

Ability of the MAX-DOAS method to derive profile information for NO₂: can the boundary layer and free troposphere be separated?

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Abstract. Multiple 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 for detailed comparisons of MAX-DOAS retrievals with other measurement techniques for NO₂, e.g. with a lidar or from space.

The retrieval algorithm used 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 models are 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 demonstrate that NO₂ in the free troposphere can only be retrieved accurately if: (i) the retrieved boundary layer profiles for aerosols and NO2 correspond to the real ones, (ii) if the right a-priori choice is made for the (average) height of free tropospheric NO₂, and (iii) if all other error sources are very low. It is shown that retrieval models that are capable of accurate NO₂ retrievals in the free troposphere, i.e. models not constrained too much by a-priori assumptions, have as a major disadvantage that they will frequently find free tropospheric NO₂, also when it is not present in reality. This is a consequence of the fact that NO_2 in the free troposphere is poorly constrained by the MAX-DOAS observations, especially for high aerosol optical thickness values in the boundary layer. Retrieval of free tropospheric NO₂ is therefore sensitive to a large number of error sources. For this reason it is advised to firmly constrain free tropospheric NO2 in MAX-DOAS retrieval models used



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for applications such as satellite validation. This effectively makes free tropospheric NO_2 a source of error for MAX-DOAS retrieval of NO_2 profiles in the boundary layer.

A comparison was performed with independent data, based on MAX-DOAS 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 well to the MAX-DOAS retrieval: a correlation was found of 0.94, and an average difference of 0.04 ppb.

1 Introduction

1.1 Background and motivation

Nitrogen dioxide (NO₂) 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 $NO_x = NO + NO_2$), 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., 2011) and GOME-2 (Richter et al., 2011). Whereas in-situ measurements have the advantage of being specific to the air that is inhalated by humans, space borne observations have the advantage of observing not only NO₂ at the surface, but the entire vertical NO₂ column. Although the first quantity is more directly related to the effect of NO₂ on human health, the second quantity is more relevant for studies of transport and trends in NO₂ 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 NO₂ abundances much less dependent on instrumental and calibration differences between national in-situ monitoring networks.

Validation of tropospheric NO₂ 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 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. Hönninger 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. Pikelnaya 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, Hendrick et al., 2004 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 $1-2 \,\mathrm{km}$ (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 Frieß et al., 2006). Under realistic conditions values above three are rarely encountered (see e.g. Clémer et al., 2010, and Sect. 4 and 5 below). 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; Clémer 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, 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 parametrization 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



Fig. 1. Height dependent sensitivity to NO₂ (height-dependent differential air mass factors) of MAX-DOAS measurements at five viewing elevations, for two cases: (i) a relatively low amount of aerosols (AOT = 0.2) in a boundary layer with a vertical extent from 0–1.5 km and (ii) a relatively high amount of aerosols (AOT = 0.5) in a boundary layer with a vertical extent from 0–0.5 km. SZA = 60°, AZIM = 180°, $\lambda = 477$ nm.

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 parametrizations 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 and Wagner et al., 2011). We study the feasibility of retrieving NO₂ above the boundary layer, by including in the retrieval model a second NO₂ layer at a fixed altitude in the free troposphere. The same is done for aerosols. Additional diagnostic information (error estimate, goodness of fit) is determined using an ensemble technique that is described in Sect. 3.3. In Sect. 4.4 it is discussed to which extent the conclusions drawn about the profiling potential of the MAX-DOAS technique are specific to the retrieval approach followed in this study, or have a more general scope.

2 MAX-DOAS measurements and uncertainties

The MAX-DOAS measurement technique has been described in detail in e.g. Hönninger 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:

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

where $P(\lambda)$ denotes a low order polynomial (order 2–5) that accounts for the broad band effects. The above equation is numerically solved for ΔN_i^S and $P(\lambda)$ using a fitting routine minimizing the differences between both sides of the equation.

In this work, the DOAS analysis is applied to measurements with a Mini MAX-DOAS instrument (Hoffmann GmbH, Germany), performed during the CINDI campaign (Sect. 5). This instrument is equipped with an Ocean Optics USB2000+ spectrometer which has a linear CCD detector with 2048 pixels and covers a wavelength range from 400 to 600 nm. The spectral resolution is approximately 0.9 nm. The DOAS fit was performed using the Qdoas software package (Fayt et al., 2011), within the spectral window from 425 to 490 nm. The zenith spectrum observed at noon served as a reference ($I_{\alpha=90^{\circ}}^{noon} = I_{ref}$). Apart from NO₂ (295 K, Vandaele et al., 1996) and O₄ (296 K, Hermans) the following absorbers were fitted: O₃ (223 K, Bogumil et al., 2003), H₂O (Vandaele et al., 2005), along with a Ring spectrum (Chance and Spurr, 1997), and a third order polynomial. We used the viewing elevations 2°, 4°, 8°, 16°, 30° and 90° (reference).

This selection of viewing elevations is chosen to find a balance between on the one hand a sufficiently small total integration time needed for the scan of one vertical profile, which is important to prevent errors due to changing atmospheric conditions, and on the other hand to make optimal use of the differences in vertical sensitivity of the various elevations (Fig. 1). This difference is largest for the smallest viewing elevations. The set of elevations is comparable to the set used in Clémer et al., 2010, but with only one instead of three elevations between 8° and 30°, since it is shown in Fig. 1 that these elevations have a quite similar (flat) vertical sensitivity. The highest elevation is needed to put a constraint on the tropospheric NO₂ column (this elevation is almost insensitive to the vertical profile shape), the lowest elevations contain most information with respect to the the aerosol and NO2 profile shapes. Although an observation for $\alpha = 1^{\circ}$ could improve the profiling potential even more (see Fig. 5 in Wagner, 2011) it was decided not to use this elevation, firstly because it cannot be used at many sites where the horizon cannot be seen, and secondly because this elevation is, for conditions with a high visibility, extremely sensitive to small errors in the instrument alignment. This affects both the aerosol and NO_2 retrieval step of the algorithm. For the set of elevations used in this study, the elevation viewing angle accuracy needs to be highest for the 2° elevation: 0.3° or better.

As there can be many changes in the atmosphere in the time between the observation of each individual spectrum and the noon reference spectrum (due to atmospheric dynamics, chemistry and the changing position of the sun), there is little to no meaning in the differential slant columns acquired with this procedure (denoted below as $\Delta N_{\alpha}^{S,\text{noon}}$). Therefore, the so-called "instantaneous" differential slant column ΔN_{α}^{S} is derived, which does not have this deficiency. It is acquired by subtracting the zenith differential slant column $\Delta N_{\alpha=90^{\circ}}^{S,\text{noon}}$ from the differential slant column at elevation α both linearly interpolated to the same time of observation (t_0):

$$\Delta N_{\alpha}^{S}(t_{0}) = \Delta N_{\alpha}^{S,\text{noon}}(t_{0}) - \Delta N_{\alpha=90^{\circ}}^{S,\text{noon}}(t_{0}).$$
⁽²⁾

Throughout this work, we will make use of these instantaneous differential slant columns, and refer to them as differential slant columns or simply as the (MAX-DOAS) measurements.

An estimate of the measurement uncertainty ϵ forms an important ingredient in the retrieval algorithm described below. It is determined for each measurement parameter $(\Delta N_{\alpha}^{S,O_4}, \Delta N_{\alpha}^{S,NO_2} \text{ and } I_{\alpha}^{\text{rel}})$ from its temporal variations. Measurement time series of the various parameters and ele-

vations are first put on the same time grid, using linear 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.

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

This procedure yields a measure for uncertainty that is generally larger than if the uncertainty estimate would be based on the residual of the DOAS fit and combined with the uncertainty estimates of the NO₂ cross section and the vertical temperature profile, although the latter approach would give a more accurate uncertainty estimate for individual differential slant column observations. From the perspective of NO₂ and aerosol profile retrieval, this alternative uncertainty estimate is however not representative since it applies to an observation at one moment in time, whereas the measurements at other viewing angles are taken at another moment in time, several minutes earlier or later, thus for changed atmospheric conditions. The uncertainty estimate defined in Eq. 3 and used in Eqs. 11 and 12 focuses on the precision of measurements given the variations in time.

3 Retrieval algorithm

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 parametrization, or conceptual model, is based on (1) the fact that tropospheric NO_2 is most often



Fig. 2. Schematic description of the aerosol and NO_2 profile parametrization of the MAX-DOAS retrieval model used in this work. The conceptual model consists of an aerosol layer (A1) and a NO_2 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.

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 aerosol extinction profile), and for this reason we parametrized our profile with a lower NO₂ 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 NO₂ 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 NO₂ 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 NO₂ retrieved in the second layer as free tropospheric NO₂. If, for example, the true NO₂ 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 NO₂ in N2, NO₂ that is in reality located in the highest part of N1. The second NO₂ layer should therefore be interpreted as "the partial NO2 column above approximately 1 km, with unknown altitude". This interpretation will be consistent with other retrievals based on alternative parametrizations for the free troposphere. If, for example, another vertical extent would have been chosen for the elevated layer, e.g. 2.5 instead of 0.5 km, but with the same average height (3.25 km), then retrievals will appear different in plots (see e.g. Fig. 12), but the integrated amount of NO₂ in the second layer (N_{N2}) would be approximately the same. Thus whereas the visual impact of other parametrizations can be high, in essence the changes may be mostly cosmetic. In Sect. 4.3.2 it is discussed if it is feasible to add a fourth free parameter for the average height of the elevated layer.

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 NO₂ layer N2, and M_{2a}^{1n} for the model with one NO₂ 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 NO₂ column: $N_{Tr} = N_{N1} + N_{N2}$
- total AOT: $\tau_{tot} = \tau_{A1} + \tau_{A2}$
- average aerosol extinction of A1: $k_{A1} = \tau_{A1}/H_{A1}$ [km⁻¹]
- average NO₂ 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 plane parallel 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. The layer height grid used in the DAK radiative transfer simulations is defined as follows: 25 layers of 1 km from 0-25 km altitude, followed by 10 layers of 2.5 km vertical extent between 25 and 50 km, and finally 10 layers of 5 km between 50 and 100 km. For forward simulations additional intermediate layers were defined. For example, the S-shape parametrization was realized using 7 sub-layers. Ozone was not included in the forward simulations since the ozone layer has almost no influence on the differential slant NO₂ columns determined with the (simultaneous) zenith observation as a reference, especially at 477 nm. For NO₂ a stratospheric profile was assumed as defined by the U.S. standard mid-latitude summer profile (Anderson et al., 1986). The forward simulations accounted for the absorption cross section temperature dependence of NO₂.

There are three types of simulated measurements contained in the look-up tables (see Sect. 3.2.1): differential slant NO₂ columns, differential slant O₄ columns, and relative intensities, for which we use the symbols $\Delta N^{S,NO_2}$, $\Delta N^{S,O_4}$, and I^{rel} respectively (S refers to slant). The slant columns of absorber *a* (either NO₂ or O₄) for elevation α are simulated for a single wavelength according to:

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

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:

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

Relative intensities are defined as:

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

3.2.1 Look-up tables

Look-up tables of differential slant NO_2 columns, differential slant O_4 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 NO_2 and aerosol layers, the aerosol optical thickness, the elevation and solar zenith angle. The range for the AOT is chosen to be realistic for the Netherlands. Depending on the measurement site, it may be needed to extend this range.

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 O_4 .

Note that it is demonstrated in Frieß et al., 2006 that combination of four wavelength bands (360, 477, 577, 630 nm) leads for aerosol extinction retrievals to one additional piece of information compared to a single wavelength approach. It depends on the wavelength range of the instrument used if this can be realized.

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

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 NO_2 consists of two parts: firstly to determine the effective NO_2 temperature, and secondly to derive two correction factors: one for the simulations and one for the measurements, see below. The effective NO_2 temperature is calculated as follows:

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

Table 1. Parameter values for which the look-up table was calculated. For each of these values, the look-up table contains simulated measurements of differential slant NO_2 columns, differential slant O_4 columns, and relative intensities. Multidimensional linear interpolation is used in the retrieval algorithm, in order to obtain simulated measurements in between the values for which the look-up table was calculated.

parameter	values
wavelength [nm]	477
single scattering albedo	0.90
asymmetry parameter	0.72
viewing elevation angle [°]	1, 2, 3, 4, 5, 8, 9, 15, 16, 17, 23, 30, 40, 50, 60, 70, 90
solar zenith angle [°]	0, 20, 30, 40, 50, 60, 67, 73, 74, 75, 81, 82, 85, 86, 87, 88, 89
relative azimuth angle [°]	0, 10, 20, 40, 60, 80, 100, 120, 140, 160, 180
surface temperature [°C]	0,25
surface pressure [hPa]	990,1030
partial aerosol opt. thickness A1	0.0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 1.0
partial aerosol opt. thickness A2	0.0, 0.05, 0.1, 0.2, 0.4, 1.0
partial trop. NO ₂ col. N1 $[10^{15} \text{molec cm}^{-2}]$	1,60
partial trop. NO ₂ col. N2 $[10^{15} \text{molec cm}^{-2}]$	0,60
height of A1 [km]	0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 2.4
height of N1 [km]	0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 2.4

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. $\Delta m^i_{\alpha}(\Psi)$ denotes the elevation and height-dependent differential air mass factor (elevation dependent vertical sensitivity to NO₂) which was calculated according to:

$$\Delta m_{\alpha}^{i}(\Psi) = \frac{\Delta N_{\alpha}^{S, \text{NO}_{2}, i+}(\Psi) - \Delta N_{\alpha}^{S, \text{NO}_{2}, \text{ref}}(\Psi)}{N^{V, i+} - N^{V, \text{ref}}},$$
(8)

by adding NO₂ to layer *i* (indicated by "*i*+"), relative to a background NO₂ profile (indicated by "ref"). N^V denotes the total vertical NO₂ column.

The elevation dependence of the effective NO₂ temperature is a consequence of the elevation dependence of Δm . T^i is determined using a US standard mid-latitude summer temperature profile scaled with the observed surface temperatures to have a close correspondence to the real atmosphere at the time of the MAX-DOAS observation.

To account for the differences between the actual effective NO₂ temperature and the fixed temperatures used in the look-up table simulations and in the DOAS fitting procedure, two temperature correction factors are derived: C_{α}^{abs} and C_{α}^{diff} . The first corrects the *simulated* differential slant NO₂ columns that were calculated for a fixed NO₂ cross section temperature $\sigma(T_{LUT})$, see Table 1. The second corrects the *measured* differential slant NO₂ columns that were derived from a DOAS fit based on an NO₂ cross section at a fixed temperature $\sigma(T_{fit})$ (295 K). Note that these correction factors do not compensate since the part of the measurement error induced by assuming a wrong temperature in the DOAS fit is related to the temperature dependency of the *differential* cross section, whereas the error in the simulated differential



Fig. 3. Schematic of the tropospheric aerosol and NO_2 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.

slant NO_2 columns is related to the temperature dependency of the cross section itself (see Fig. 4).

 C_{α}^{abs} is calculated at 477 nm according to:

$$C_{\alpha}^{\rm abs} = \frac{\sigma\left(T_{\rm LUT}\right)}{\sigma\left(T_{\alpha}^{\rm eff}\right)}.$$
(9)

 C_{α}^{diff} is calculated as:

$$C_{\alpha}^{\text{diff}} = \frac{\Delta\sigma\left(T_{\text{fit}}\right)}{\Delta\sigma\left(T_{\alpha}^{\text{eff}}\right)},\tag{10}$$



Fig. 4. NO₂ cross section spectrum σ at two different temperatures (Vandaele et al., 1998). The figure illustrates that a change in effective NO₂ 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 NO₂ columns, since they are derived from a DOAS fit performed with an NO₂ 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 .

using an average of several local maxima and minima of the NO₂ cross section in the DOAS spectral fitting window, one of which is indicated in Fig. 4. In a typical situation where $T^{\text{eff}} = 283$ K and $T_{\text{fit}} = T_{\text{LUT}} = 298$ K, we have $C^{\text{abs}} = 1.02$ and $C^{\text{diff}} = 0.92$.

Note that the most important aspect of the temperature correction is the use of the independent observations of the surface temperature. This allows a first order temperature correction, based on an assumed vertical profile shape. The temperature correction factors are most accurate for cases where the real NO₂ profile is adequately described by the NO₂ profile parametrization in the retrieval model, and where in addition the temperature profile is comparable to the U.S. standard profile scaled with the surface temperature. The effect of an error in the temperature profile has been tested (for the same settings as in sensitivity study F), and it was found that if the temperature of the NO₂ layer at 3-3.5 km is estimated wrong by 10°C, then the error on the partial NO₂ column retrieved for this layer (N_{N2}) is about 1%. This indicates that the errors due to the assumed temperature profile shape are small compared to the uncertainties in the NO₂ profile shape. However, errors in the profile retrieval due to a wrong temperature profile assumption are generally higher than that, due to the fact that the temperature correction factors C_{α}^{abs}

and C_{α}^{diff} are frequently determined for the wrong NO₂ profile shape. This effect is included in the results reported in the sensitivity studies in Sect. 4.

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 NO₂ parameters. As the aerosol retrieval is not completely independent of the NO₂ retrieval, due to the broad band absorption by NO₂, which is more pronounced at small elevations, an iteration is performed after the first retrieval, where an improved guess of the NO₂ profile is used in the aerosol retrieval. The initial value used for NO₂ in the first step of the algorithm (aerosol retrieval) is: $N_{N1}=15 \times 10^{15}$ molec cm⁻², $H_{N1}=0.4$ km. The initial aerosol extinction state is: $\tau_{A1}=0.5$ and $H_{A1}=0.4$ km. In the subsequent NO₂ retrieval, the first guess for NO₂ is: $N_{N1}=30 \times 10^{15}$ molec cm⁻² and $H_{N1}=0.4$ km.

The cost functions that are minimized, are:

$$\chi_{\text{aero}}^{2} = \sum_{i=1}^{5} \left(\frac{f_{sc} \cdot \Delta N_{\alpha_{i}}^{S,O_{4}} - \widehat{\Delta N_{\alpha_{i}}^{S,O_{4}}}}{\epsilon_{\alpha_{i}}^{O_{4}}} \right)^{2} + \left[\left(\frac{I_{\alpha_{i}}^{\text{rel}} - \widehat{I_{\alpha_{i}}^{\text{rel}}}}{\epsilon_{\alpha_{i}}^{\text{rel}}} \right)^{2} \right]_{\text{optional}}$$

and

$$\chi^{2}_{\text{NO}_{2}} = \sum_{i=1}^{5} \left(\frac{C_{\alpha_{i}}^{\text{diff}} \cdot \Delta N_{\alpha_{i}}^{S,\text{NO}_{2}} - C_{\alpha_{i}}^{\text{abs}} \cdot \Delta \widehat{N_{\alpha_{i}}^{S,\text{NO}_{2}}}}{\epsilon_{\alpha_{i}}^{\text{NO}_{2}}} \right)^{2}, \quad (12)$$

where ϵ to 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). 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.



Fig. 5. Examples of the ensemble of 200 retrievals of the NO₂ layer height (left) and of the NO₂ volume mixing ratio (right). Note that the right plot has a logarithmic scale on the y-axis. This example demonstrates that although the ensemble average and median of H_{N1} differ by only a small amount (4 %), which indicates that the distribution of H_{N1} is almost symmetric, the corresponding ensemble of X_{N1} can be highly asymmetric, and consequently have a large difference between median and average (42 %). For this reason, the median is used for the volume mixing ratio, see also Fig. 7.

The empirical scaling factor f_{sc} was first reported by Clémer et al. (2010), also used in Zieger et al. (2011), and found to have the approximate value of 0.8. Clémer et al. found that measured differential slant O₄ 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 O₄ columns. We did a similar study as Clémer 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 (NO₂ and O₄ 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. The perturbations are independent for each elevation and for each parameter. The final aerosol and NO2 solutions, after 200 steps, are defined by the average aerosol and NO₂ model parameters within the ensemble of retrieval outcomes. Only for the volume mixing ratio (X_{N1}) and the aerosol extinction (k_{A1}) , which are "derived parameters", and not directly fitted (Sect. 3.1), the ensemble median is used instead of the ensemble average. The reason for this is that their distributions are frequently asymmetric due to the fact that they are proportional to the reciprocal of H_{N1} and H_{A1} respectively. The skewness is especially large if H is low, and if in addition the uncertainty in H is high, as illustrated in Fig. 5. 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. The number of 200 repetitions is selected to have a reasonable description of the ensemble properties and at the same time to have a reasonable computing time. Without special efforts to optimize for speed, a performance was realized of 16 seconds for 200 runs. For a typical day with 12 hours of observation, with an analysis for each half hour, the total analysis time would be 6 minutes. Although more runs would lead to a more accurate distribution for each retrieval parameter, tests have shown that the average and extremes of the distribution are almost unaffected by increasing the number of repetitions to 2000. For fewer runs (e.g. 20), these values become unstable.

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 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 ($\chi^2_{\nu,median}$), based on 200 runs, is a more reliable quantity from which to judge the appropriateness of the retrieval model. Note that "reduced", denoted with ν , here refers to a correction for the

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 10¹⁶ 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}
В	2	0	0.8	n.a.	1	0.2	0	0.05-2.3	n.a.	1	0–15 %	$M_{1a}^{1\ddot{n}}, M_{1a}^{2\ddot{n}}$
С	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}
Е	1.5	0	0.6	n.a.	1	0.2	0.2	0.6	0.05-20	1	0%	M_{1a}^{1n}, M_{2a}^{1n}
F	0	1	n.a.	0.05–20	1	0.2	0	0.6	n.a.	1	0–15 %	$M_{1a}^{1\ddot{n}}, M_{1a}^{2\ddot{n}}$

Table 3. Comparison of NO₂ volume mixing ratios derived from in-situ monitors and MAX-DOAS. The average difference is defined as (MAX-DOAS (y) minus in-situ (x)), and the linear fit parameters are defined for the in-situ values on the horizontal and the MAX-DOAS values on the vertical axis. The upper part of the table shows the results of the comparison when each observation is considered independent, the bottom part shows the results when all observations (within the five days) that fall within the same hour of the day are averaged prior to the statistical analysis (see Fig. 15).

Retrieval Model	Correlation	Av. x [ppb]	Av. y [ppb]	Av. Diff. [ppb]	Slope	Intercept [ppb]
one NO ₂ layer	0.75	4.69	3.85	-0.84	1.14	-1.51
two NO ₂ layers	0.80	4.69	4.77	0.07	1.31	-1.39
selection based on $\chi^2_{NO_2}$	0.79	4.69	4.73	0.04	1.31	-1.43
(averaged) one NO ₂ layer	0.93	4.66	3.82	-0.85	0.83	-0.07
(averaged) two NO ₂ layers	0.94	4.66	4.75	0.10	1.10	-0.34
(averaged) selection based on $\chi^2_{NO_2}$	0.94	4.66	4.70	0.04	1.09	-0.36

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 $\chi^2_{\nu,median}$ 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 $\chi^2_{\nu,median}$ is illustrated in the next section. For simplicity we will use the notation $\chi^2_{NO_2}$ or χ^2_{aer} in the remainder of this work, meaning $\chi^2_{\nu,median,NO_2}$ and $\chi^2_{\nu,median,aerosol}$, 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, i.e. homogeneously mixed NO₂ and aerosol layers (sensitivity studies A and B). Here we also

study the effect of noise. In sensitivity studies C and D we perform tests to see the effect on the retrieval accuracy of inhomogeneous mixing of NO₂ and aerosols in the lowest layers, whereas homogeneous mixing is assumed in the retrieval model. Finally we test the sensitivity to elevated layers of aerosols (sensitivity study E), including the role of relative intensities in the cost function, and study how effective the algorithm retrieves elevated NO₂ layers (sensitivity study F).

In most sensitivity studies below, just one aerosol layer was used in the retrieval models (M_{1a}^{1n} , M_{1a}^{2n}), only in the study of elevated aerosol layers a second aerosol layer was added to the retrieval model (M_{2a}^{1n}). All sensitivity studies were done for a solar zenith angle of 40°, and a relative azimuth angle of 180°, which is representative for summer time measurements with an instrument located in the Netherlands, looking towards the North. The dependence on the solar position is not further studied. It may however be expected that this geometry is relative advantageous to determine aerosol extinction and NO₂ profile characteristics because retrievals for a relatively small relative azimuth angle (< 60°) would be more challenging due to the increased sensitivity to the aerosol phase function, which is fixed in our approach.



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).

4.1 Homogeneous boundary layer

In sensitivity study A we simulated measurements with various heights for the lowest NO₂ layer (N1), none of which corresponds exactly to one of the heights on the look-up table grid. The aerosol layer height (H_{A1}) was fixed at 0.8 km. All other parameters were as the fixed parameters in the lookup table (Sect. 3.2.1), except for the temperature (20 °C) and pressure (1013 hPa). The results are shown in Fig. 7. The top row shows relatively accurate retrievals for the one NO₂ layer model (M_{1a}^{1n}), of the NO₂ layer height, tropospheric NO₂ column and NO₂ mixing ratio. Increasing the level of Gaussian noise slightly affects the ensemble average of the tropospheric NO₂ column retrieval, leads to a small systematic underestimation of the NO₂ layer height and an overestimation of the NO₂ volume mixing ratio, 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 parametrize 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-parametrization 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 $\chi^2_{NO_2}$. For both constituents, it can be seen that values of S < 1 lead to an 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_{N1} 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



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 (which are almost covered by the solid red lines) indicate prescribed values in the sensitivity study, i.e. the truth in the simulation.



Fig. 8. Sensitivity study C (top row) and D (bottom row): inhomogeneous boundary layer distributions of aerosols and NO_2 . 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.

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 $\chi^2_{NO_2}$. High values for $\chi^2_{NO_2}$ 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 0.6 km and partial AOT = 0.2. These choices for the elevated aerosol profile are considered to be realistic for the Netherlands, where the mean total aerosol extinction optical thickness observed by the AERONET sun photometer in Cabauw (2007-2009) is 0.26 ± 0.20 ($\lambda = 440$ nm). The vertical extent of the elevated layer (0.1 km) was considered realistic for a residual aerosol layer and in addition much less relevant than the vertical extent of aerosol layers starting at the surface. The NO₂ profile here consists of a block profile extending from the surface, with a height of 0.4 km and an NO₂ column of $1.5 \times 10^{16} \text{ molec cm}^{-2}$.

Figure 9 shows the results of this sensitivity study. First of all it may be concluded from these results that the effect of elevated aerosol layers on the tropospheric NO_2 column is relatively small, independent of the aerosol retrieval model and cost function. Secondly, it is clear from this study that the use of relative intensities in the cost function significantly improves the aerosol optical thickness retrieval, especially in the double aerosol layer model where the addition of relative intensities leads to a better separation of low and high aerosols; this was already found by Frieß et al. (2006). Despite this improvement, Fig. 9 also demonstrates that several other parameters are negatively affected by the inclusion of relative intensities in the cost function. The second and third column of Fig. 9 show the effect of the different aerosol cost functions on the retrieval of aerosol extinction and NO₂ volume mixing ratio. Here we see that using the two layer aerosol model in combination with relative intensities improves the aerosol extinction and NO2 volume mixing ratio for low elevated aerosol layers (< 3 km) with respect to the O₄ based aerosol retrievals, but that there is a larger inaccuracy of these two parameters for high elevated aerosol layers (> 5 km, even in the two-layer aerosol retrieval model. The increased sensitivity to high aerosol layers, due to the use of relative intensities, causes the retrieval to put aerosols in the highest possible model layer, which is either A1 (retrieval model M_{1a}^{1n}) or A2 (retrieval model M_{2a}^{1n}). In both cases the resulting aerosol distribution in the model does not correspond to the reality. This leads to a discrepancy between O₄ differential slant columns simulated for the sensitivity study and those in the look-up table. This discrepancy is larger than for the relative intensities because O4 measurements contain more information on the exact vertical distribution of aerosols (in the lowest kilometers). Especially in the single aerosol layer model, this leads to high values of χ^2_{aer} .

Altogether we conclude that from the perspective of aerosol profile retrieval alone, it is advantageous to use a second aerosol layer, and possibly a third at 10 km, together with relative intensities in the cost function since only then elevated aerosol layers can accurately be retrieved. Please note that this aerosol profile retrieval, is only possible under cloud free conditions. From the perspective of NO₂ 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 NO₂ 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 NO₂

Here we test the effectiveness 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 NO₂ layer with a vertical extent of 0.1 km and with a partial NO₂ column of 1×10^{16} moleccm⁻² placed at different heights. The aerosol profile is fixed in this study: a block



Fig. 9. Sensitivity study E (elevated aerosol layers). The top row shows aerosol retrievals based solely on differential slant column measurements of O_4 . The retrievals shown in the bottom row are done with a cost function where not only O_4 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.

profile with a height of 0.6 km and AOT = 0.2, see also Fig. 6. The results of this sensitivity study are shown in Fig. 10.

The one NO₂ layer model underestimates NO₂ already by more than 30 % if it is located at 1 km, and this underestimation rapidly decreases with altitude. The two NO₂ layer model is clearly more sensitive to elevated NO₂, underestimating the partial column only > 3 km and even overestimating if it is below <3 km (due to the choice to locate the second NO₂ layer between 3 and 3.5 km in the model). Note that relatively high overestimation (up to 40 % of the tropospheric NO₂ column) only applies to that part of the total tropospheric NO₂ column that is actually found in an elevated layer; in this study no NO₂ was located near the surface.

If the second NO₂ 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 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 behavior of $\chi^2_{NO_2}$ 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 $\chi^2_{NO_2}$ values show a much stronger dependence. The lower absolute values of $\chi^2_{NO_2}$ 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 $\chi^2_{NO_2}$, see Eq. (12).

Not only the absolute level of the $\chi^2_{NO_2}$ curves changes as a result from noise, but, more interestingly, also the shape. Especially for the two NO₂ layer model (M^{2n}_{1a}) it is clear that the minimum of $\chi^2_{NO_2}$ 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. This implies



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.

that for realistic situations, a-priori assumptions about the free tropospheric part of the NO_2 profile are critical. Flexible a-priori assumptions allow more accurate retrievals, but frequently with low precision. Less flexible a-priori assumptions may have a higher precision, but only for specific cases where the a-priori assumption corresponds to the real situation at the time of measurement.

To decide for a given measurement situation which retrieval model is preferable, the one or the two NO₂ layer retrieval model (or alternative parametrizations), it is best to look at the model with the lowest value of $\chi^2_{NO_2}$. 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.

A final conclusion that may be drawn from Fig. 10 is that both the single and double NO_2 layer retrieval have little, but still some, sensitivity to NO_2 to the low stratosphere (a typical stratospheric NO_2 profile may start at approximately 10 km and peak at around 25 km, see Hendrick et al., 2004).

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

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

Retrieval approaches to derive NO₂ profile information from MAX-DOAS observations can roughly be separated in those using the "optimal estimation method" (OE-method) (Rodgers, 2000) and those using a "parametrized profile method" (PP-method). In the following, we refer to the OEmethod specifically as those implementations of OE which use a profile parametrization for aerosols and NO₂ that is defined for a relatively high number of independent layers, each with a vertical extent of typically 200 meters (see e.g. Frieß et al. (2006) and Clémer et al. (2010)). With the PP-method, we here refer to retrieval approaches where the vertical profile (of aerosols and/or NO_2) is parametrized by a low number of well-selected parameters, which may have different dimensions, such as a column amount and a scale height (see this paper, Sinreich et al. (2005), Li et al. (2010) and Wagner et al. (2011)). The number of selected parameters is usually approximately equal to a realistic estimate of the number of independent pieces of information contained in the MAX-DOAS measurements, and may vary between 1 (overdetermined) and no more than 5 (under-determined). The solution is found by a least-squares minimization of differences between the measurements and forward simulations.

A major advantage of OE-method is the flexibility to retrieve a wide range of different profile shapes. In the here presented sensitivity study it has been shown that the MAX-DOAS measurements are sensitive to the profile shapes (of aerosol extinction and NO₂) especially for the lowest part of the boundary layer. In this part of the troposphere, such shapes can be retrieved using the OE-method without assuming them in the a-priori. A disadvantage of the OE-method is that under some conditions the retrievals tend to be unstable and consequently yield profiles showing unrealistic oscillations. This effect is highest in that part of the troposphere (typically above 1-2 km) where the MAX-DOAS sensitivity functions (Fig. 1) are parallel, and therefore do not contribute with independent pieces of information. This height significantly decreases for higher AOT.

In this study, where the PP-method is used, it has been shown that a too much simplified description of the boundary layer profile shape, e.g. assuming homogeneous distribution of aerosols and NO₂, may lead to errors in the retrieval of both boundary layer and free tropospheric NO₂. For PP-approaches this problem may be solved by adding a third free parameter to describe the NO_2 and aerosol boundary layer profiles, such as the parametrization as used in the sensitivity studies, using the shape factor S. A similar approach is taken by Wagner et al. (2011). The need for nonhomogeneous boundary layer profile descriptions is also supported by Morgan et al. (2010) where aerosol extinction profiles are reported that typically show an increase with altitude in the boundary layer.

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

With respect to the free troposphere both approaches are equally limited by fact that the vertical sensitivity functions of all elevation viewing angles are flat, and in addition decrease to zero towards the top of the free troposphere. This implies that for both approaches a-priori assumptions are critical in this part of the atmosphere. When the NO₂ radiosonde (Sluis et al., 2010) will be further developed and validated, a long-term data set of profiles NO₂ can be used to make a realistic, well-founded a-priori assumption for free tropospheric NO₂. Such an assumption would probably have to take seasonal variations into account.

4.4.1 Consequences for satellite validation

MAX-DOAS observations of tropospheric NO₂ can be used for validation of satellite observations. A comparison of individual tropospheric column measurements of satellite and MAX-DOAS should take into account the differences in assumed profile shapes and the difference in vertical sensitivities, as described by Rodgers and Connor, 2003. For example, the profile shape assumed for the OMI tropospheric NO₂ product (DOMINO) is taken from the TM4 chemistry transport model (Boersma et al., 2011). For MAX-DOAS a basic profile shape can be retrieved from the observations themselves, but, as noted above, the retrieval strongly depends on a-priori assumptions. Space-borne observations are more sensitive to NO_2 in the free troposphere than to NO_2 in the boundary layer (see Fig. 1 in Boersma and Eskes, 2003), whereas the opposite is the case for ground based MAX-DOAS observations (Fig. 1 shown above). Flexible a-priori assumptions are the only way to accurately retrieve free tropospheric NO₂ if it is present. However, for most of the time this will not be the case: the boundary layer partial NO₂ column is usually much higher than the free tropospheric partial column. As a consequence, flexible a-priori assumptions for the free troposphere will for the majority of cases lead to less accurate and less precise retrievals.

Long term data sets of MAX-DOAS profile observations can be used to validate the profile description generated by chemistry transport models, which are used as an input for the satellite retrieval. For this application it is especially important that the MAX-DOAS profile retrievals produce realistic first order profile descriptions for NO₂ in the boundary layer.

5 Application to measurements performed at the CINDI campaign

The single and double NO₂ layer retrieval algorithms are applied 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 et al., 2011, and Roscoe et al., 2010).

5.1 Retrieval results for selected days

We have selected six days (18, 23, 24, 30 June, 2 and 4 July 2009) from the CINDI campaign to illustrate the outcome of the retrieval algorithm for three parameters: aerosol optical thickness, tropospheric NO₂ columns, and average NO₂ volume mixing ratio (see Fig. 11). The last five days are "category A" days according to Piters et al. 2011, and for this reason are most optimal for the retrieval approach which assumes cloud free conditions. In practice, such conditions occurred mostly in the mornings. The algorithm is applied also under cloudy conditions, to illustrate the effect of such conditions on the accuracy of the retrieval (which decreases significantly, especially for the two layer retrieval model). The in-situ observations show that the five category A days have quite the same behavior in terms of the temporal evolution of the volume mixing ratio measured at the surface. June 18 is shown in addition as an example of a day with an a-typical behavior in this respect. 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 χ^2_{NO2} 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 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



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 $\chi^2_{NO_2}$, 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.

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 2.0 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. In addition, external stray light levels are higher at small relative azimuth angles. This might also contribute to larger differences between AERONET and MAX-DOAS aerosol optical thickness. 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.

The retrievals of tropospheric NO₂ columns (Fig. 11), are relatively stable in time and internally consistent in the mornings, but tend to have larger uncertainties in the afternoons. As noted above, discontinuities in the AERONET data (first column of Fig. 11) indicate the presence of clouds. These discontinuities sometimes coincide with high uncertainties in the tropospheric NO₂ column. For periods in which the frequency of AERONET observations is high (continuous cloud free periods), the uncertainty estimates for N_{Tr} are relatively low. Scattered clouds lead to a significant increase in the uncertainty estimate of the measurements, which is defined in Sect. 2. In combination with the double layer retrieval model, which is less stable than the single layer model, this may lead to large uncertainties in the tropospheric NO₂ column.

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 24 June, 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_{N1}) since the NO₂ column – the other model parameter from which X_{N1} 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 for NO₂ 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. Does the selection of the two layer model indicate that NO₂ is present above the boundary layer? For most days the answer cannot be given by the lidar measurements, as they do not go high enough. For 24 June however, evidence for the presence of an elevated NO₂ layer is also found with the NO₂ radiosonde (Sluis et al. (2010), Fig. 11c), launched around 10:30 UTC. Note that the large difference with the NO₂ sonde on 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., 2012), 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



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). Note that NO₂ retrieved in the second layer of the two layer retrieval model should be interpreted as: NO₂ above approximately 1 km, with unknown altitude (see Sect. 3.1).

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.

The following procedure was followed to select a pair of partial tropospheric NO₂ measurements out of each simultaneous measurement of MAX-DOAS and lidar: First a choice was made between the single and double NO₂ layer MAX-DOAS retrieval models: the retrieval model with the lowest value of $\chi^2_{NO_2}$ was selected. Then, if the single NO₂ layer model was selected, the retrieved NO₂ layer height (H_{N1}) was compared with the maximum height up to which the lidar profile was reported ($H_{\text{lidar}}^{\text{max}}$). When this maximum height was lower than H_{N1} , then the fraction of the tropospheric NO₂ column of the MAX-DOAS retrieval was determined that was below $H_{\text{lidar}}^{\text{max}}$ and the fractional column was used in the comparison. For $H_{\text{lidar}}^{\text{max}} > H_{N1}$, nothing was changed.



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.

A similar procedure could not be applied if the double NO₂ layer model was selected due to the uncertain height of the NO₂ that is retrieved in the second layer. For example, NO₂ retrieved in the second layer could in reality be located at around 4 km, but just as well at 1 km: the information is not included in the measurements, as discussed in Sect. 3.1. We therefore made the pragmatic choice not to change the retrieved total tropospheric NO₂ column from the MAX-DOAS retrieval, as in the case of the single NO2 layer model, but only to select the pair of MAX-DOAS and lidar NO₂ columns if the maximum reported *lidar* height was above 1.5 km. This procedure is meant to exclude cases where the MAX-DOAS retrieval indicates possible elevated NO2 layers (because the double NO2 layer model has the lowest value of $\chi^2_{NO_2}$) and where the lidar measurements stop at relative low altitude.

An example of a lidar NO_2 profile is shown in Fig. 13. An interpolation method needs to be defined in order to calculate partial NO_2 column from the lidar profile. The lidar profile is defined for discrete vertical layers that may or may not overlap. For each of those layers the NO_2 volume mixing ratio and its uncertainty is reported in the lidar data files. We applied the following interpolation procedure to obtain a best, lower and upper estimate of the partial NO_2 column: for the best estimate, linear interpolation was used in between heights where either no volume mixing ratio was reported, or where two regions showed overlap. The lowermost profile layer was extended to the surface without changing the volume mixing ratio. The same method was applied for 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 $(0.1 \pm 0.2 \times 10^{15} \text{ molec cm}^{-2})$, and slope of linear fit (0.92 ± 0.05) indicate that the two measurement techniques compare quite well. A bi-variate fitting method was used, where the squared orthogonal distance of each x-y point to the fitted line was minimized. Errors were taken into account by varying each x and each y within its uncertainty estimate (using random Gaussian noise) and repeating the fit procedure a thousand times (the fit results did not change significantly when this number would either be ten times lower or ten times higher). The resulting fit parameters were found to change as expected after the x- and y-axis were interchanged. It is remarkable that the slope found in this comparison is comparable to the slope reported in Roscoe et al., 2010 (their Fig. 6), where differential slant column measurements from the KNMI instrument used in this study are compared to an average of other MAX-DOAS instruments used at the CINDI campaign. If the MAX-DOAS measurements used in this study would be artificially corrected using those results, then a slope would have been found of almost one, and a small intercept. Note that the result of this lidar versus MAX-DOAS comparison 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 NO_2 and the average NO_2 volume mixing



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 χ^2_{NO2} , see text. The solid line shows a linear fit. 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).

ratios in the lower NO_2 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 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. 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 a partial explanation for the systematic underestimation of the NO₂ volume mixing ratio found in their study in the morning hours.



Fig. 15. Diurnal cycle of the 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 for a composite retrieval approach where the choice between the one and two NO₂ layer retrieval model is based on the lowest value of $\chi^2_{NO_2}$. The thin vertical lines indicate the root mean square error.

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

With respect to the averaged diurnal evolution, a good agreement is found between the in-situ observations and the MAX-DOAS derived NO₂ volume mixing ratios. The general pattern of the diurnal evolution - showing a dilution caused by thermal convection -is captured best by the two NO₂ layer retrieval model and the combined product of the two models (where for each observation the model selection is based on $\chi^2_{NO_2}$). Those two retrieval products agree with the in-situ observations within their uncertainty range. The one layer model tends to underestimate the volume mixing ratios a little: the MAX-DOAS values are 18% lower than the in-situ values. For the two NO₂ layer model a correlation is found of 0.94 and an average difference of 0.10 ppb. The combined product has the same correlation, and an even smaller average difference: 0.04 ppb. The slope of the linear fit, obtained with the same fitting method as used in the comparison between MAX-DOAS and lidar (Sect. 5.2.1), is 1.10 for the two layer model.

The comparison based on individual observations shows larger differences, see Table 3. The morning hours sometimes show an over- or underestimation relative to the in-situ monitor (Fig. 11). This effect in the morning is not always due to clouds or measurement noise in combination with low NO₂ layers, see the discussion above, but may also be due to errors in the assumed profile shapes for aerosols and NO₂. For compact NO₂ layers close to the surface (which are typical for the morning), volume mixing ratios can only be retrieved accurately from the MAX-DOAS measurements if there is an almost exact agreement between the real profile shape and the profile shape assumed in the retrieval model (see Sect. 4).

6 Summary and conclusions

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 parametrize the aerosol and NO₂ profile. The retrieval model 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 model versions were 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 retrieval uncertainties.

Sensitivity studies were performed to test the retrieval accuracy for various levels of noise, NO₂ and aerosol boundary layer profiles being different from those assumed in the retrieval model, and elevated NO₂ and aerosol layers. This led to the following conclusions:

- If NO₂ is present only in a homogeneously mixed boundary layer (BL), then the amount of NO₂ in this BL, and its height, can be retrieved accurately. The effect of noise is different in the one and two NO₂ layer model. In the one layer model, noise does not affect the accuracy of the tropospheric NO₂ column, but leads to an underestimation of the NO₂ layer height. In the two layer model, noise leads to a small overestimation of the tropospheric NO₂ column, which is related to the fact that NO₂ is retrieved in the upper model layer N2, although in the simulations it was only present in the lowest layer N1.
- If NO₂ is also present in the free troposphere, then its presence will be confirmed by the retrieval of the two NO₂ layer model, even for high measurement uncertainties. However, the altitude of this elevated NO₂ layer can only be determined for high measurement accuracy, and accurate aerosol extinction retrieval. The 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 %.

- NO₂ retrieved in the second layer of the two layer model should not be interpreted as NO₂ between 3 and 3.5 km, but instead as NO₂ above approximately 1 km with unknown altitude.
- When using the two NO₂ layer retrieval model, elevated NO₂ layers are frequently found for the wrong reason, i.e. not because there is an elevated NO₂ layer in the real atmosphere, but due to a low signal to noise ratio, or due to a BL profile parametrization for aerosols or NO₂ that does not correspond to the real situation. This effect may lead to an error in the tropospheric NO₂ column up to 10%. Probably an optimal estimation approach would be more accurate for a wider range of aerosol and NO₂ BL profile shapes.
- Frequent retrieval of "fictitious" elevated NO₂ layers is unwanted, especially from the perspective of satellite validation. MAX-DOAS NO₂ profile retrieval approaches should therefore focus first of all on the BL. Retrieval models assuming homogeneous distribution of aerosols and NO₂ in the BL are too much restricted in scope. It is advised to use BL profile parametrizations similar to those in the sensitivity studies, based for example on an amount, a height and a shape description (see also Wagner et al. (2011)).
- Accurate MAX-DOAS retrieval of NO₂ in the free troposphere is possible only when (i) there are no clouds, (ii) the AOT is sufficiently low, (iii) the aerosol extinction and NO₂ profiles are sufficiently constant in time, (iv) the signal to noise ratio of the MAX-DOAS measurements is sufficiently high, (v) the BL profile parametrizations for aerosols and NO₂ adequately describe the real profile shapes, and (vi) the vertical temperature and pressure profiles correspond to those in the retrieval model. Only when these conditions are fulfilled, then it may be possible to retrieve the height and concentration of a free tropospheric NO2 layer. The accuracy and precision for retrieval of NO2 in the free troposphere therefore strongly depend on a-priori assumptions. This conclusion is not limited to the retrieval approach chosen in this work, but equally applies to retrieval methods based on optimal estimation.
- The use of relative intensity measurements (in addition to O_4 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 O_4 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 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, but only under ideal conditions (see above). 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 NO_2 columns and profile shapes from NO_2 lidar measurements, and NO_2 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 profile shapes 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.
- 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 0.94, and an average difference of 0.04 ppb.

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 et al. (2011).

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References

- Anderson, G. P., Clough, S. A., Kneizys, F. X., Chetwynd, J. H., and Shettle, E. P.: Atmospheric Constituent Profiles (0–120 km), Air Force Geophysics Laboratory Report, AFGL-TR-86-0-10, Environmental Research paper no. 954, 1986.
- Berkhout, A. J. C., van der Hoff, G. R., Bergwerff, J. B., Gast, L. M., Peters, E., and Swart, D. P. J.: Comparison of nitrogen dioxide measurements by lidar and by chemiluminescence monitors, in preparation, Atmos. Meas. Tech., 2012.

- Blond, N., Boersma, K. F., Eskes, van der A, R. J., Van Roozendael, M., De Smedt, I., Bergametti, G., and Vautard, R.: Intercomparison of SCIAMACHY nitrogen dioxide observations, in situ measurements and air quality modeling results over Western Europe, J. Geophys. Res., 112, D10311, doi:10.1029/2006JD007277, 2007.
- Eskes, H. J. and Boersma, K. F.: Averaging kernels for DOAS totalcolumn satellite retrievals, Atmos. Chem. Phys., 3, 1285–1291, doi:10.5194/acp-3-1285-2003, 2003.
- Boersma, K. F., Eskes, H. J., and Brinksma, E. J.: Error analysis for tropospheric NO2 retrieval from space, J. Geophys. Res., 109, D04311, doi:10.1029/2003JD003962, 2004.
- Boersma, K. F., Jacob, D. J., Trainic, M., Rudich, Y., De Smedt, I., Dirksen, R., and Eskes, H. J.: Validation of urban NO₂ concentrations and their diurnal and seasonal variations observed from the SCIAMACHY and OMI sensors using in situ surface measurements in Israeli cities, Atmos. Chem. Phys., 9, 3867–3879, doi:10.5194/acp-9-3867-2009, 2009.
- Boersma, K. F., Eskes, H. J., Dirksen, R. J., van der A, R. J., Veefkind, J. P., Stammes, P., Huijnen, V., Kleipool, Q. L., Sneep, M., Claas, J., Leitão, J., Richter, A., Zhou, Y., and Brunner, D.: An improved tropospheric NO₂ column retrieval algorithm for the Ozone Monitoring Instrument, Atmos. Meas. Tech., 4, 1905– 1928, doi:10.5194/amt-4-1905-2011, 2011.
- Bogumil, K., Orphal, J., Homann, T., Voigt, S., Spietz, P., Fleischmann, O. C., Vogel, A., Hartmann, M., Kromminga, H., Bovensmann, H., Frerick, J., and Burrows, J. P.: Measurements of Molecular Absorption Spectra with the SCIAMACHY Pre-Flight Model: Instrument Characterization and Reference Data for Atmospheric Remote-Sensing in the 230–2380 nm Region, J. Photochem. Photobiol. A., 157, 167–184, 2003.
- Brinksma, E. J., Pinardi, G., Volten, H., Braak, R., Richter, A., Schoenhardt, A., Van Roozendael, M., Fayt, C., Hermans, C., Dirksen, R. J., Vlemmix, T., Berkhout, A. J. C., Swart, D. P. J., Oetjes, H., Wittrock, F., Wagner, T., Ibrahim, O., de Leeuw, G., Moerman, M., Curier, R. L., Celarier, E. A., Cede, A., Knap, W. H., Veefkind, J. P., Eskes, H. J., Allaart, M., Rothe, R., Piters, A. J. M., and Levelt, P. F.: The 2005 and 2006 DANDELIONS NO2 and aerosol intercomparison campaigns, J. Geophys. Res., 113, D16S46, doi:10.1029/2007JD008988, 2008.
- Chan, A. W. H., Chan, M. N., Surratt, J. D., Chhabra, P. S., Loza, C. L., Crounse, J. D., Yee, L. D., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Role of aldehyde chemistry and NO_x concentrations in secondary organic aerosol formation, Atmos. Chem. Phys., 10, 7169–7188, doi:10.5194/acp-10-7169-2010, 2010.
- Chance, K. and Spurr, R. J. D.: Ring effect studies: Rayleigh scattering including molecular parameters for rotational Raman scattering, and the Fraunhofer spectrum, Appl. Opt., 36, 5224–5230, 1997.
- Clémer, K., Van Roozendael, M., Fayt, C., Hendrick, F., Hermans, C., Pinardi, G., Spurr, R., Wang, P., and De Mazière, M.: Multiple wavelength retrieval of tropospheric aerosol optical properties from MAXDOAS measurements in Beijing, Atmos. Meas. Tech., 3, 863–878, doi:10.5194/amt-3-863-2010, 2010.
- Crutzen, P.: The influence of nitrogen oxides on the atmospheric ozone content, Quart. J. Roy. Meteor. Soc., 96, 320–325, 1970.
- De Haan, J. F., Bosma, P. B., and Hovenier, J. W.: The adding method for multiple scattering calculations of polarized light, Astron. Astrophys., 183, 371–393, 1987.

- Fayt, C., De Smedt, I., Letocart, V., Merlaud, A., Pinardi, G., and Van Roozendael, M.: QDOAS Software user manual, http: //uv-vis.aeronomie.be/software/QDOAS/index.php, 2011.
- Frieß U., Monks, P. S., Remedios, J. J., Rozanov, A., Sinreich, R., Wagner, T., and Platt, U.: MAX-DOAS O4 measurements: A new technique to derive information on atmospheric aerosols: 2. Modeling studies, J. Geophys. Res., 111, D14203, doi:10.1029/2005JD006618, 2006.
- Greenblatt, G. D., Orlando, J. J., Burkholde, J. B., and R., R. A.: Absorption Measurements of Oxygen Between 330 and 1140 nm, J. Geophys. Res., 95, D11, 18577–18582, doi:10.1029/2005JD006618, 1990.
- Hains, J., Boersma, K. F., Kroon, M., and Dirksen, R. J.: Testing and Improving OMI DOMINO Tropospheric NO2 Using Observations from the DANDELIONS and INTEX-B Validation Campaigns, J. Geophys. Res., 115, D05301, doi:10.1029/2009JD012399, 2010.
- Hendrick, F., Barret, B., Van Roozendael, M., Boesch, H., Butz, A., De Mazière, M., Goutail, F., Hermans, C., Lambert, J.-C., Pfeilsticker, K., and Pommereau, J.-P.: Retrieval of nitrogen dioxide stratospheric profiles from ground-based zenith-sky UV-visible observations: validation of the technique through correlative comparisons, Atmos. Chem. Phys., 4, 2091–2106, doi:10.5194/acp-4-2091-2004, 2004.
- Hermans, C.: O₄ absorption cross-sections, http://spectrolab. aeronomie.be/o2.htm.
- Hönninger, G., von Friedeburg, C., and Platt, U.: Multi axis differential optical absorption spectroscopy (MAX-DOAS), Atmos. Chem. Phys., 4, 231–254, doi:10.5194/acp-4-231-2004, 2004.
- Irie, H., Kanaya, Y., Akimoto, H., Iwabuchi, H., Shimizu, A., and Aoki, K.: First retrieval of tropospheric aerosol profiles using MAX-DOAS and comparison with lidar and sky radiometer measurements, Atmos. Chem. Phys., 8, 341–350, doi:10.5194/acp-8-341-2008, 2008a.
- Irie, H., Kanaya, Y., Akimoto, H., Tanimoto, H., Wang, Z., Gleason, J. F., and Bucsela, E. J.: Validation of OMI tropospheric NO₂ column data using MAX-DOAS measurements deep inside the North China Plain in June 2006: Mount Tai Experiment 2006, Atmos. Chem. Phys., 8, 6577–6586, doi:10.5194/acp-8-6577-2008, 2008.
- Irie, H., Takashima, H., Kanaya, Y., Boersma, K. F., Gast, L., Wittrock, F., Brunner, D., Zhou, Y., and Van Roozendael, M.: Eight-component retrievals from ground-based MAX-DOAS observations, Atmos. Meas. Tech. Discuss., 4, 639–690, doi:10.5194/amtd-4-639-2011, 2011.
- Knap, W.: Basic measurements of radiation at station Cabauw (2009-06), doi:10.1594/PANGAEA.669511, 2009.
- Levelt, P. F., van den Oord, G. H. J., Dobber, M. R., Mälkki, A., Visser, H., de Vries, J., Stammes, P., Lundell, J., and Saari, H.: The Ozone Monitoring Instrument, IEEE Trans. Geo. Rem. Sens. (Special Issue on the EOS-Aura mission), 44, 1199–1208, 2006.
- Li, X., Brauers, T., Shao, M., Garland, R. M., Wagner, T., Deutschmann, T., and Wahner, A.: MAX-DOAS measurements in southern China: retrieval of aerosol extinctions and validation using ground-based in-situ data, Atmos. Chem. Phys., 10, 2079– 2089, doi:10.5194/acp-10-2079-2010, 2010.
- Morgan, W. T., Allan, J. D., Bower, K. N., Esselborn, M., Harris, B., Henzing, J. S., Highwood, E. J., Kiendler-Scharr, A., McMeeking, G. R., Mensah, A. A., Northway, M. J., Osborne,

S., Williams, P. I., Krejci, R., and Coe, H.: Enhancement of the aerosol direct radiative effect by semi-volatile aerosol components: airborne measurements in North-Western Europe, Atmos. Chem. Phys., 10, 8151–8171, doi:10.5194/acp-10-8151-2010, 2010.

- Nelder, J. A. and Mead, R.: A simplex method for function minimization, Computer Journal, 7, 308–313, 1965.
- Pikelnaya, O., Hurlock, S. C., Trick, S., and Stutz, J.: Intercomparison of multiaxis and long-path optical absorption spectroscopy measurements in the marine boundary layer, J. Geophys. Res., 112, D10S01, doi:10.1029/2006JD007727, 2007.
- Piters, A., Boersma, K. F., Kroon, M., Hains, J. C., Van Roozendael, M., Wittrock, F., Abuhassan, N., Adams, C., Akrami, M., Allaart, M. A. F., Apituley, A., Bergwerff, J. B., Berkhout, A. J. C., Brunner, D., Cede, A., Chong, J., Clémer, K., Fayt, C., Frieß, U., Gast, L. F. L., Gil-Ojeda, M., Goutail, F., Graves, R., Griesfeller, A., Grossmann, K., Hemerijckx, G., Hendrick, F., Henzing, B., Herman, J., Hermans, C., Hoexum, M., van der Hoff, G. R., Irie, H., Johnston, P. V., Kanaya, Y., Kim, Y. J., Klein Baltink, H., Kreher, K., de Leeuw, G., Leigh, R., Merlaud, A., Moerman, M. M., Monks, P. S., Mount, G. H., Navarro-Comas, M., Oetjen, H., Pazmino, A., Perez-Camacho, M., Peters, E., du Piesanie, A., Pinardi, G., Puentedura, O., Richter, A., Roscoe, H. K., Schönhardt, A., Schwarzenbach, B., Shaiganfar, R., Sluis, W., Spinei, E., Stolk, A. P., Strong, K., Swart, D. P. J., Takashima, H., Vlemmix, T., Vrekoussis, M., Wagner, T., Whyte, C., Wilson, K. M., Yela, M., Yilmaz, S., Zieger, P., and Zhou, Y.: The Cabauw Intercomparison campaign of Nitrogen Dioxide Measuring Instruments (CINDI): design, execution and early results, Atmos. Meas. Tech. Discuss., 2011.
- Platt, U. and Stutz, J.: Differential Optical Absorption Spectroscopy, Springer-Verlag Berlin Heidelberg, 2008.
- Pommereau, J. P. and Goutail, F.: O₃ and NO₂ ground based measurements by visible spectrometry during Arctic winter and spring 1988, Geophys. Res. Lett., 15, 891–894, doi:10.1029/GL015i008p00891, 1988.
- Richter, A. and Burrows, J. P.: Tropospheric NO2 From Gome Measurements, Adv. Space Res., 29, 1673–1683, 2002.
- Richter, A., Begoin, M., Hilboll, A., and Burrows: An improved NO₂ retrieval for the GOME-2 satellite instrument, Nature, 437, 129–132, 2005.
- Richter, A., Burrows, J. P., Nuess, H., Ganier, C., and Niemeier, U.: Increase in tropospheric nitrogen dioxide over China observed from space, Atmos. Meas. Tech. Discuss., 4, 213–246, doi:10.5194/amtd-4-213-2011, 2011.
- Rodgers, C. D.: Inverse methods for atmospheric sounding: Theory and Practice, Ser. Atmos. Oceanic Planet. Phys., World Scientific Publishing, 2000.
- Rodgers, C. D. and Connor, B. J.: Intercomparison of remote sounding instruments, J. Geophys. Res., 4116, doi:10.1029/2002JD002299, 2003.
- Roscoe, H. K., Van Roozendael, M., Fayt, C., du Piesanie, A., Abuhassan, N., Adams, C., Akrami, M., Cede, A., Chong, J., Clémer, K., Friess, U., Gil Ojeda, M., Goutail, F., Graves, R., Griesfeller, A., Grossmann, K., Hemerijckx, G., Hendrick, F., Herman, J., Hermans, C., Irie, H., Johnston, P. V., Kanaya, Y., Kreher, K., Leigh, R., Merlaud, A., Mount, G. H., Navarro, M., Oetjen, H., Pazmino, A., Perez-Camacho, M., Peters, E., Pinardi, G., Puentedura, O., Richter, A., Schönhardt, A., Shaiganfar, R.,

Spinei, E., Strong, K., Takashima, H., Vlemmix, T., Vrekoussis, M., Wagner, T., Wittrock, F., Yela, M., Yilmaz, S., Boersma, F., Hains, J., Kroon, M., Piters, A., and Kim, Y. J.: Intercomparison of slant column measurements of NO_2 and O_4 by MAX-DOAS and zenith-sky UV and visible spectrometers, Atmos. Meas. Tech., 3, 1629–1646, doi:10.5194/amt-3-1629-2010, 2010.

- Shindell, D. T., Faluvegi, G., Dorothy, M. K., Schmidt, G. A., Unger, N., and Bauer, S. E.: Improved Attribution of Climate Forcing to Emissions, Science, 326, 716–718, doi:10.1126/science.1174760, 2009.
- Sinreich, R., Frieß U., Wagner, T., and Platt, U.: Multi axis differential optical absorption spectroscopy (MAX-DOAS) of gas and aerosol distributions, Faraday Discuss., 130, 153–164, 2005.
- Sluis, W. W., Allaart, M. A. F., Piters, A. J. M., and Gast, L. F. L.: The development of a nitrogen dioxide sonde, Atmos. Meas. Tech., 3, 1753–1762, doi:10.5194/amt-3-1753-2010, 2010.
- Stammes, P.: Spectral radiance modeling in the UV-visible range, IRS2000: Current problems in atmospheric radiation, Eds. W.L. Smith and Y.M. Timofeyev, A. Deepak Publ., Hampton (VA), 1, 385–388, 2001.
- Stammes, P., de Haan, J. F., and Hovenier, J. W.: The polarized internal radiation field of a planetary atmosphere, Astron. Astrophys., 225, 239–259, 1989.
- van der A, R. J., Eskes, H. J., Boersma, K. F., van Noije, T. P. C., Van Roozendael, M., De Smedt, I., Peters, D. H. M. U., and Meijer, E. W.: Trends, seasonal variability and dominant NO_x source derived from a ten year record of NO2 measured from space, J. Geophys. Res., 113, D04302, doi:10.1029/2007JD009021, 2008.
- Vandaele, A. C., Hermans, C., Simon, P. C., Van Roozendael, M., Guilmot, J. M., Carleer, M., and Colin, R.: Fourier transform measurement of NO2 absorption cross-section in the visible range at room temperature, J. Atmos. Chem., 25, 289–305, 1996.
- Vandaele, A. C., Hermans, C., Simon, P. C., Carleer, M., Colin, R., Fally, S., Merienne, M. F., Jenouvrier, A., and Coquart, B.: Measurements of the NO2 Absorption Cross-section from 42000 cm⁻¹ to 10000 cm⁻¹ (238–1000 nm) at 220 K and 298 K, J. Quant. Spectr. Radiat. Transfer, 59, 171–184, 1998.
- Vandaele, A. C., Fayt, C., Hendrick, F., Hermans, C., Humbled, F., Van Roozendael, M., Gil, M., Navarro, M., Puentedura, O., Yela, M., Braathen, G., Stebel, K., Tornkvist, K., Johnston, P., Kreher, K., Goutail, F., Mieville, A., Pommereau, J.-P., Khaikine, S., Richter, A., Oetjen, H., Wittrock, F., Bugarski, S., Frieß U., Pfielsticker, K., Sinreich, R., Wagner, T., Corlett, G., and Leigh, R.: An intercomparison campaign of ground-based UVvisible measurements of NO₂, BrO and OCLO slant columns: Methods of analysis and results for NO₂, J. Geophys. Res., doi:10.1029/2004JD005423, 2005.
- Vlemmix, T., Piters, A. J. M., Stammes, P., Wang, P., and Levelt, P. F.: Retrieval of Tropospheric NO₂ using the MAX-DOAS method combined with relative intensity measurements for aerosol correction, Atmos. Meas. Tech., 3, 1–19, doi:10.5194/amt-3-1-2010, 2010.
- Volten, H., Brinksma, E. J., Berkhout, A. J. C., Hains, J., Bergwerff, J. B., Van der Hoff, G. R., Apituley, A., Dirksen, R. J., Calabretta-Jongen, S., and Swart, D. P. J.: NO₂ Lidar Profile Measurements for Satellite Interpretation and Validation, J. Geophys. Res.-Atmos., 114, D24301, doi:10.1029/2009JD012441,

2009.

- Wagner, T., Dix, B., von Friedeburg, C., Frieß U., Sanghavi, S., Sinreich, R., and Platt, U.: MAX-DOAS O4 measurements: A new technique to derive information on atmospheric aerosols – Principles and information content, J. Geophys. Res., 109, D22205, doi:10.1029/2004JD004904, 2004.
- Wagner, T., Beirle, S., Brauers, T., Deutschmann, T., Frieß, U., Hak, C., Halla, J. D., Heue, K. P., Junkermann, W., Li, X., Platt, U., and Pundt-Gruber, I.: Inversion of tropospheric profiles of aerosol extinction and HCHO and NO₂ mixing ratios from MAX-DOAS observations in Milano during the summer of 2003 and comparison with independent data sets, Atmos. Meas. Tech. Discuss., 4, 3891–3964, doi:10.5194/amtd-4-3891-2011, 2011.
- Wittrock, F., Oetjen, H., Richter, A., Fietkau, S., Medeke, T., Rozanov, A., and Burrows, J. P.: MAX-DOAS measurements of atmospheric trace gases in Ny-Ålesund – Radiative transfer studies and their application, Atmos. Chem. Phys., 4, 955–966, doi:10.5194/acp-4-955-2004, 2004.
- Zieger, P., Weingartner, E., Henzing, J., Moerman, M., de Leeuw, G., Mikkilä, J., Ehn, M., Petäjäa T., Clémer, K., van Roozendael, M., Yilmaz, S., Frieß, U., Irie, H., Wagner, T., Shaiganfar, R., Beirle, S., Apituley, A., Wilson, K., and Baltensperger, U.: Comparison of ambient aerosol extinction coefficients obtained from in-situ, MAX-DOAS and LIDAR measurements at Cabauw, Atmos. Chem. Phys., 11, 2603–2624, doi:10.5194/acp-11-2603-2011, 2011.