the fact that the instrument was looking in the direction of the sun in that period (the instrument was always looking towards the North-West). Such observations for a small relative azimuth angle more critically depend on a proper modeling of the forward scattering by aerosols (described by the asymmetry parameter). As the asymmetry parameter is not included as a free model parameter – the look-up table is calculated for just one fixed value of the asymmetry parameter – the retrieval uncertainties will increase with decreasing relative azimuth angle.

The sometimes large differences between tropospheric NO₂ columns (second column of Fig. 11) from lidar and MAX-DOAS, seen in about half of the cases, catch the eye. We think that in many cases this difference is not an indication of a large retrieval error, but due to the limited height up to which the lidar profile is reported (as was mentioned above). This is most apparent on the 24 June 2009. The first five retrievals of lidar and MAX-DOAS agree within their uncertainty estimates, whereas the last four show large differences. These differences coincide with a sharp decrease in the maximum height up to which lidar measurements are done, as shown in the fourth column.

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The retrievals of tropospheric NO₂ columns, shown in the second column of Fig. 11, are relatively stable in time and internally consistent in the mornings, but tend to have larger uncertainties in the afternoons. The uncertainty estimate is usually smaller for the cases where the single NO₂ layer model was selected. We suspect that the increase in uncertainty for the double NO₂ layer model may be related to the occurrence of clouds, which will have most effect on the estimate of NO₂ in elevated NO₂ layers. Clouds not only lead to different sky radiances (the look-up table is calculated for cloud free conditions) but also to a reduced intensity of skylight, thereby lowering the signal to noise ratio and increasing the measurement uncertainty.

The agreement between average NO₂ volume mixing ratio derived from the MAX-DOAS retrieval and in situ measurements at the surface and 200 meters altitude in general looks reasonable (third column of Fig. 11). The most striking moments of disagreement between the in situ measurements and the MAX-DOAS retrievals are seen in some of the mornings.

When looking in more detail at the 24th, it can be argued that the underestimation of volume mixing ratios by MAX-DOAS is due to an overestimate of the NO₂ layer height (H_{N_2}) since the NO₂ column – the other model parameter from which X_{N_2} is determined – shows good agreement with the column measured with the lidar, which was up to relatively high altitude for this specific morning (see Fig. 11, row three, columns two and four). This overestimation may be explained by the difference between the actual NO₂ profile shape indicated by the lidar and the profile shapes assumed by the MAX-DOAS retrieval model, as shown in Fig. 12.

The sensitivity study in the previous section has shown that sometimes fictitious elevated NO₂ layers are retrieved by the double NO₂ layer retrieval algorithm, for various possible reasons (measurement uncertainty, other profile shapes, inaccurate aerosol extinction retrieval). This may raise the question how realistic the retrievals of the two NO₂ layer model are. For most days the answer cannot be given by the lidar measurements, as they do not go high enough. For June the 24th however, a strong confirmation is given by the measurement of an NO₂ radiosonde (Sluis et al. (2010),

Fig. 11c), which also shows an elevated NO₂ layer around 10:30 UTC. Note that the large difference with the NO₂ sonde on the 30 June may well be due to instrumental effects affecting the sonde observations that were tested in this week for the first time (Sluis, personal communication, 2011).

5.2 Comparison to other NO₂ measurement techniques

5.2.1 Partial Tropospheric NO₂ columns: MAX-DOAS and Lidar

Lidar measurements of NO₂ profiles in the low troposphere taken during the CINDI campaign have shown to be very accurate when compared to in situ monitors at 3, 100 and 200 m altitude (Berkhout et al., 2011), and therefore provide a good standard against which the profiling capabilities of the MAX-DOAS technique can be tested (see also Volten et al., 2009). It should however be emphasized that the vertical representativeness of the two techniques is different.

MAX-DOAS NO₂ retrievals based on either the single or the double NO₂ layer models (see above), are sensitive to NO₂ in the entire troposphere, although sensitivity is decreasing with altitude (Fig. 10). The MAX-DOAS measurements do not contain the information to assign a height to NO₂ above an altitude of 1–2 km (Sect. 3.1).

Lidar observations on the other hand are not expected to have a height dependent bias, but are limited in the height up to which measurements can be made, due to loss of return signal. Measurements taken during the CINDI campaign rarely exceeded an altitude of 2 km. The highest altitude up to which NO₂ concentrations were reported was determined for each measurement sequence separately, based on the quality of the lidar return signal. A decrease in the quality of the lidar signal does not necessarily coincide with low NO₂ concentrations, which means that NO₂ concentrations above the last reported altitude should be considered unknown. A comparison between MAX-DOAS and lidar thus needs to take into account this difference in vertical representativeness.

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the upper estimate, however based on the upper estimate of the average volume mixing ratio of each layer. The method used for the lower column estimate was based on the lower estimate of the volume mixing ratios, and on the additional assumption that no NO₂ was measured in regions that are not covered by the measurements (in between non-overlapping layers).

The results of the lidar versus MAX-DOAS comparison are shown in Fig. 14. The correlation of 0.78 ± 0.03 , low average difference ($0.1 \pm 0.2 \times 10^{15}$ molec cm^{-2}), and slope of linear fit (0.92 ± 0.05) indicate that the two measurement techniques compare quite well. However, the result does not apply to tropospheric NO₂ columns in general, but only to partial tropospheric NO₂ columns up to the maximum height where lidar measurements are reported.

5.2.2 NO₂ Volume Mixing Ratio: MAX-DOAS and In-situ monitor

The in-situ measurements of the NO₂ volume mixing ratios were performed with an M200E chemiluminescence nitrogen oxides analyzer from Teledyne Advanced Pollution Instrumentation. It was equipped with a photolytic converter, from the same company, to make it insensitive to nitrogen compounds other than NO₂ and NO. The lowest detection limit of the instrument was 0.4 ppb for NO and NO_x and 0.8 ppb for NO₂. Its precision was 0.5 % of the reading or of the lowest detection limit, whichever was greater.

A comparison with MAX-DOAS volume mixing ratios derived with the algorithm described in this paper should be interpreted with care, as the observed surface volume mixing ratio of NO₂ and the average NO₂ volume mixing ratios in the lower NO₂ layer of the MAX-DOAS retrieval model (layer N1) are two distinct physical quantities. A certain amount of disagreement may be due to differences in assumed profile shape (model versus true profile, also for aerosols) or to uncertainties in the measurements.

Because the look-up table was created for cloud free conditions, the presence of clouds will generally increase the errors in the retrieval, e.g. of the layer NO₂ layer height H_{N1} and as a consequence on the NO₂ mixing ratio X_{N1} . The effect of clouds on

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the retrieved mixing ratio is strongest for situations where the NO₂ is relatively close to the surface, mostly in the morning hours, because then the largest relative errors in the retrieval of the NO₂ layer height will occur. Due to the inverse relation between the X_{N1} and H_{N1} , as discussed in Sect. 3.3, this will more often lead to larger overestimations than underestimations of X_{N1} .

For this reason, a selection was made of CINDI days included in this comparison. Only days with cloud free mornings were selected: the 23, 24 and 30 June and the 2 and 4 July. Observations from the Baseline Surface Radiation Network (BSRN) at Cabauw were used to examine the occurrence of clouds (Knap, 2009).

It should be noted that the sensitivity to clouds in combination with low NO₂ layers, would not occur if a fixed NO₂ layer height would have been chosen, such as in Irie et al. (2011), their Fig. 8. However, their choice for a fixed layer height (1 km) may also provide an explanation for the systematic underestimation of the NO₂ volume mixing ratio found in their study in the morning hours.

The results of the comparison are shown in Fig. 15, and Table 3. On average there is quite a good agreement between the in situ observations and the MAX-DOAS derived NO₂ volume mixing ratios, especially for the two NO₂ layer model: a correlation of 0.8, and an average difference of 0.2 ppb. The general pattern of the diurnal evolution – showing a dilution caused by thermal convection – is captured by the both the one and two NO₂ layer retrieval model, although the one layer model tends to underestimate the volume mixing ratios in the morning hours.

When looking on a day-to-day basis, 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 NO₂ layers, see the discussion above, but may also be due to errors in the assumed profile shape. For low NO₂ layers, 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).

6 Conclusions and outlook

This paper describes a retrieval algorithm developed to derive a first order description of the vertical distribution of NO_2 in the troposphere from MAX-DOAS measurements. Such profile information is essential in validation studies in which MAX-DOAS retrievals play a role.

A conservative approach was followed in order not to overestimate the number of degrees of freedom to parameterize the aerosol and NO_2 profile. The retrieval model is based on a pre-calculated look-up table and assumes homogeneous mixing of aerosols and NO_2 in layers extending from the surface to a variable height. Two retrieval model versions were compared: one including and one excluding an elevated NO_2 layer at a fixed altitude in the free troposphere. An ensemble technique is applied to derive retrieval uncertainties.

Sensitivity studies were performed to test the retrieval accuracy for various levels of noise, NO_2 and aerosol boundary layer profiles being different from those assumed in the retrieval model, and elevated NO_2 and aerosol layers. This led to the following conclusions:

- If NO_2 is present only in a homogeneously mixed boundary layer (BL), then the amount of NO_2 in this BL, and its height, can be retrieved accurately. The effect of noise is different in the one and two NO_2 layer model. In the one layer model, noise does not affect the accuracy of the tropospheric NO_2 column, but leads to an underestimation of the NO_2 layer height. In the two layer model, noise leads to a small overestimation of the tropospheric NO_2 column, which is related to the fact that NO_2 is retrieved in the upper model layer N2, although in the simulations it was only present in the lowest layer N1.
- If NO_2 is also present in the free troposphere, then its presence will be confirmed by the retrieval of the two NO_2 layer model, even for high measurement uncertainties. However, the altitude of this elevated NO_2 layer can only be determined for high measurement accuracy, and accurate aerosol extinction retrieval. The

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accuracy of the partial NO₂ column of the elevated layer is therefore in practice often quite low. In the one layer model, NO₂ above 2 km is underestimated by more than 50 %.

- Error sources for NO₂ profile retrieval, such as measurement uncertainty and inappropriate parameterizations of the NO₂ or aerosol profiles, have a higher impact on the retrieval accuracy of the NO₂ profile shape, than on the integrated tropospheric NO₂ column.
- The two retrieval model versions explored in this study are relatively inaccurate when elevated NO₂ layers are found at heights other than those included in the retrieval model. The inappropriateness of the retrieval models under such conditions is indicated, for conditions with low noise, by relatively high values of $\chi_{\text{NO}_2}^2$ (order 10 or higher). This indicates that the information to retrieve such elevated layers more accurately is to some extent contained in the measurements, and that a different profile parameterization could give results that are arguably better.
- It is advised apply both the one and the two NO₂ layer retrieval model to the measurements, and to use the outcome of the retrieval model with the lowest value for $\chi_{\text{NO}_2}^2$.
- The use of relative intensity measurements (in addition to O₄ slant column measurements) leads to a higher accuracy of the aerosol optical thickness retrieval (AOT), especially if aerosols are present in elevated layers, than if only O₄ measurements would have been used (this was also concluded by Friess et al. (2006)). However, this improvement in AOT retrieval does not have a noticeable effect on the retrieval of the vertical distribution of NO₂ and for some cases (aerosol layers above 5 km) it does even lead to considerable underestimation of the NO₂ layer height. Taking this into account, together with the unwanted increased sensitivity to clouds, it is from the perspective of NO₂ profile retrieval

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advisable not to use relative intensity measurements in the aerosol retrieval in combination with an elevated aerosol layer with a fixed height.

The various aspects of the sensitivity study indicate that the profile retrieval potential of MAX-DOAS can be classified into two vertical domains. Firstly, a domain from the surface to roughly 0.5–1.5 km (the vertical extent decreases with increasing aerosol extinction in the BL). In this domain NO₂ can be retrieved with at most three degrees of freedom. Secondly, a domain above the first, having one (occasionally two) degree(s) of freedom. Note that the transition level between those lower and upper domains is not always related to the “meteorological” BL height: NO₂ retrieved in the upper domain may be located in the BL, or in the free troposphere, even at high altitudes, or both.

The retrieval model was applied to observations performed at the CINDI campaign, held in the Netherlands in 2009. Results were compared with independent observations: aerosol optical thickness from AERONET direct sun observations, partial tropospheric NO₂ columns and profile shapes from NO₂ lidar measurements, and NO₂ volume mixing ratios from in-situ observations at the surface. These comparisons lead to the following conclusions:

- The MAX-DOAS retrievals of aerosol optical thickness, based on a retrieval model with a single aerosol BL, and using only O₄ observations (instead of combining it with relative intensity measurements), compare well to AERONET.
- The MAX-DOAS and lidar have quite a good agreement in partial tropospheric NO₂ columns (correlation of 0.78, average difference of 0.1×10^{15} molec cm^{-2}). The differences between NO₂ profiles measured by the lidar and retrieved from the MAX-DOAS were sometimes quite large. This is partly explained by the fact that lidar measurements did not cover the full free troposphere, and partly caused by the assumptions made for the NO₂ and aerosol profile shapes in the MAX-DOAS retrieval model, as indicated by the several sensitivity studies performed in this work.

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– The diurnal evolution of the NO₂ volume mixing ratio measured at the surface and averaged over five days with cloud free mornings, compares quite well to the volume mixing ratio derived from the MAX-DOAS retrieval: a correlation was found of 0.8, and an average difference of 0.2 ppb for the two layer retrieval model.

As the lidar measurements during the CINDI campaign could often not be done above a few kilometers altitude, future intercomparison campaigns are needed for further validation of the MAX-DOAS NO₂ retrieval in the free troposphere, e.g. by comparison with NO₂ sondes.

To fundamentally improve the NO₂ profile retrieval accuracy, especially the free tropospheric part, more constraints on the NO₂ profile are needed than can be given by the MAX-DOAS technique alone. An important step forward could be the combination of different DOAS techniques: MAX-DOAS (to measure NO₂ in the lower troposphere), zenith sky (NO₂ in stratosphere) and direct sun (total NO₂ column). Measurements from the three techniques should then be combined in one consistent retrieval algorithm. Important progress towards such an approach has already been made by several groups that have developed MAX-DOAS instruments capable of observing scattered sunlight in all directions (as opposed to MAX-DOAS instruments that have a fixed viewing azimuth) as well as direct sunlight, see e.g. Piters (2011), to be submitted.

Acknowledgements. The authors would like to thank M. Van Roozendael and C. Fayt from the Belgian Institute for Space and Aeronomy (IASB/BIRA) for providing the Qdoas software that was used for the DOAS analysis, and for giving valuable support and advice.

Furthermore we would like to thank S. Kraus and T. Lehmann of the Institute for Environmental Physics at the University of Heidelberg for providing the DOASIS software package.

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We also acknowledge the free use of tropospheric NO₂ column data from the OMI sensor from www.temis.nl.

We greatly acknowledge the contributions of P. Stammes to this manuscript.

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- 5 This work has been financed by User Support Program Space Research via the project “Atmospheric chemistry instrumentation to strengthen satellite validation of CESAR” (EO-091).

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Table 2. Overview of the variable settings in the sensitivity studies. In each sensitivity study, the retrieval is tested for different values of the variable of which the range is indicated in boldface. Measurements are simulated for the settings given by the table, and analyzed with the retrieval models given in the final column. Note that the variables S_{N1} , S_{A1} , H_{N2} , and H_{A2} , have fixed values in the retrieval models, but are varied in the simulation of measurements for this sensitivity study. All partial NO₂ columns (N_{N1} and N_{N2}) are given in 10^{16} molec cm⁻² and all heights are given in km.

	N_{N1}	N_{N2}	H_{N1}	H_{N2}	S_{N1}	τ_{A1}	τ_{A2}	H_{A1}	H_{A2}	S_{A1}	noise	retr. models
A	2	0	0.05–2.3	n.a.	1	0.2	0	0.8	n.a.	1	0–15 %	M_{1a}^{1n}, M_{1a}^{2n}
B	2	0	0.8	n.a.	1	0.2	0	0.05–2.3	n.a.	1	0–15 %	M_{1a}^{1n}, M_{1a}^{2n}
C	2	0	0.5	n.a.	1	0.2	0	0.5	n.a.	0–2	0 %	M_{1a}^{1n}, M_{1a}^{2n}
D	2	0	0.5	n.a.	0–2	0.2	0	0.5	n.a.	1	0 %	M_{1a}^{1n}, M_{1a}^{2n}
E	1.5	0	0.6	n.a.	1	0.2	0.2	0.6	0.05–20	1	0 %	M_{1a}^{1n}, M_{1a}^{2n}
F	0	1	n.a.	0.05–20	1	0.2	0	0.6	n.a.	1	0–15 %	M_{1a}^{1n}, M_{1a}^{2n}

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Table 3. Comparison of NO₂ volume mixing ratios derived from in situ monitors and MAX-DOAS. The average difference is defined as (MAX-DOAS minus in situ), and the linear fit parameters are defined for the insitu values on the horizontal and the MAX-DOAS values on the vertical axis.

Retrieval Model	Correlation	Av. Diff. [ppb]	Slope	Offset [ppb]
one NO ₂ layer	0.75	−0.71	1.15	−1.39
two NO ₂ layers	0.80	0.24	1.31	−1.20
selection based on $\chi^2_{\text{NO}_2}$	0.77	0.22	1.32	−1.23

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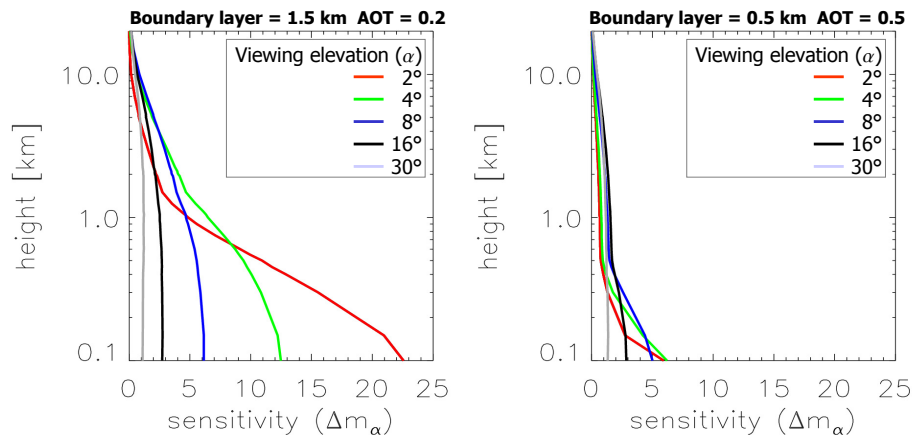


Fig. 1. Height dependent sensitivity to NO_2 of MAX-DOAS measurements at five viewing elevations, for two cases: (i) a relatively low amount of aerosols ($\text{AOT} = 0.2$) in a boundary layer with a vertical extent from 0–1.5 km and (ii) a relatively high amount of aerosols ($\text{AOT} = 0.5$) in a boundary layer with a vertical extent from 0–0.5 km. $\text{SZA} = 60^\circ$, $\text{AZIM} = 180^\circ$, $\lambda = 477 \text{ nm}$.

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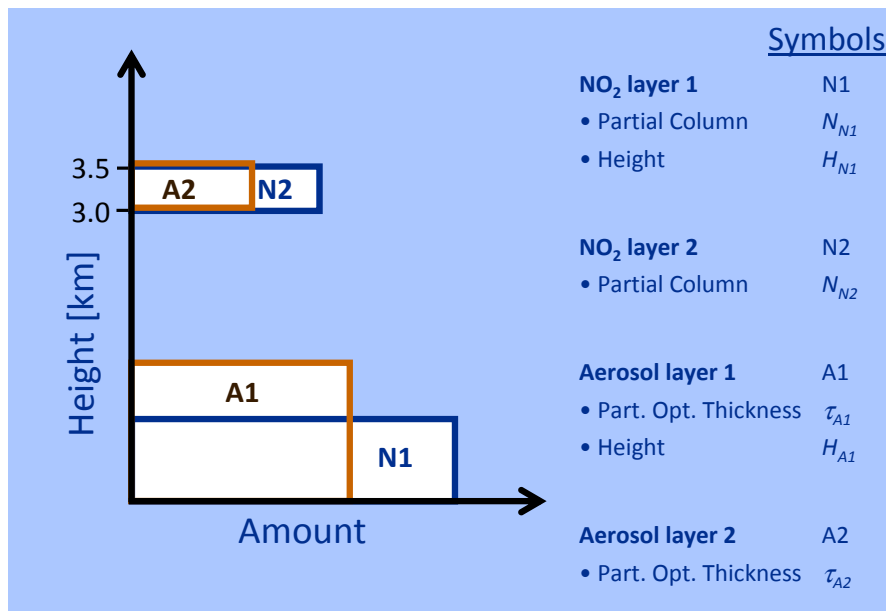


Fig. 2. Schematic description of the aerosol and NO₂ profile parameterization of the MAX-DOAS retrieval model used in this work. The conceptual model consists of an aerosol layer (A1) and a NO₂ layer (N1), which both go from the surface to a variable height, optionally extended with one or two second layers: A2 and N2, placed at a fixed altitude (3–3.5 km). The retrieval model thus has a minimum of four and a maximum of six free parameters. The use of the two optional layers (A2 and N2) is studied in Sect. 4.

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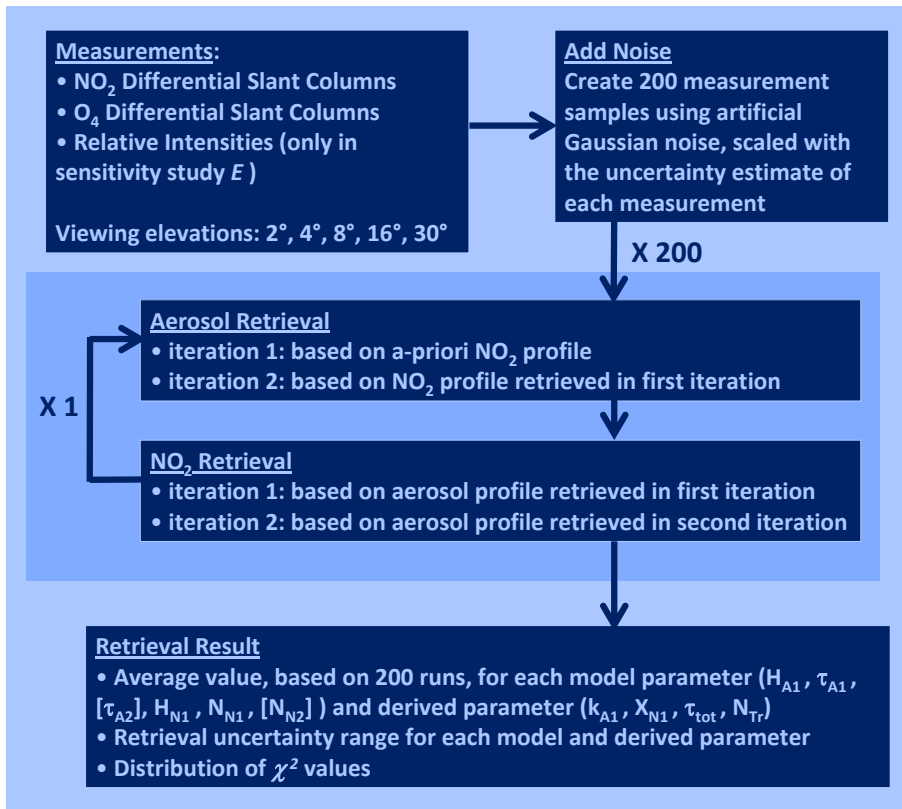


Fig. 3. Schematic of the tropospheric aerosol and NO₂ retrieval algorithm. This algorithm is used both in the sensitivity study (using simulated measurements) and in the analysis of measurements taken during the CINDI campaign.

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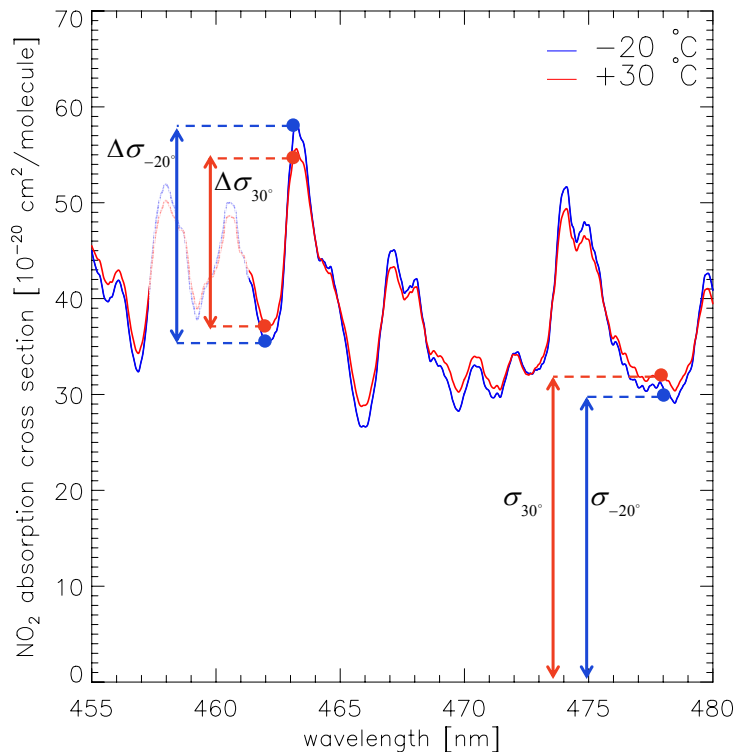


Fig. 4. NO_2 cross section spectrum σ at two different temperatures (Vandaele et al., 1998). The figure illustrates that a change in effective NO_2 temperature (see Sect. 3.2.2) leads to a relative change in the *differential* cross section ($\Delta\sigma$), used in the DOAS fitting, that is larger than the relative change of the cross section itself. A correction based on the temperature dependency of $\Delta\sigma$ is applied to the measured differential slant NO_2 columns, since they are derived from a DOAS fit performed with a NO_2 cross section of 295 K. A correction of simulated measurements (that are calculated in the look-up table for only two values of the surface temperature (Sect. 3.2.1)) is based on the temperature dependency of σ .

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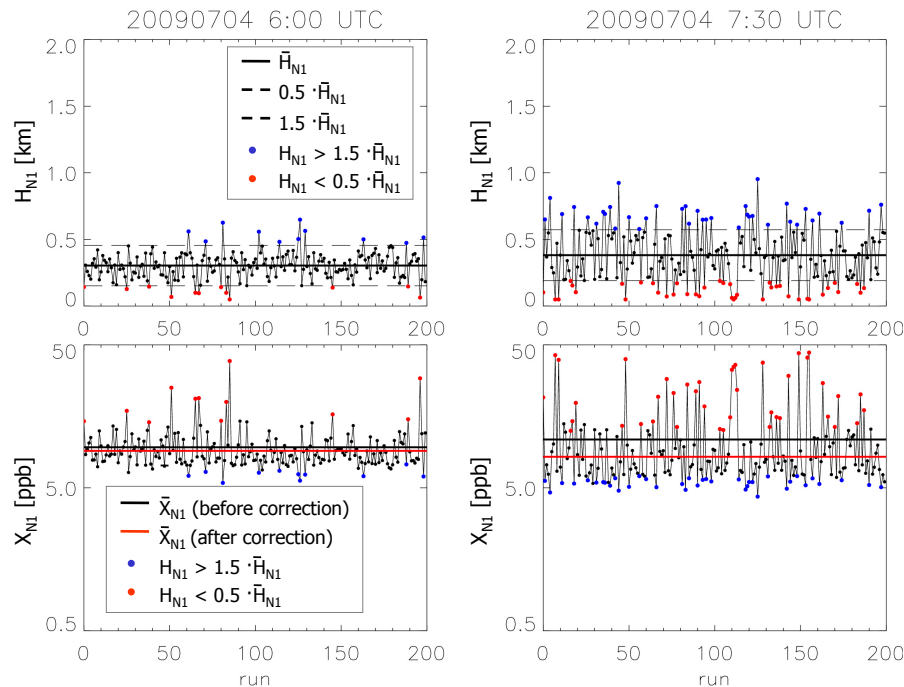


Fig. 5. Two examples of the ensemble of 200 retrievals of NO₂ layer height (H_{N1}) and NO₂ volume mixing ratio (X_{N1}). Note that the plots on the bottom row have a logarithmic y-axis. These examples are selected to demonstrate the effect of the procedure where ensemble runs are deselected to avoid overestimation of the NO₂ volume mixing ratio due to a retrieval uncertainty in H_{N1} (Sect. 3.3). This deselection applies only to the colored points on the lower two plots (X_{N1}). On the left this procedure leads to a change of -5% , on the right to -25% . Horizontal bars in the legends denote average values.

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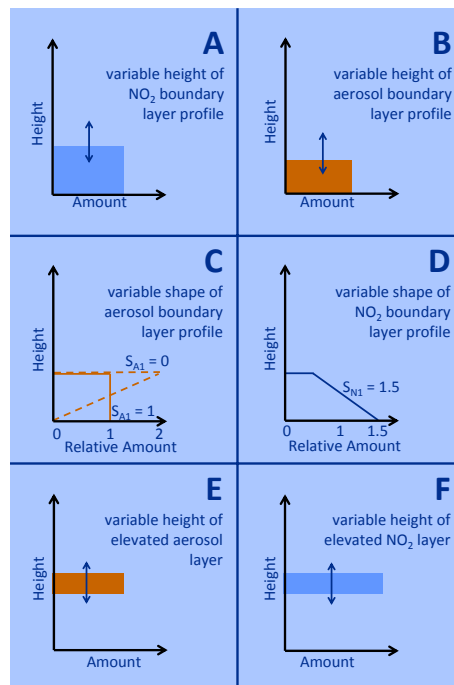


Fig. 6. Schematic of the six sensitivity studies (A–F) performed to test the behavior and robustness of the NO₂ profile retrieval algorithm. Each diagram only shows the parameter that is changed, other fixed parameters are given in Table 2. The top row shows the first two studies, that were done to check the behavior of the algorithm for various levels of artificial noise, under conditions that coincide with the model assumptions. The second row illustrates the study that was done to test the effect of inhomogeneous distributions within the boundary layer of aerosols or NO₂ (whereas the retrieval model assumes homogeneous distributions for both). The shape parameter S defines the various profile shapes. Finally we tested the sensitivity of the NO₂ retrieval to elevated aerosol and NO₂ layers (third row).

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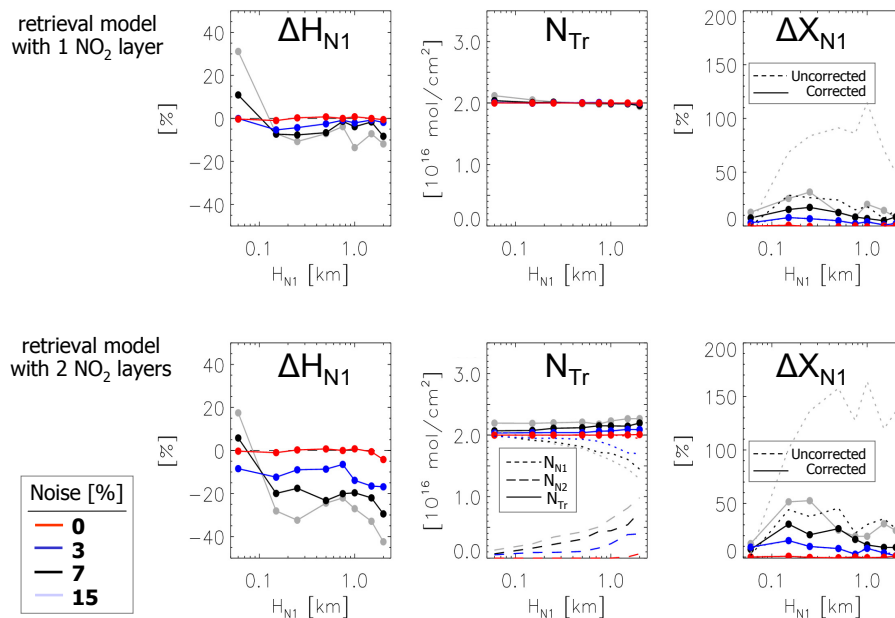


Fig. 7. Sensitivity study A. The retrieval accuracy of the NO₂ layer height, NO₂ column amounts and NO₂ volume mixing ratio for the 1 NO₂ layer model (top row) and the 2 layer model (bottom row), for different levels of Gaussian noise, as a function of the NO₂ layer height H_{N1} . The black dashed lines indicate prescribed values in the sensitivity study, i.e. the truth in the simulation. The correction method applied in the last column is described in Sect. 3.3.

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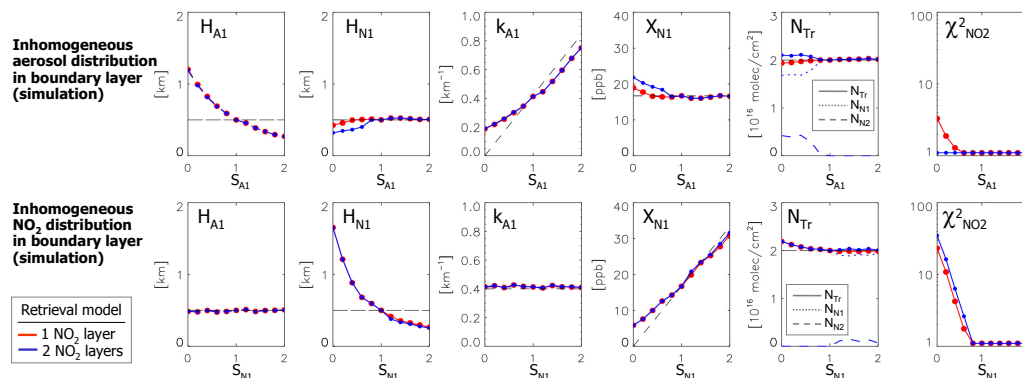


Fig. 8. Sensitivity study C (top row) and D (bottom row): inhomogeneous boundary layer distributions of aerosols and NO₂. The black dashed lines indicate prescribed values in the sensitivity study, i.e. the truth in the simulation. The aerosol retrieval was performed with the single aerosol layer retrieval model.

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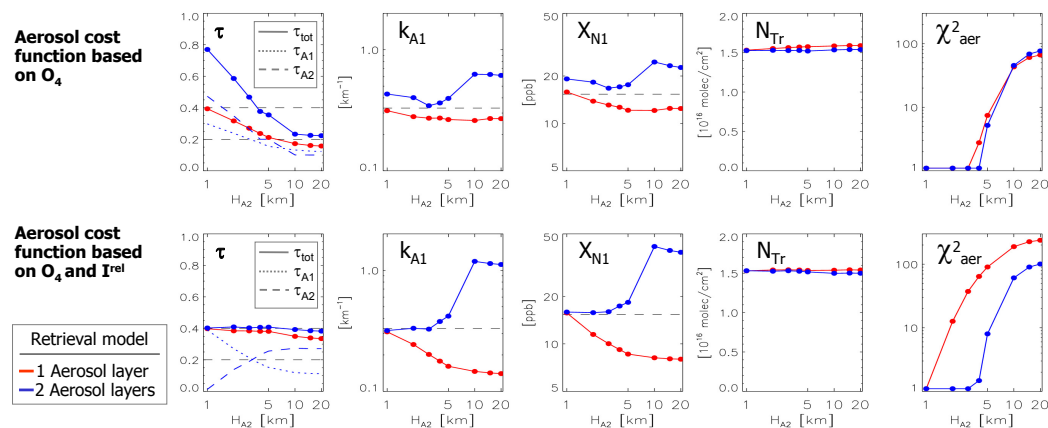


Fig. 9. Sensitivity study E (elevated aerosol layers). The top row shows aerosol retrievals based solely on differential slant column measurements of O₄. The retrievals shown in the bottom row are done with a cost function where not only O₄ but also relative intensity measurements were used. The black dashed lines indicate prescribed values in the sensitivity study, i.e. the truth in the simulation. In the first column not only the total AOT is shown (0.4), but also the AOT of the boundary layer (0.2). Only the 1 NO₂ layer retrieval model was used for the NO₂ retrieval. Note that the 2nd, 3rd and 5th column have a logarithmic scale on the y-axis.

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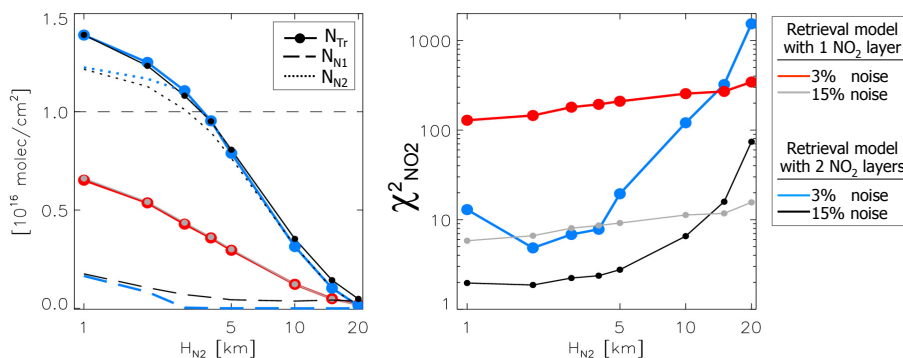


Fig. 10. Sensitivity study F (elevated NO₂ layers). On the left partial and total NO₂ columns are shown for both the one and two NO₂ layer retrieval model, for two noise levels. On the right $\chi^2_{NO_2}$ values are shown for both models and noise levels. The elevated NO₂ layer in this experiment had a partial NO₂ column of 1.0×10^{16} molec cm⁻². Note that height of the elevated NO₂ layer (H_{N2}) is varied in this sensitivity study, whereas it is fixed in the two NO₂ layer retrieval model, see Sect. 3.1.

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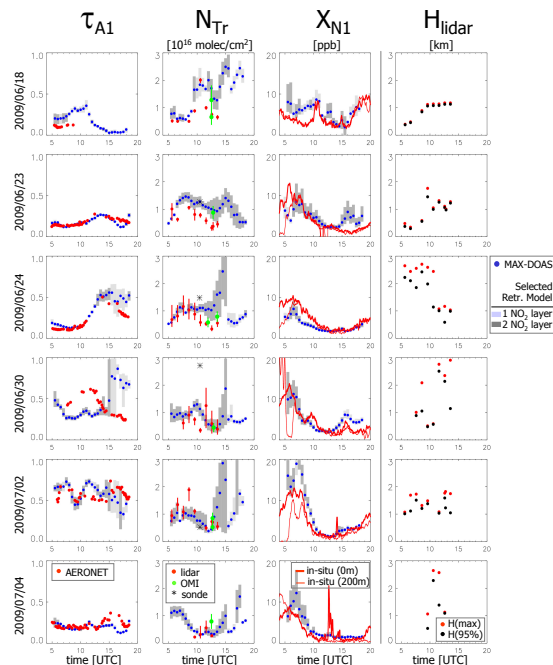


Fig. 11. Results of retrieval algorithm applied to MAX-DOAS observations on six selected days during the CINDI campaign, and comparison with independent observations: aerosol optical thickness from AERONET (first column), tropospheric NO₂ columns from lidar, OMI and sonde (second column), and NO₂ volume mixing ratios from in-situ monitors located at two different altitudes in the Cabauw tower (third column). MAX-DOAS retrievals based on the one NO₂ layer model are indicated with a light gray error bar, whereas dark gray indicates the use of the two NO₂ layer model. The selection of the retrieval model is based on the lowest value of $\chi^2_{\text{NO}_2}$, see also Sect. 5.1. The fourth column shows the height up to which the lidar profile was reported, and the height below which altitude 95 % of the lidar NO₂ column was found. For OMI only the pixel with its center closest to Cabauw was selected. On two occasions Cabauw was exactly between two pixel centers, and both were plotted.

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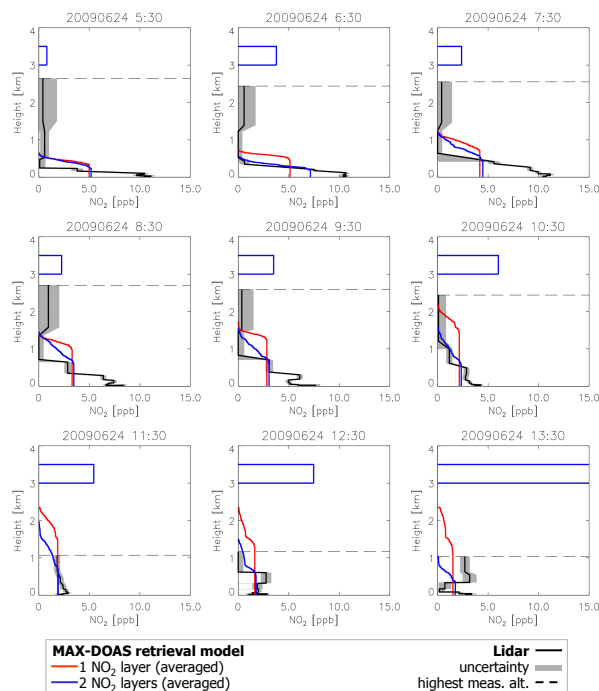


Fig. 12. Lidar NO₂ profiles and MAX-DOAS retrievals measured at the CINDI campaign on the 24 June 2009. The lidar profile is shown in black, with uncertainty estimate in gray and the highest measurement altitude shown with the dashed horizontal line. The average profiles retrieved with the MAX-DOAS one and two NO₂ layer algorithms are shown in red and blue respectively, they are obtained by averaging all block shaped profiles of the ensemble of 200 runs. During the first part of this day the agreement between the two measurements techniques in terms of tropospheric NO₂ columns was high, whereas the average NO₂ volume mixing ratio derived from MAX-DOAS was significantly below the NO₂ volume mixing ratio measured at the surface (Sect. 5.1).

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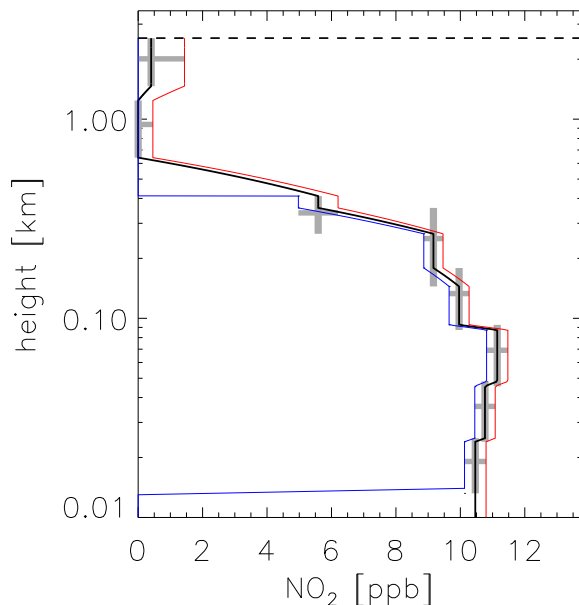


Fig. 13. Example of lidar NO_2 profile measured at the CINDI campaign. In gray the individual lidar measurements are shown, where the vertical bar shows the range to which the concentration applies, and the horizontal bar shows the uncertainty range of the average concentration. Note that the vertical ranges sometimes do and sometimes do not overlap. The black line shows the continuous profile derived from the discrete measurements (according to a procedure explained in Sect. 5.2.1) that is used to determine the integrated partial NO_2 column. The blue and red profiles are used to define the uncertainty range of the partial NO_2 column: the blue profile is based on conservative estimates, the red on non-conservative estimates. The horizontal dashed black line indicates the height above which no measurements were reported.

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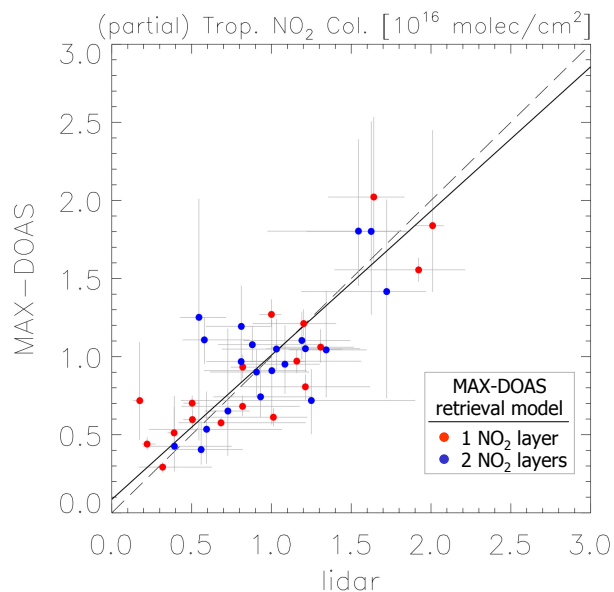


Fig. 14. Comparison of partial tropospheric NO₂ columns retrieved from lidar and MAX-DOAS at the CINDI campaign. For each lidar measurement, a choice was made which MAX-DOAS retrieval to compare with: the single (red) or double NO₂ layer retrieval (blue). This choice was based on the value of the reduced $\chi^2_{\text{NO}_2}$, see text. The solid line shows the result of the linear regression. It has a slope of 0.92 and an intercept of 0.9×10^{15} molec cm⁻². The two data sets have a correlation of 0.78 and an average difference of 0.1×10^{15} molec cm⁻² ($n = 39$).

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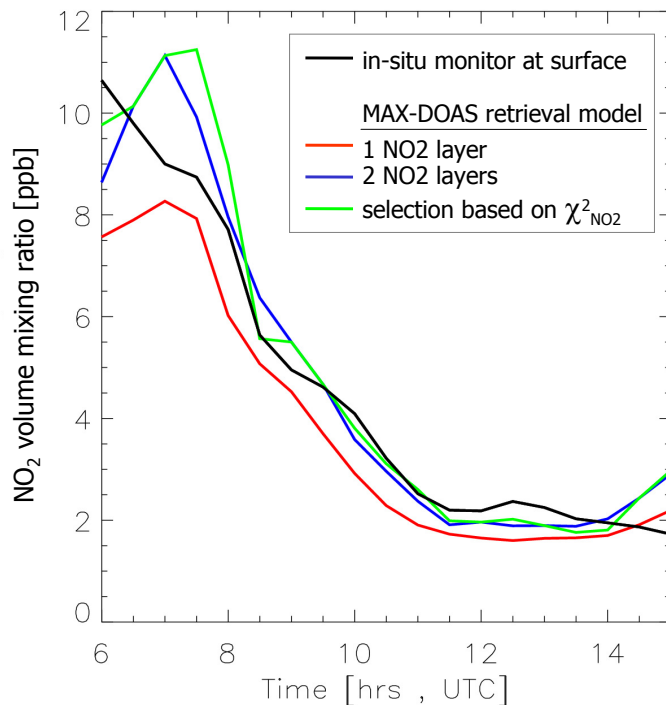


Fig. 15. Comparison of tropospheric NO₂ volume mixing ratio measured with an in-situ monitor at the surface, averaged over five days of the CINDI campaign with cloud free mornings (Sect. 5.2.2), and average NO₂ volume mixing ratio derived by the MAX-DOAS, for the one and two NO₂ layer retrieval models, and when the choice between the one and two NO₂ layer retrieval model is based on the lowest value of $\chi^2_{NO_2}$.

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