

An improved tropospheric NO₂ retrieval for OMI observations in the vicinity of mountainous terrain

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Abstract. We present an approach to reduce topography-related errors of vertical tropospheric columns (VTC) of NO₂ retrieved from the Ozone Monitoring Instrument (OMI) in the vicinity of mountainous terrain. This is crucial for reliable estimates of air pollution levels over our particular area of interest, the Alpine region and the adjacent planes, where the Dutch OMI NO₂ product (DOMINO) exhibits significant biases due to the coarse resolution of surface parameters used in the retrieval. Our approach replaces the coarse-gridded surface pressures by accurate pixel-average values using a high-resolution topography data set, and scales the a priori NO₂ profiles accordingly. NO₂ VTC reprocessed in this way for the period 2006–2007 suggest that NO₂ over the Po Valley in Italy and over the Swiss plateau is underestimated by DOMINO by about 15–20% in winter and 5% in summer under clear-sky conditions (cloud radiance fraction <0.5). A sensitivity analysis shows that these seasonal differences are mainly due to the different a priori NO₂ profile shapes and solar zenith angles in winter and summer. The comparison of NO₂ columns from the original and the enhanced retrieval with corresponding columns deduced from ground-based in situ observations over the Swiss Plateau and the Po Valley illustrates the promise of our new retrieval. It partially reduces the underestimation of the OMI VTCs at polluted sites in winter and fall and generally improves the agreement in terms of slope and correlation at rural stations. It does not solve, however, the issue that the OMI DOMINO product tends to overestimate very low columns observed at rural sites in spring and summer.

1 Introduction

Nitrogen dioxide (NO₂) is an important air pollutant affecting human health and ecosystems and playing a major role in the production of tropospheric ozone (Seinfeld and Pandis, 1998; Finlayson-Pitts, 2000). Nitrogen oxides (NO_x=NO+NO₂) have both substantial anthropogenic sources due to combustion of fossil fuels and human-induced biomass burning, and natural sources such as microbial production in soils, wildfires, and lightning. NO_x concentrations exhibit large spatial gradients due to the inhomogeneous distribution of sources and the relatively short lifetime of NO_x in the planetary boundary layer. Observations at high spatial resolution are therefore crucial to reliably assess exposure levels and corresponding environmental impacts.

Complementary to ground-based monitoring networks, which provide detailed information of local near-surface air pollution, satellite remote sensing can extend the spatial coverage and provide area-wide data of NO₂ vertical tropospheric column densities (VTCs). Satellite observations of tropospheric NO₂ using UV/VIS spectrometers began in 1995 with the Global Ozone Monitoring Experiment (GOME) (Burrows et al., 1999) on ERS-2, followed by the Scanning Imaging Absorption spectrometer for Atmospheric Chartography (SCIAMACHY) (Bovensmann et al., 1999) on Envisat, the Ozone Monitoring Instrument (OMI) (Levelt et al., 2006a, b) on Aura, and GOME-2 (Callies et al., 2000) on MetOp. The global coverage available from spaceborne instruments has been proven useful in estimating the large-scale distribution of NO_x sources in studies combining the satellite data with information from global scale models (Martin et al., 2003; Jaeglé et al., 2005; van der A et al., 2008; Boersma et al., 2008a). The gradually improving spatial resolution of space-borne UV/VIS instruments (GOME pixel size: 40×320 km², GOME-2: 40 km×80 km²,



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SCIAMACHY: 30×60 km², OMI: up to 13×24 km² at nadir) increasingly allows them to detect NO₂ pollution features on a regional scale. Bertram et al. (2005), for example, used SCIAMACHY measurements to investigate the daily variations in regional soil NO_x emissions, and Blond et al. (2007) compared columns from a mesoscale model with SCIAMACHY columns over Western Europe. The comparatively high resolution of the OMI instrument was demonstrated valuable in analyzing urban-scale pollution and its changes in time (Wang et al., 2007; Boersma et al., 2009).

A good knowledge of the precision and accuracy of the observations is important for many applications. However, due to the complex retrieval procedure this is more challenging to achieve for satellite observations than for ground-based in situ measurements. A detailed general error analysis for satellite NO₂ retrievals was presented by Boersma et al. (2004). It shows that the retrieval uncertainties are dominated by the uncertainty in the estimate of the tropospheric air mass factor, which is of the order of 20–30% for polluted pixels. Key input parameters for the calculation of the tropospheric air mass factor are cloud fraction, surface albedo, aerosol, and a priori NO₂ profile shape, each having its own uncertainty. Extending on this work, Boersma et al. (2007) described an additional error source associated with the improved spatial resolution of recent sensors like OMI. True variations of surface albedo and NO₂ profile shapes at the scale of individual satellite pixels can no longer be resolved by the input data sets used in the retrievals which are traditionally obtained from coarse global climatologies and models. To illustrate this problem, Fig. 1 shows the OMI overpass over central Europe on 3 January 2006 together with the outlines of two input parameter grids used in the Dutch OMI NO₂ (DOMINO) retrieval (Boersma et al., 2008b).

Our prime motivation for this study was to obtain reliable NO₂ column estimates over Switzerland. In Switzerland as well as in most other countries in Europe, NO₂ is a key air pollutant that is still frequently exceeding the air quality limits despite significant reductions since the late 1980s due to the introduction of exhaust after-treatment for stack emissions, 3-way catalysts and other measures. This is particularly true for the heavily industrialized and densely populated Po Valley in Northern Italy which is one of the most polluted places in Europe and which affects air quality in southern Switzerland. The Swiss plateau and the Po Valley are thus our principal areas of interest. Both are located in the vicinity of the Alps (see Fig. 1) which creates additional challenges to the retrieval.

The altitude or pressure of a surface, in addition to its albedo, is an important input for the retrieval as it affects the pathways of photons and hence the sensitivity of the satellite to measure NO₂ in a given atmospheric layer. The surface altitude (pressure) is a parameter that in principle can be estimated accurately. However, the way the topography is treated differs quite strongly between different retrieval algorithms and the details of the procedures are usually not well

documented. Furthermore, the a priori NO₂ profile, which is typically only available at a coarse resolution, often starts at a different altitude than the high-resolution topography and therefore needs to be adjusted. Today, most retrieval algorithms employ a high-resolution topography data. However, the algorithms differ in the way the a priori profile is adjusted to the high-resolution topography. For instance, in the standard OMI algorithm of NASA (Bucseala et al., 2006) the profile is simply cut if the true altitude is higher (E. Celarier, personal communication, 2009) while in the standard GOME and GOME-2 algorithms (ATBD GDP 4.0, 2004; GOME-2 ATBD, 2007) as well as in the Dalhousie University product (Martin et al., 2002; R. Martin, personal communication, 2009) some method for rescaling is applied. To our knowledge, meteorological variability in surface pressure is not accounted for in these algorithms.

In the DOMINO retrieval, conversely, the surface pressure is obtained at the same coarse resolution as the a priori profiles from the TM4 model, which is driven by meteorological fields of the ECMWF (European Centre for Medium Range Weather Forecast) model. Schaub et al. (2007) demonstrated that this can lead to significant systematic errors over and in the surroundings of mountainous terrain. The potential errors were quantified based on a sensitivity analysis for a few selected clear sky SCIAMACHY pixels and a priori profile shapes.

Although the effects of the topography on the retrieval are well known in the satellite community, a detailed quantitative analysis of this problem is still missing in the peer-reviewed literature. In this paper we therefore extend on the study of Schaub et al. (2007) and present a simple approach for a more accurate treatment of the surface topography than currently applied in DOMINO. The effect of these changes on the retrieved NO₂ columns are quantified by reprocessing extended time periods with accurate pixel-average surface pressures. A sensitivity study is then performed to investigate the dependence of the topography-related error on other forward model parameters including a priori profile shape, surface albedo, solar zenith angle (SZA) and cloud parameters. Finally, to demonstrate the potential improvement of this approach, NO₂ columns from the original and enhanced retrieval are compared with ground-based in situ observations over the Swiss plateau (station Taenikon) and selected stations in the Po Valley in Italy where the effects of inaccurate surface pressure are the largest.

While some details of our approach are specific to DOMINO, the basic concepts can easily be adapted to other algorithms and the results will add to a better understanding of the differences between the different satellite data products. Despite our focus on the Alpine domain, the method proposed here will be applicable to any other region of the globe with complex topography.

2 Data and methods

2.1 OMI tropospheric NO₂ observations

The Dutch-Finnish OMI instrument onboard the Earth Observing System (EOS) Aura satellite launched in 2004 offers greatly enhanced spatial and temporal (daily global coverage) resolution as compared to its predecessors. The Aura satellite (Schoeberl et al., 2006) passes over the equator in a sun-synchronous ascending polar orbit at 13:45 local time (LT). A near-real time retrieval algorithm has been developed for the rapid generation of NO₂ columns within 3 h of the actual OMI measurement (Boersma et al., 2007). The Dutch OMI NO₂ (DOMINO) offline product (in the following referred to as the DOMINO product) is based on the near-real time algorithm, but with the following improvements: it is a more accurate post-processing data set based on a more complete set of OMI orbits, improved Level 1B (ir)radiance data (collection 3, Dobber et al., 2008), analyzed meteorological fields rather than forecast data, and actual spacecraft data. These improvements make the offline product the recommended product for scientific use (Boersma et al., 2008b). The improved instrument calibration parameters used in collection 3 lead to much lower across-track variability, or stripes, in the OMI NO₂ products and therefore no de-stripping is currently applied. Whenever an OMI viewing scene contains snow or ice, this is detected based on the NISE ice and snow cover data set (Nolin et al., 2005) using passive microwave observations. The albedo from the TOMS/GOME albedo data set is then overwritten with a value of 0.6 for snow over land. Detailed descriptions of the algorithm for the DOMINO data products are given in Boersma et al. (2008b, 2009). The NO₂ vertical columns studied in this work are basically calculated in the same way as the DOMINO product data (version 1.0.2) available from ESA's TEMIS project (Tropospheric Emission Monitoring Internet Service, www.temis.nl). Deviations will be detailed in Sect. 2.2. Data is available since October 2004.

The starting point in this study is the tropospheric slant columns (SCD_{trop}) obtained from the measured slant columns by subtraction of the stratospheric slant columns. In the DOMINO retrieval the stratospheric slant columns are obtained with a data-assimilation approach using the TM4 global chemistry transport model (Dentener et al., 2003). The vertical tropospheric column (VTC) is then derived by dividing SCD_{trop} by the tropospheric air mass factor (AMF_{trop}).

AMF_{trop} depends on the a priori trace gas profile x_a and a set of forward model parameters \hat{b} including cloud parameters (cloud fraction, cloud pressure), surface albedo, surface pressure and viewing geometry. For small optical thickness, the altitude dependence of the measurement sensitivity to the atmospheric species of interest (calculated with a radiative transfer model) can be decoupled from the shape of the vertical trace gas profile (calculated e.g. with an atmospheric

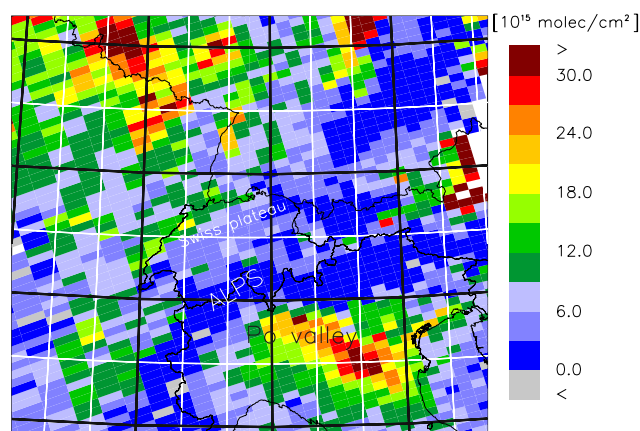


Fig. 1. NO₂ tropospheric vertical columns over central Europe from a single OMI overpass on 3 January 2006. The pixel size varies in across-track direction within the swath, with the highest resolution of about $0.15^\circ \times 0.2^\circ$ at nadir. For comparison, the grid of the albedo data set ($1^\circ \times 1^\circ$) is overlaid as white lines and the grid of the TM4 chemistry-transport-model ($2^\circ \times 3^\circ$) as black lines. The TM4 model (Dentener et al., 2003) determines the resolution of both the a priori profile and the surface pressure, with one grid cell almost as big as Switzerland.

chemistry transport model). The AMF_{trop} can then be written as follows (Palmer, 2001; Boersma et al., 2004):

$$AMF_{\text{trop}} = \frac{\sum_l m_l(\hat{b}) x_{a,l} c_l}{\sum_l x_{a,l}} \quad (1)$$

where l is an index denoting the atmospheric layer, m_l are the altitude dependent box air mass factors, and x_a the layer subcolumns (molecules cm^{-2}) of the a priori NO₂ profile. The coefficients c_l are layer-specific correction terms that describe the temperature dependence of the NO₂ absorption cross-section.

The box air mass factors m_l are calculated with a pseudo-spherical version of the DAK radiative transfer model (Stammes, 2001; de Haan et al., 1987). For computational efficiency, a lookup-table with precalculated box air mass factors at discrete points of the forward model parameters is used, and the values for a given set of parameters are obtained by linear interpolation.

The a priori NO₂ profile x_a for every location is obtained from the TM4 model. The profiles are collocated daily with a model output at overpass time of the satellite. The TM4 model version used for DOMINO has a horizontal resolution of 2° latitude by 3° longitude and 34 terrain-following hybrid layers extending from the surface to 0.38 hPa with approximately 15 layers in the troposphere (below 11 km) and 6 layers in the boundary layer (below 2 km) to assure a good representation of the vertical structure of air pollution near the surface. The layers are defined by two sets of hybrid level coefficients a and b :

$$p_{b,l} = a(l) + p_{\text{TM4}} \cdot b(l)$$

$$p_{t,l} = a(l + 1) + p_{\text{TM4}} \cdot b(l + 1) \quad (2)$$

where $p_{b,l}$ and $p_{t,l}$ are the bottom and top pressure of layer l ($l=1 \dots 34$), and p_{TM4} is the TM4 model surface pressure which corresponds to the bottom pressure of layer one (since $a(1)=0$ and $b(1)=1$). The mid pressure of each layer is defined as the mean of $p_{b,l}$ and $p_{t,l}$. Over marked topography, p_{TM4} may strongly deviate from the effective pixel-average surface pressure (denoted p_{eff} in the following) due to the coarse resolution of the TM4 model data, which is responsible for the systematic retrieval errors discussed in this study.

In Sect. 3.3 we will show that these errors are particularly important for cloudy scenes. The AMF for a partly cloudy scene is determined with the independent pixel approach (Boersma et al., 2007), which assumes that the air mass factor can be written as a linear combination of a cloudy and a clear sky air mass factor:

$$\text{AMF}_{\text{trop}} = w \text{AMF}_{\text{cloud}}(p_c) + (1-w) \text{AMF}_{\text{clear}}(p_s) \quad (3)$$

where $\text{AMF}_{\text{cloud}}$ is the AMF for a completely cloudy pixel, and $\text{AMF}_{\text{clear}}$ the AMF for a completely cloud-free pixel. A single cloud pressure p_c is assumed within a given viewing scene, p_s is the surface pressure. The $\text{AMF}_{\text{cloud}}$ is obtained with Eq. (1) with $m_l=0$ for all layers below cloud. The cloud radiance fraction w is defined as

$$w = \frac{f_{cl} I_{cl}}{f_{cl} I_{cl} + (1 - f_{cl}) I_{cr}} \quad (4)$$

where f_{cl} is the OMI effective cloud fraction, and I_{cl} and I_{cr} are the radiances for cloudy and clear scenes, respectively. I_{cl} mainly depends on the viewing geometry and the assumed cloud albedo (Koelemeijer et al., 2001) and I_{cr} depends on surface albedo and viewing geometry. The retrieval method for OMI cloud parameters uses the top-of-atmosphere reflectance as a measure to determine cloud fraction, and the depth of the O₂-O₂ band as a measure to determine cloud pressure (Acarreta et al., 2004).

2.2 Retrieval with effective pixel-average surface pressures

To calculate more accurate effective pixel-average surface pressures, the topography height from the global digital elevation model GTOPO30 (<http://eros.usgs.gov/products/elevation/gtopo30/gtopo30.html>) available on a high resolution ($\sim 1 \times 1 \text{ km}^2$) was averaged over each OMI pixel. The resulting effective terrain height h_{eff} of each pixel was converted to an effective surface pressure p_{eff} based on the TM4 surface temperature T_{surf} , surface pressure p_{TM4} and topography height h_{TM4} available in the DOMINO product. The conversion follows the hypsometric equation and the assumption that temperature changes linearly with height, which is often used for reducing measured surface pressures to sea level (Wallace and Hobbs, 1977):

$$p_{\text{eff}} = p_{\text{TM4}} \times \left(\frac{T_{\text{surf}}}{(T_{\text{surf}} + \Gamma(h_{\text{TM4}} - h_{\text{eff}}))} \right)^{-g/R\Gamma} \quad (5)$$

where $R=287 \text{ J kg}^{-1} \text{ K}^{-1}$ is the gas constant for dry air, $\Gamma=6.5 \text{ K km}^{-1}$ the lapse rate, and $g=9.8 \text{ m s}^{-2}$ the acceleration by gravity.

The absolute difference between effective and TM4 terrain height $\Delta h = h_{\text{eff}} - h_{\text{TM4}}$ is plotted in Fig. 2, which demonstrates the large mismatch in the Alpine region. In the TM4 model, the topography is averaged over extended grid elements (cf. Fig. 1) leading to an underestimation of the effective elevation of up to 1400 m for the highest mountains near the border between Switzerland, France and Italy. Conversely, there is an overestimation in the surrounding areas of up to 500 m over the Swiss plateau and more than 700 m over the Po Valley in Italy.

With the other forward model parameters kept the same as in the DOMINO product, the AMF_{trop} and NO₂ VTC was first calculated for the TM4 surface pressure p_{TM4} , and then recalculated for the effective surface pressure p_{eff} for all the pixels within the domain of interest (latitude between 44° N and 52° N, longitude between 5° E and 12° E) from January 2006 to May 2008. The retrieval with p_{TM4} in principle reproduces the DOMINO product. However, we eliminated a problem in the calculation of box air mass factors close to the surface which was detected at the beginning of this investigation. For any given pressure the algorithm interpolates the box AMF between the values at the two neighboring pressure levels of the lookup table, but the lower level may be located below the surface. In that case the box AMF at the lower level was assigned a value of zero which resulted in a too low interpolated box AMF. The magnitude of this error largely depended on the position of the actual surface pressure relative to the reference points in the lookup table and therefore its impact on the estimated NO₂ VTC differed with location and time. The averaged relative difference between the NO₂ VTC (cloud radiance fraction <50%) before and after elimination of this error was between 10 and 26% over the Swiss Plateau and the Po valley depending on season. Elimination of this error increases the air mass factors and therefore decreases the NO₂ columns. This problem will be eliminated in future versions of the DOMINO product. Thus, it should be kept in mind that even our product retrieved with p_{TM4} is not identical to the DOMINO data set up to date.

For the retrieval with p_{eff} the a priori NO₂ profiles had to be rescaled vertically to be consistent with p_{eff} . This scaling is performed in a way that preserves mixing ratios rather than subcolumns to account for the fact that only mixing ratios are conserved when a vertical column of air is compressed or expanded:

$$x_{a,l}^{\text{eff}} = x_{a,l} \times \left(\frac{p_{b,l}^{\text{eff}} - p_{t,l}^{\text{eff}}}{p_{b,l} - p_{t,l}} \right) \quad (6)$$

where $x_{a,l}^{\text{eff}}$ and $x_{a,l}$ are the a priori NO₂ profile with p_{eff} and p_{TM4} , respectively. $p_{b,l}^{\text{eff}}$ and $p_{t,l}^{\text{eff}}$ are obtained following Eq. (2) with p_{eff} replacing p_{TM4} in the formula. An example for the difference between original and rescaled profile is

presented in Fig. 8. Preserving mixing ratios or subcolumns makes almost no difference for the calculation of AMFs and NO₂ VTCs since it is only the shape of the a priori profile that matters but not the absolute values.

3 Results and discussion

3.1 Monthly mean and annual cycle

The relative change in retrieved NO₂ VTC defined as $(VTC_{\text{eff}} - VTC_{\text{TM4}}) / VTC_{\text{TM4}}$ was calculated for all snow-free (surface albedo <0.6) clear sky OMI pixels. Corresponding monthly mean maps are plotted exemplarily for December and June 2006 in Figs. 3 and 4, respectively, and for two different thresholds for the cloud radiance fraction of 50% (a), and 10% (b). Observations over snow were eliminated because for these pixels it is known that the contrast between cloud and the surface is too low to make a proper distinction between the two, leading to an incorrect effective cloud fraction (King et al., 1992), and therefore an ill-determined cloud pressure and less reliable retrieval.

Comparing the relative change in retrieved NO₂ VTCs in Figs. 3 and 4 to Δh in Fig. 2 shows that for negative Δh ($h_{\text{eff}} < h_{\text{TM4}}$, e.g. over the Swiss Plateau and the Po Valley) NO₂ VTCs are underestimated when retrieved with TM4 surface pressure while for positive Δh ($h_{\text{eff}} > h_{\text{TM4}}$, e.g. over the Alps) the columns are overestimated by more than 20% near the highest mountain ranges. Since NO₂ is generally low over the mountain regions and the retrieval is more uncertain due to the complex topography and snow, we focus on the more polluted areas over the planes. Comparing Figs. 3 and 4 further suggests that the relative changes in NO₂ VTCs are depending on season. For example, NO₂ VTCs are underestimated by more than 25% over some places in the Po Valley in December whereas in June the differences do not exceed 15%. Another interesting finding is that there is an obvious difference in the results for the different cloud radiance fraction criteria. For areas with negative Δh , a 50% threshold results in more serious underestimation of NO₂ VTCs than a 10% threshold, and this difference is much more obvious in December than in June. The large sensitivity of the results to the selected threshold implies that the relative change in NO₂ VTCs is particularly large for the cloudy part of the pixels, especially in winter. This issue will be discussed in Sect. 3.3.

For illustration of the seasonal differences, two small areas were selected over the Swiss Plateau and the Po Valley (labels A and B in Fig. 2), respectively. The averaged Δh of the selected areas are about 400 and 700 m, respectively, corresponding to a difference of about 45 hPa and 80 hPa between p_{TM4} and p_{eff} . Figures 5 and 6 show the time series of monthly averaged NO₂ VTCs from January 2006 to May 2009 for all pixels centered in areas A and B, respectively, retrieved with p_{TM4} (black solid line with square symbols)

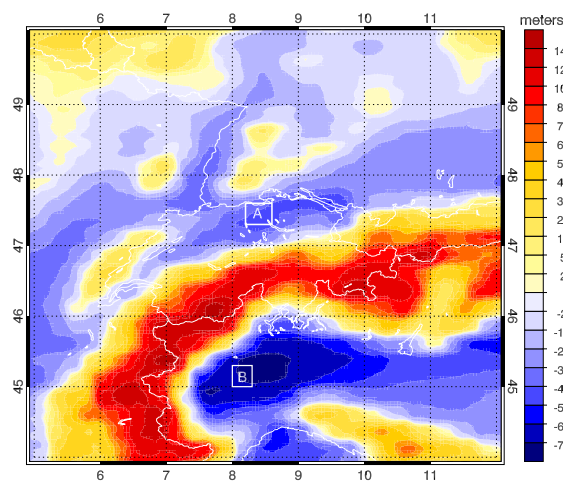


Fig. 2. Difference between effective and TM4 model terrain height ($h_{\text{eff}} - h_{\text{TM4}}$) in meters (averaged over January, 2006). The heights h_{eff} and h_{TM4} are first determined for each OMI pixel separately and then mapped onto a fine regular grid by averaging over all pixels covering a given grid cell. Two areas of interest over the Swiss Plateau and the Po Valley in northern Italy referred to in the text are highlighted with labels A (latitude between 47.3° N and 47.6° N, longitude between 8.2° E and 8.6° E) and B (latitude between 45° N and 45.3° N, longitude between 8° E and 8.3° E), respectively.

and p_{eff} (black dashed line with diamonds). Winter months have much higher NO₂ VTCs than summer months due to the increased lifetime of NO₂ (Schaub et al., 2007). At the same time, both the absolute (black solid lines with crosses) and relative changes in NO₂ VTCs (grey lines) exhibit a seasonal cycle with higher values in winter months. However, the seasonal cycle of the changes does not necessarily align with the seasonal cycle of NO₂ VTCs itself. For pixels with a cloud radiance fraction lower than 50% the underestimation of NO₂ VTCs reaches values larger than 20% in both areas in some winter months (Figs. 5a and 6a). The changes in NO₂ VTCs are generally smaller over the Swiss Plateau than over the Po Valley consistent with the smaller altitude shift. In summer, the relative change is typically of the order of 5% and the absolute change is rather small due to the much lower NO₂ VTCs. With a cloud radiance fraction threshold of 10%, the changes in NO₂ VTCs have a much less pronounced seasonal cycle for both areas (Figs. 5b and 6b). The cause of this difference will be discussed in Sect. 3.3.

3.2 Sensitivity analysis for cloud free pixels

According to Eq. (1) the AMF_{trop} is entirely determined by the profile of the altitude dependent box air mass factors m_l and by the a priori NO₂ profile shape obtained from the TM4 model. The effect of a surface pressure change on these profiles is illustrated in Figs. 7 and 8 for the two selected pixels separately. Comparing Fig. 7a and b it can be seen that the profiles of m_l differ significantly between the two pixels due

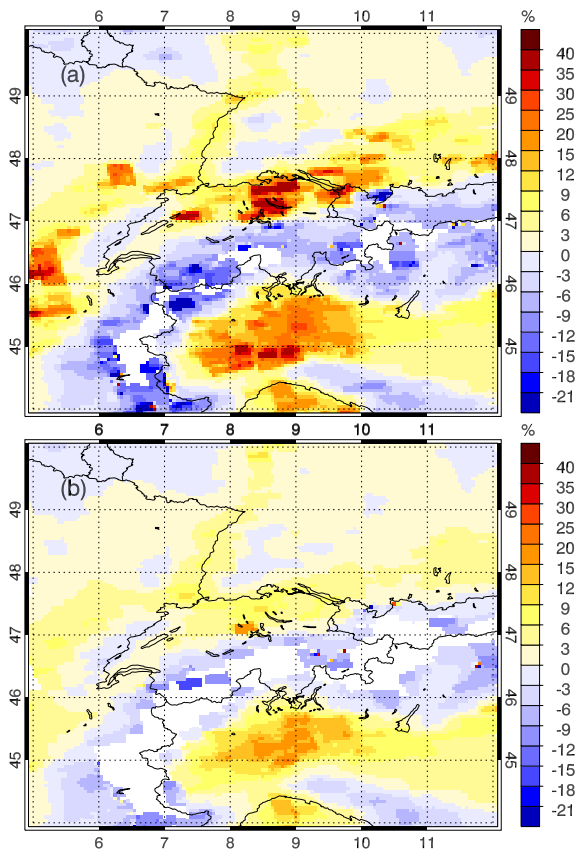


Fig. 3. Relative change in NO₂ VTC retrieved with effective surface pressure p_{eff} instead of TM4 surface pressure p_{TM4} for December 2006. (a) Cloud radiance fraction <50% (corresponds to a cloud fraction of only about 20%, and has often been used in previous studies to distinguish between clear and cloudy pixels), (b) Cloud radiance fraction <10% (much more stringent than (a) and reduces the data set to virtually cloud-free pixels).

to the large difference in the forward parameters. In the upper atmosphere the values approach the geometric air mass factor which is determined by the SZA and viewing zenith angle (VZA) (Palmer, 2001). The trends of the two profiles are similar with decreasing m_l towards the ground, which represents the decreasing sensitivity of the satellite instrument towards the surface due to increased scattering of light above the level of interest.

The effect of a vertical displacement of the surface on the box AMF profile may be summarized as follows: For a given atmospheric layer at a fixed altitude, the box AMF is reduced over an elevated surface because fewer photons will be scattered from the atmospheric layers below. However, for a layer at a fixed altitude *relative* to the surface (e.g. 0–100 m above ground) the box AMF is enhanced over the elevated surface because fewer photons are scattered by the atmosphere above and hence more light reaches the elevated surface.

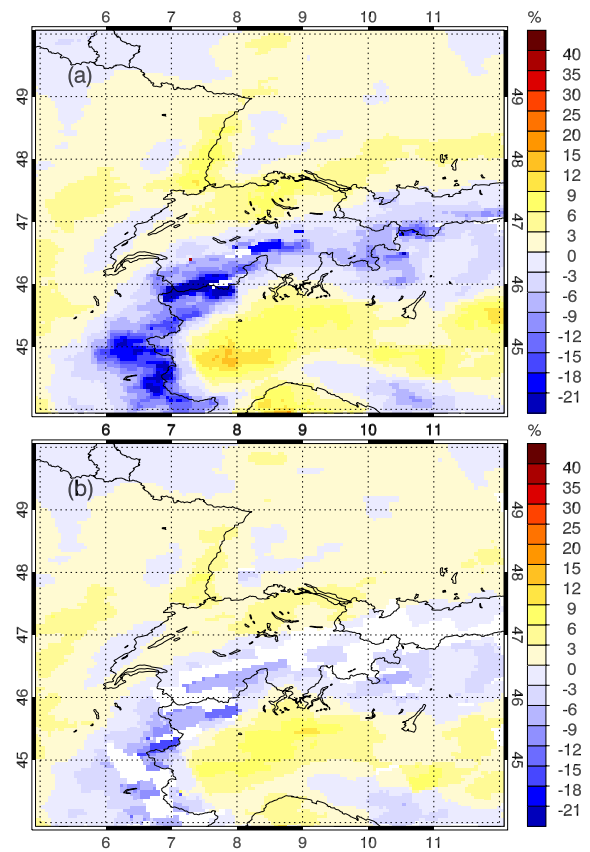


Fig. 4. Same as Fig. 3 but for June 2006. (a) Cloud radiance fraction <50%, (b) <10%.

For a systematic analysis of the influence of the different retrieval parameters on the topography-related NO₂ error, two sets of forward parameters and a priori NO₂ profiles corresponding to the two pixels on 4 August and 1 December 2006 were selected to represent typical summer and winter conditions over the Po valley, respectively. The individual effects of the a priori NO₂ profile, SZA, and albedo as well as their combined effects were then investigated by systematically replacing each parameter by its value of the opposing season. The corresponding retrieval parameter settings are listed in Table 1, and the results are shown in Fig. 9. The TM4 surface pressure was assumed to be 928 hPa in all cases as a reference point and the effective surface pressure p_{eff} was varied about this point over a realistic range thereby shifting up or down the profiles of box air mass factors and a priori profiles as described in Sect. 2.2. In the Po Valley, the differences between p_{eff} and p_{TM4} are of the order of 80 hPa. The relative changes in AMF_{trop} and NO₂ VTCs for this specific point on the sensitivity lines in Fig. 9 are summarized in Table 1.

The shape of the a priori NO₂ profile is an important factor in determining the AMF_{trop} (see Eq. 1). Due to the poor spatial resolution of the TM4 model the a priori NO₂ profile

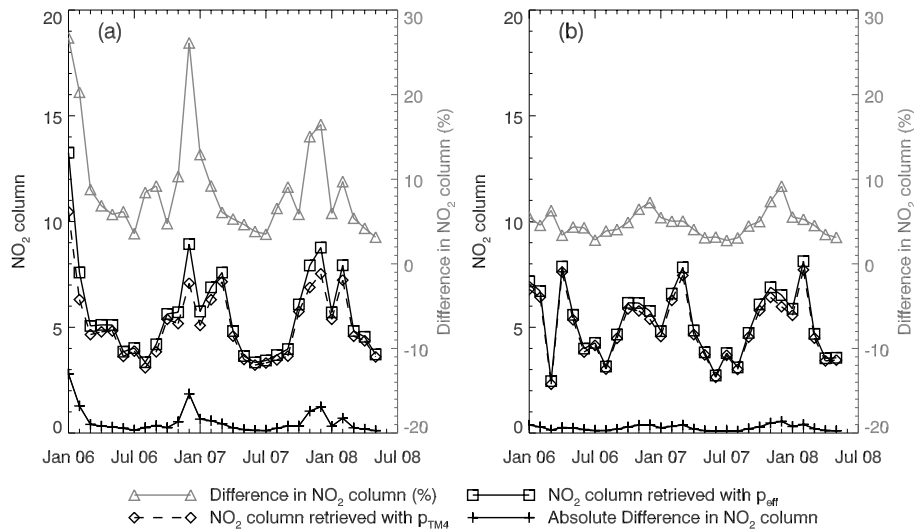


Fig. 5. Seasonal cycles of NO₂ VTC retrieved with effective surface pressure p_{eff} (black solid line with squares) and with TM4 surface pressure p_{TM4} (dashed line with diamonds) in area A over the Swiss Plateau. Also shown are the absolute (black solid line with crosses) and relative differences (grey line, right axis) between the two. (a) Cloud radiance fraction <50%, (b) <10%.

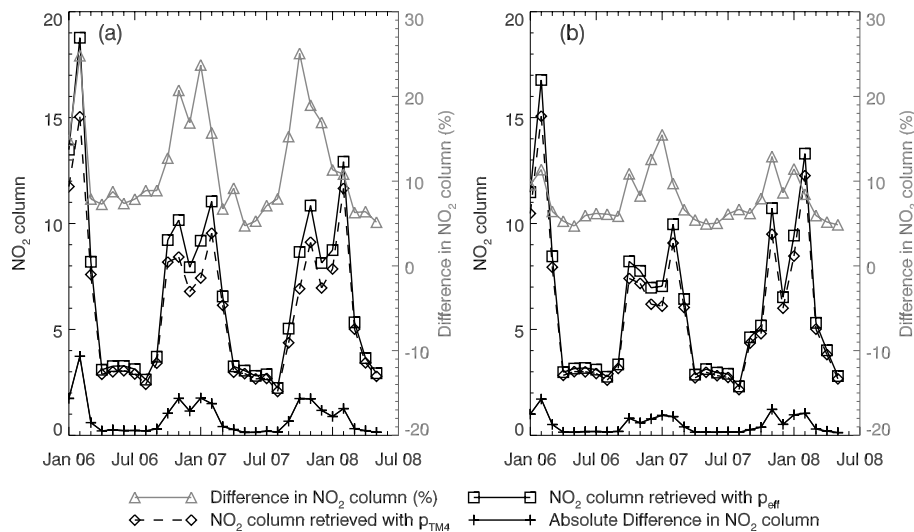


Fig. 6. Same as Fig. 5 but for area B in the Po Valley. (a) Cloud radiance <50%, (b) <10%.

varies only slowly in space such that our selected profile is representative for large parts of the Po Valley. As seen in Fig. 8, the selected winter profile exhibits a pronounced peak in the boundary layer since vertical mixing is generally weak in winter, and both the lifetime of NO_x and the emissions are enhanced in this season (Richter et al., 2002; Jaeglé et al., 2005). In contrast, the selected summer profile shows a much lower NO₂ abundance near the ground resulting from enhanced vertical mixing and a reduced lifetime. Figure 9a shows how the sensitivities of the AMF_{trop} and NO₂ VTCs to varying surface pressure change when replacing the winter profile by the summer profile while keeping all other parameters constant. In comparison to summer, the more pronounced a priori NO₂ profile in winter results in a

stronger sensitivity of the retrieved NO₂ VTCs to errors in the assumed surface pressure. This is understandable since changes in surface pressure most strongly affect the box air mass factors m_l at the lowest levels, and this effect is amplified in the computation of AMF_{trop} if the a priori profile predicts most of the NO₂ at these levels.

A similar analysis was made for the other two retrieval parameters changing strongly with season, solar zenith angle and albedo. As seen in Fig. 9b, for the larger SZA in winter, the relative changes in AMF_{trop} and NO₂ VTCs are more sensitive to differences between p_{TM4} and p_{eff} than for the smaller angles in summer. This effect thus adds to the differences observed between winter and summer. Fig. 9c shows that, in contrast to the two previous parameters, the

Table 1. Retrieval parameter settings in the case studies of retrieval parameter effects on sensitivity of relative changes in AMF_{trop} (Δ AMF_{trop}) and NO₂ VTC (Δ NO₂ VTC) respect to change in surface pressure, and the results of selected surface pressure (reference point $p_{\text{TM4}}=928$ hPa, $p_{\text{eff}}=1008$ hPa).

Case	Parameter varied	a priori profile	Albedo	SZA	VZA	AZA	Δ AMF _{trop}	Δ NO ₂ VTC
A1	a priori profile	winter profile	0.116	70°	11.5°	122.8°	-7.4%	8.0%
A2		summer profile	0.116	70°	11.5°	122.8°	-5.0%	5.3%
B1	SZA	summer profile	0.116	70°	11.5°	122.8°	-5.0%	5.3%
B2		summer profile	0.116	31°	11.5°	122.8°	-3.7%	3.86%
C1	albedo	summer profile	0.116	31°	11.5°	122.8°	-3.7%	3.86%
C2		summer profile	0.057	31°	11.5°	122.8°	-3.8%	3.94%
C3	combined	winter profile	0.116	70°	11.5°	122.8°	-7.4%	8.0%
C4		summer profile	0.057	31°	11.5°	122.8°	-3.8%	3.94%

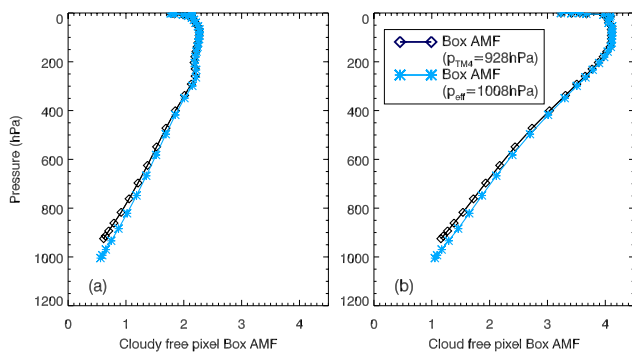


Fig. 7. Profiles of box air mass factors for cloud free pixels in the Po Valley on (a) 4 August 2006 (longitude: 8.3°, latitude: 45.14°, albedo=0.057, SZA=31°, AZA=136°, VZA=3°) and (b) 1 December 2006 (longitude: 8.22°, latitude: 45.12°, albedo=0.116, SZA=70°, AZA=122.8°, VZA=11.5°). Black lines: For surface pressure p_{TM4} . Blue lines: for effective surface pressure p_{eff} . Each symbol in the curves represents the value at the middle of one of the 34 layers in the TM4 model from the ground to the model top. Due to the hybrid coordinate system, the location of these layers scales with the surface pressure (see Eq. 2).

sensitivity of relative changes in AMF_{trop} and NO₂ VTCs to changing surface pressure is almost the same in winter and in summer, even though the largely different albedos have a significant effect on the absolute values of the AMF_{trop}.

Figure 9d finally illustrates the combined effect of the three parameters above. For the selected location in the Po valley, where p_{TM4} is 928 hPa and p_{eff} is 1008 hPa, the relative NO₂ VTCs change for cloud-free pixels is about 8% in winter and 4% in summer. The sensitivity of the retrieval error to the surface pressure error is thus almost twice as large in winter as in summer which is mainly a consequence of the differences in a priori profile shape and SZA as described above. The other forward model parameters VZA and relative azimuth angle (AZA) were not included in this sensitivity study as they do not vary with season but rather within a single swath.

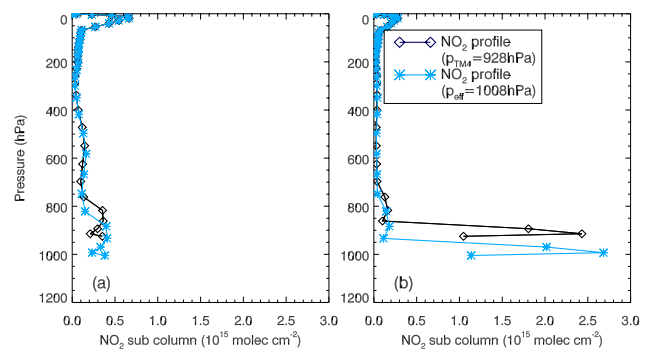


Fig. 8. Same as Fig. 7 but for a priori NO₂ profiles.

3.3 Sensitivity analysis for cloudy pixels

To illustrate the effect of the inaccurate topography for partly cloudy pixels, we took the same forward model parameters as for the cloud-free pixel presented in Fig. 7b but assumed a cloud fraction of 15% and a cloud pressure of 900 hPa. The profile of box AMFs of the completely cloudy part is shown in Fig. 10a, and the corresponding profile of the partly cloudy pixel in Fig. 10b, which is the weighted sum of the values in Figs. 7b and Fig. 10a. Clouds are modeled as opaque Lambertian reflectors with an albedo of 0.8 (Acarreta et al., 2004). The sensitivity is enhanced above the bright cloud but drops to zero below the top of the opaque cloud as seen in Fig. 10a. The box AMF corresponding to the pressure just larger than the cloud pressure (903 hPa) behaves like a transition point, since the cloud is located within this layer, and the fraction of the layer above the cloud still has non-zero m_l . This sudden change in m_l is also reflected in the profile of effective box AMFs of the partly cloudy pixel shown in Fig. 10b. Below cloud the box AMFs drop to values much smaller than for the cloud free case in Fig. 7b.

AMF_{trop} is determined by the m_l of the partly cloudy pixel and the a priori NO₂ profile according to Eq. (1). Figures 3 and 4 suggest that the AMF_{trop} is generally more sensitive to

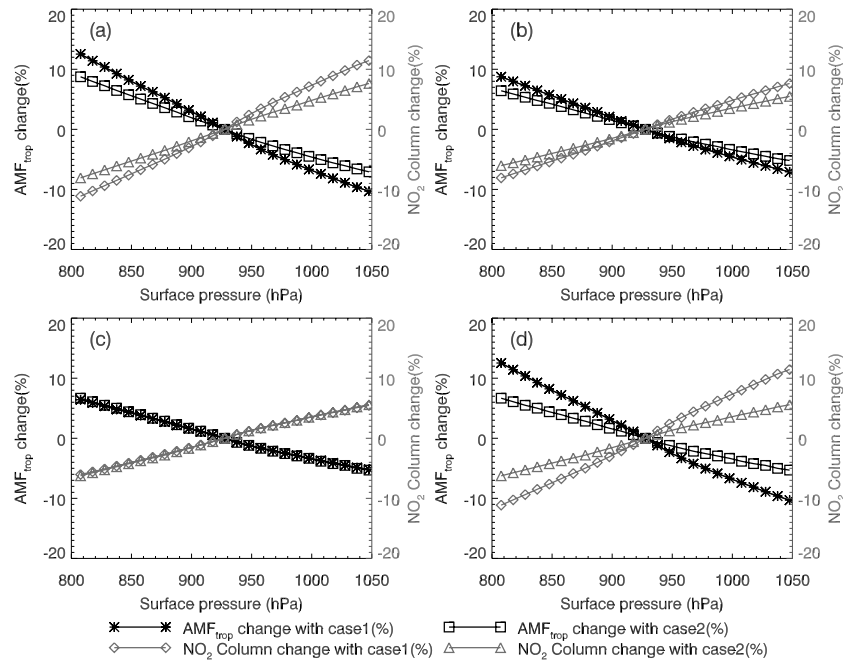


Fig. 9. Effect of different retrieval parameters on the sensitivity of the change in AMF_{trop} (black lines) and NO₂ VTC (grey lines) to a change in surface pressure. The corresponding retrieval parameter settings are listed in Table 1. (a) Effect of a priori NO₂ profile (case A1: winter profile, case A2: summer profile), (b) solar zenith angle (case B1: SZA=70°, case B2: SZA=31°), (c) albedo (case C1: albedo=0.116, case C2: albedo=0.057°), (d) combined effect (case D1: winter, case D2: summer).

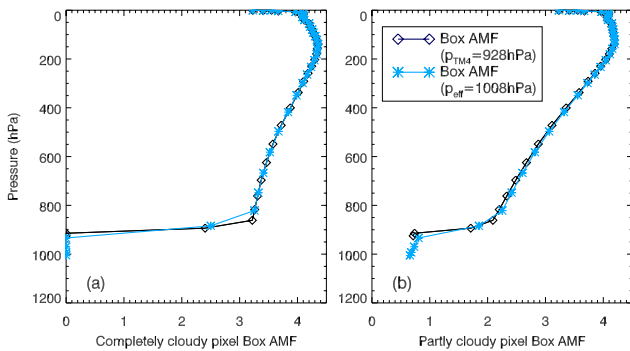


Fig. 10. Profiles of box air mass factors for (a) a completely cloudy pixel (cloud albedo=0.8, cloud pressure=900 hPa, SZA=70°, AZA=122.8°, VZA=11.5°) and (b) for the same pixel but assumed to be only partly cloudy (surface albedo=0.116, cloud fraction=15%, cloud radiance fraction=38%, cloud pressure=900 hPa). Black lines: For original surface pressure p_{TM4} . Blue lines: for effective surface pressure p_{eff} .

the change in terrain height for cloudy pixels than for cloud free pixels. The reason for this high sensitivity is illustrated in Fig. 11 showing the situation for a partly cloudy pixel and a low level cloud. Shifting the surface to a lower effective pixel altitude (right hand part of Fig. 11), e.g. over the Po Valley, results in more levels becoming poorly visible to the satellite and effectively places a larger fraction of the polluted

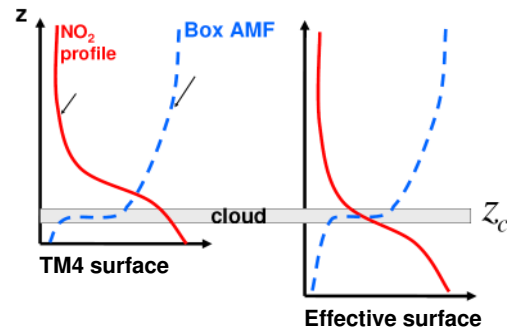


Fig. 11. Illustration of the inaccurate topography effect on partly cloudy pixels. Red lines are the a priori NO₂ profiles, blue dashed lines the box air mass factors. The cloud level remains unchanged when the surface is lowered to the effective altitude in the right hand part of the figure. The a priori NO₂ profile is scaled to the new surface level with all polluted layers now located below cloud top where the sensitivity of the measurement is very low.

part of the NO₂ profile below the cloud (red line in Fig. 11b). This results in a much lower AMF_{trop} and correspondingly higher NO₂ VTC.

The sensitivity to the surface pressure change depends on cloud pressure, cloud radiance fraction, and the a priori NO₂ profile shape. To demonstrate the cloud pressure dependence the relative changes in AMF_{trop} and NO₂ VTC are shown in Fig. 12 as a function of the change in surface pressure for

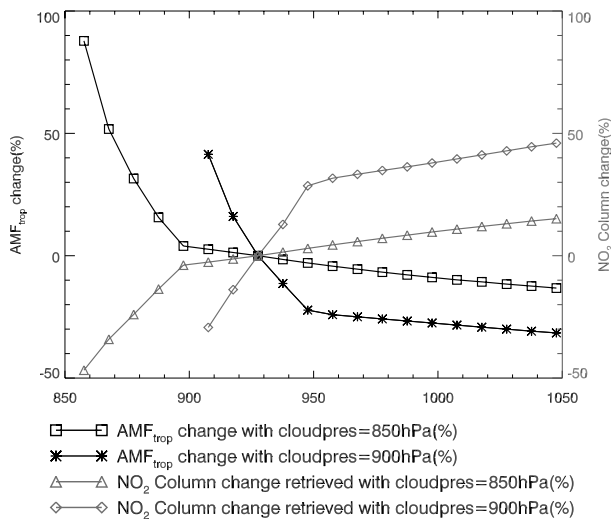


Fig. 12. Effect of cloud pressure on the sensitivity of the change in AMF_{trop} (black lines) and NO₂ VTC (grey lines) to a change in surface pressure (reference point $p_{TM4}=928$ hPa, cloud fraction=15%).

two different cloud pressures for the winter pixel (retrieval parameters as in case A1 in Table 1). The NO₂ VTC retrieved with $p_{eff}=1008$ hPa instead of $p_{TM4}=928$ hPa is close to 40% higher when the cloud is located close to the surface (cloud pressure=900 hPa), which is a much larger change than for the cloud free situation. However, when the cloud is located higher at 850 hPa the increase is only about 10%. Obviously, these numbers also depend on the assumed cloud radiance fraction. By varying the cloud radiance fraction between 0% and 50% for the pixel shown in Fig. 12 (with $p_{TM4}=928$ hPa and $p_{eff}=1008$ hPa), for example, we found that the NO₂ VTC difference varies linearly from about 8% (cloud radiance fraction=0%) to 55% (cloud radiance fraction=50%) for a cloud with a pressure of 900 hPa, but only from 8% to 12.5% for a cloud with a pressure of 850 hPa.

Interestingly, the very high sensitivity to surface pressure only occurs over a range of about 50 hPa below cloud, which corresponds to the depth of the boundary layer with elevated NO₂ in Fig. 8b. Thus, for a cloud located inside the polluted boundary layer the retrieval error due to inaccurate surface pressure is large, especially in the winter season with pronounced NO₂ in the boundary layer. Conversely, when the cloud is located above the boundary layer, the retrieval error is comparatively small and similar to the cloud free case. Low clouds were frequently observed over some areas in the Po Valley during winter. For example, the monthly mean cloud pressure over area B in Fig. 2 was 917 hPa in December 2006, which contrasts with a much lower pressure of 789 hPa in June 2006. The predominance of low clouds likely explains the very high relative changes in retrieved NO₂ VTCs in December 2006 over some areas in Fig. 3a.

The high sensitivity of our results to the cloud pressure highlights the importance of an accurate retrieval of cloud parameters. However, a recent comparison of the OMI cloud retrieval with other cloud products indicated that the uncertainty in retrieved cloud pressures is probably larger than 50 hPa and can be significantly larger for small cloud fractions below 20% (Sneep et al., 2008). Improvements in the representation of the surface may thus easily be offset by cloud effects. It should be noted that by adopting the GTOPO30 data set the NO₂ retrieval becomes more consistent with the OMI cloud retrieval which is already using a high-resolution topography data set.

4 Validation

4.1 Calculation of tropospheric NO₂ VTCs from ground-based measurements

In-situ ground-based measurements of NO₂ for the period January 2006 to December 2007 were obtained from two sources, from the Swiss National Air Pollution Monitoring Network (NABEL) (<http://www.bafu.admin.ch/luft/00612/00625/index.html>) for stations over the Swiss plateau, and from the Lombardy Regional Agency for Environmental Protection (ARPA), Italy, for stations in the Po Valley/Milano area (<http://www.ambiente.regione.lombardia.it>). From a total of more than 100 stations only 35 were selected for the validation. All the selected stations are background stations not affected by local traffic or industrial pollution sources, and have a data coverage of more than 80% at the time of the OMI overpass during the analysis period. At these stations, nitrogen oxides are measured using commercial instruments with molybdenum converters. NO₂ is catalytically converted to NO on a heated molybdenum surface, and then measured as NO by chemiluminescence after reaction with ozone. It is well known that these converters do not only convert NO₂ but also other odd nitrogen species such as PAN, HNO₃ and organic nitrates to NO (Winer et al., 1974; Grosjean and Harrison, 1985; Steinbacher et al., 2007). Nevertheless, it is the standard method applied in air quality monitoring networks. In a similar study using the Lombardy station network for validation of GOME observations, Ordóñez et al. (2006) quantified the interference in the molybdenum converter at GOME overpass time based on simultaneous measurements of surface NO₂ performed with a photolytic converter (selective for NO₂ only) and a molybdenum converter at the rural site Taenikon (47.47° N, 8.90° E, 539 m a.s.l.), Switzerland, during the period 1995–2001. The ratios of the monthly medians of these two measurements on sunny days (photolytic divided by molybdenum) at GOME overpass time (~10:30 LT) were then used as factors to correct the molybdenum converter measurements. As a first approximation, we followed the same approach yet quantifying the interference at the overpass time of OMI instead of GOME. The

calculated monthly correction factors are shown in Table 2. The ratios show a clear seasonal cycle with a summertime minimum. This is expected since during the warm season the photochemistry leads to a higher production of oxidized nitrogen species such as HNO₃ and PAN which results in a more pronounced overestimation of the NO₂ surface concentrations. The ratios at OMI overpass time differ by less than 5% from those of Ordóñez et al. (2006) at GOME overpass time from October to January but are about 10% lower in the other months due to the more pronounced diurnal cycles of the interference with a larger overestimation of NO₂ concentrations in the afternoon than in the morning (Steinbacher et al., 2007).

Monthly mean ratios can not reflect the potentially large temporal and spatial variations in the ratios due to varying photochemistry. In this study we therefore adopt the refined correction method proposed by Steinbacher et al. (2007) which models the ratios by a multiple linear regression approach using daily O₃ mixing ratios as a proxy for photochemical activity and month as a factor variable to estimate the seasonal variation. We used the same regression coefficients as Steinbacher et al. (2007) which are based on an analysis of the same Taenikon data used by Ordóñez et al. (2006). We then corrected the NO₂ measurements for each station separately using the ozone data of the respective station if available. For 7 out of 35 stations no ozone measurements were available and therefore the monthly median ratios of the Taenikon data had to be used. For comparison, Table 2 also lists the monthly median correction factors deduced from the regression approach for the 28 stations with O₃ measurements. The regression-based median ratios are slightly smaller (up to -6.3%) in winter but are significantly higher (that is closer to one corresponding to a smaller correction) in the other seasons compared to Taenikon monthly median ratios with a maximal relative difference as high as 58.4% in August. The reason for this is that the Po valley stations tend to be more polluted and closer to the pollution sources than the station Taenikon and therefore the interferences from higher oxidized NO_y species tend to be smaller. In winter the overestimation of NO₂ by molybdenum converters is smallest and therefore the results are more reliable in this season.

Hourly NO₂ measurements averaged over 13:00–14:00 LT were used for the comparison with the NO₂ VTCs measured from OMI at about 13:30 LT. Only measurements coincident with a valid OMI observation (see selection criteria below) and only days with a surface NO₂ mixing ratio larger than 1 ppb were considered since the instrument detection limit for NO₂ is approximately 1 ppb (NABEL, 2007). For quantitative comparison with the satellite observations, corrected NO₂ mixing ratios measured at the surface were scaled to NO₂ VTCs using the same TM4 vertical NO₂ profiles used also as a priori. These profiles are representative for the time and location of each OMI observation. The “ground based

Table 2. Monthly medians of the ratio of NO₂ measurements performed with photolytic and molybdenum converters at Taenikon, Switzerland, under clear-sky conditions (sunshine fraction of at least 0.8) from 13:00 to 14:00 LT during the period January 1995 to mid-August 2001 (applied for the 7 stations without ozone measurements). The second column shows monthly medians of the correction factors (mean corrected NO₂ divided by mean measured NO₂ for each station) based on regression analysis of the 28 stations with ozone measurements. The relative differences between the two median ratios ((regression ratio-Taenikon ratio)/Taenikon ratio) are also shown.

Month	Median ratio	Median ratio	Relative difference (%)
	(Taenikon)	(Regression)	
January	0.850	0.822	-3.3
February	0.774	0.726	-6.3
March	0.667	0.696	4.4
April	0.537	0.653	21.6
May	0.463	0.669	44.6
June	0.488	0.668	36.9
July	0.466	0.722	54.9
August	0.517	0.819	58.4
September	0.647	0.856	32.3
October	0.767	0.866	12.9
November	0.806	0.870	7.9
December	0.873	0.855	-2.1

in-situ NO₂ VTCs” were calculated according to:

$$\text{VTC}_G = \frac{\text{VTC}_{\text{TM4}}}{S_{\text{TM4}}} \times S_G \quad (7)$$

where S represents the surface level mixing ratio and subscript G denotes ground based measurement. VTC_{TM4} is calculated by summing up the TM4 model subcolumns from the surface to the tropopause level. S_{TM4} is the NO₂ mixing ratio of the model at the lowest level. For comparison with the OMI NO₂ VTCs retrieved with p_{TM4} , the original TM4 profile was used. For comparison with the OMI NO₂ VTCs retrieved with p_{eff} , however, the profile scaled to the effective surface pressure following Eq. (6) was used. Due to our choice of preserving mixing ratios in the rescaled NO₂ profile, the VTC_G calculated with p_{TM4} are somewhat smaller than those calculated with the higher effective surface pressure p_{eff} . These differences are of a similar order but generally smaller than the differences between the satellite NO₂ VTC obtained for p_{TM4} and p_{eff} . Note that, as mentioned at the end of Sect. 2, the differences in the OMI NO₂ VTC are a result of the differences in the box AMFs near the surface rather than of the conservation of mixing ratios.

The selection of OMI pixels was based on the following criteria: (1) pixel center within 10 km of the station and east-west extension of the pixel of less than 70 km, (2) cloud radiance fraction lower than 50%, (3) albedo smaller than 0.6 to

exclude snow cover. If there was more than one pixel meeting the criteria on the same day then the OMI pixel with the smallest effective cloud fraction was selected. The thresholds for these criteria were set to balance data quality with a sufficient number of measurements for good statistics.

4.2 Comparison of in situ and OMI tropospheric NO₂ VTCs

Figure 13 shows the correlation coefficients (r) between in-situ and OMI NO₂ VTCs retrieved with p_{eff} . For most of the stations, the in-situ NO₂ VTCs are well correlated with the satellite observations, with r ranging from 0.6 to 0.82 for, on average, 180 data points per station. Poorer correlations are observed for a few elevated stations in the pre-Alps. Due to enhanced spatial variability, both the representativeness of the surface measurement itself and the representativeness of the a priori profile for these stations become more uncertain.

The measurement sites are classified by land use type as rural, suburban and urban. The medians of the ratios at each station between seasonal means of the OMI and in-situ NO₂ VTCs are shown in Fig. 14 for each station type separately. For urban stations, the ratios are closer to unity in all four seasons compared to rural and suburban stations. As reported by Boersma et al. (2009), good agreement between OMI and in situ measurements was also found for Israeli urban stations. The retrieval with accurate surface pressure p_{eff} improves the agreement in winter for both urban and suburban stations where the retrieval with p_{TM4} underestimates NO₂ VTCs. For rural and suburban stations, the ratios exhibit a pronounced seasonal variation with highest ratios in spring months suggesting a significant overestimation of the OMI NO₂ VTCs in this season. It is important to note, however, that in these cases the absolute values and also the absolute differences between OMI and in-situ NO₂ VTCs are small, with an average absolute overestimation of 4.3 and 3.4 (10^{15} molecules cm^{-2}) for rural and suburban stations, respectively. Lamsal et al. (2008) reported similar differences between OMI and in situ measurements over North America with strongest overestimation in summer. They concluded that the larger seasonal bias at rural sites suggests an incomplete removal of stratospheric NO₂ which has a larger relative effect where tropospheric NO₂ columns are lower. However, different from Lamsal et al. (2008), the ratios are larger than one in most of the seasons for rural and suburban stations in our study, which may be explained by the use of different OMI NO₂ products (standard product from NASA versus our modified DOMINO product). As suggested by Bucsel et al. (2008), the NASA and KNMI algorithms produce significantly different tropospheric NO₂ amounts mainly due to the different retrieval parameters used.

Two examples of the comparison between OMI and in-situ NO₂ VTCs at individual stations are shown in Fig. 15 for the rural station Motta (45.29° N, 9° E) and the urban station Pavia (45.19° N, 9.16° E). The OMI VTCs follow the sea-

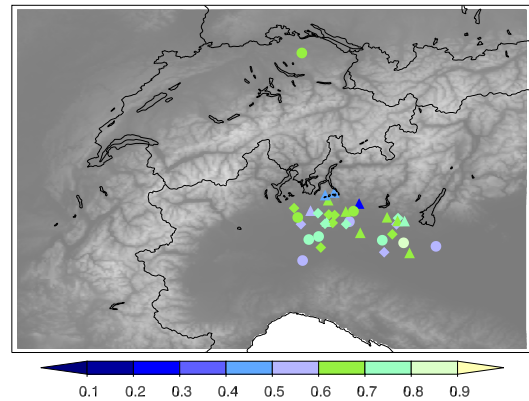


Fig. 13. Topographic map of the Alpine domain with all in situ measurement stations used for validation shown as colored symbols. Colors are correlation coefficients (r) between the in-situ and OMI NO₂ VTCs retrieved with effective surface pressure p_{eff} for measurements in 2006 and 2007. Circles represent rural, triangles suburban and diamonds urban stations.

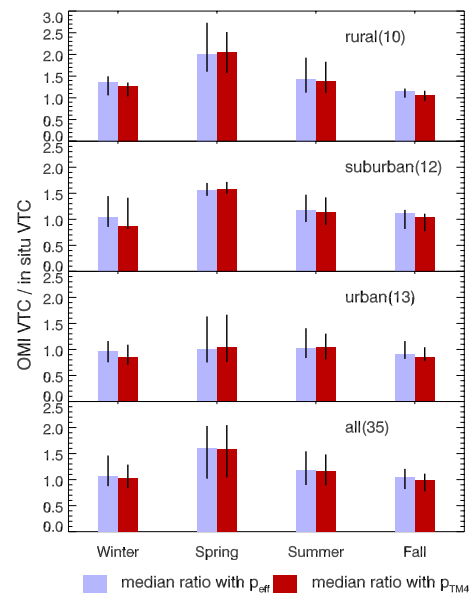


Fig. 14. Medians of the ratios of seasonal mean of OMI NO₂ VTCs and seasonal mean of in-situ NO₂ VTCs (OMI mean divided by in situ mean for each station). The vertical lines depict the central half of the data between the lower ($q_{0.25}$) and the upper quartile ($q_{0.75}$). The measurement sites are classified by land use type as rural, suburban and urban. The number of stations included is given in parentheses.

sonal variation of the in situ VTC data very well, but the OMI columns tend to be too high at the rural station Motta in all months, and to be too low at the urban station Pavia in winter and fall. A weighted least squares orthogonal regression was performed for each station which considers the uncertainties in both measurements and minimizes the distances in both y- and x-direction by a chi-square minimization procedure (Press et al., 1992). The uncertainties of the OMI NO₂ VTCs

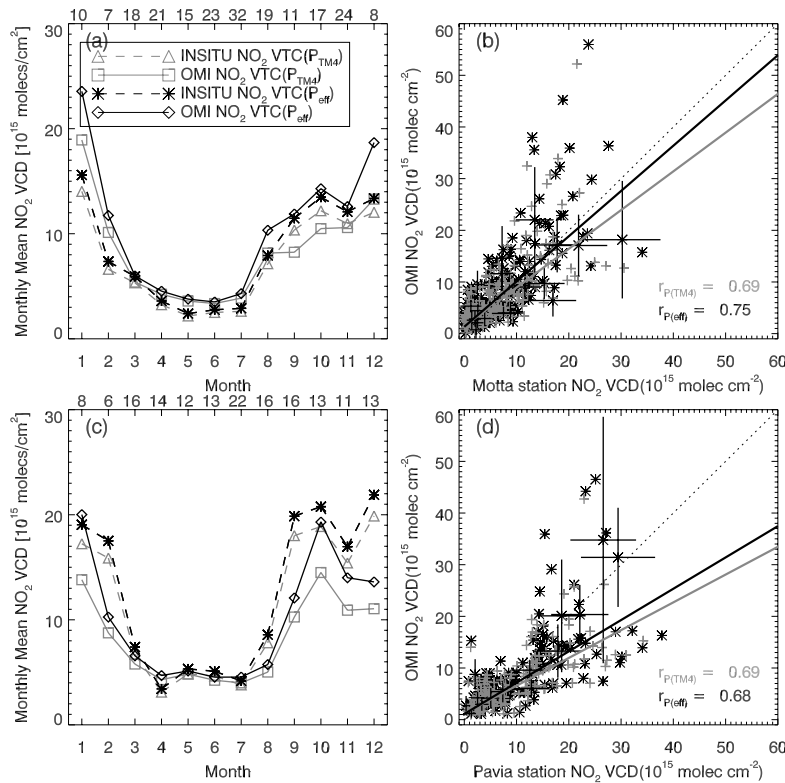


Fig. 15. The left column shows the seasonal cycles of monthly means of in situ and OMI NO₂ VTCs at (a) the rural station Motta and (c) the urban station Pavia. Numbers above each panel refer to the number of cloud-free (cloud radiance fraction lower than 50%) and snow-free (albedo lower than 0.6) days considered for each month during the two year period 2006–2007. The right column shows the corresponding regression analysis for all individual OMI NO₂ VTCs versus in situ NO₂ VTCs at (b) Motta and (d) Pavia. Black stars indicate VTCs retrieved with p_{eff} , grey crosses with p_{TM4} . Dotted lines are the 1:1 lines, black and grey solid lines are the weighted orthogonal fits to the data with p_{eff} and p_{TM4} , respectively.

were taken to be the estimates of the tropospheric column error as provided in the DOMINO product following the approach of Boersma et al. (2004). For the majority of the OMI pixels, this uncertainty ranges from 30% to 60% of the NO₂ VTCs. The uncertainties of the in-situ NO₂ VTCs were computed as the square root of the sum of the squares of two independent errors: (1) The representativeness uncertainty, which depends on how well the TM4 NO₂ vertical profile used in calculating the in-situ NO₂ column represents the real NO₂ profile at the location of the station, and also how well the station NO₂ represents the NO₂ abundance over the whole extent of an OMI pixel. This uncertainty is assumed to be 20% of the in-situ NO₂ VTCs. (2) The uncertainty due to the in situ measurement error, which is estimated as the sum of the instrument detection limit (1 ppb) and a measurement accuracy of 10% of the NO₂ mixing ratio (NABEL, 2007). The uncertainty of the in situ NO₂ is converted to a column uncertainty using Eq. (7).

For both stations the slope of the regression line is closer to one when retrieved with p_{eff} implying a better agreement between in situ and OMI VTCs. For the station Pavia this is clearly a result of the better agreement of OMI NO₂ columns

retrieved with p_{eff} in winter and fall. It is interesting to see that both slope and correlation are improved with p_{eff} for the rural station Motta while the corresponding monthly mean OMI VTCs tend to be more strongly overestimated. This may be explained by the fact that the points with strong overestimation in the upper left part of the figure have little influence on the regression analysis due to their high uncertainties while they significantly contribute to the monthly means. In summary, it may be concluded that the amplitude of the seasonal variations of NO₂ VTCs over the Po Valley and the Swiss Plateau is better captured with our enhanced retrieval due to the increases in autumn and winter while the problem of overestimation of the lowest columns in spring and summer remains.

5 Discussion and conclusions

An improved NO₂ retrieval for satellite observations over mountainous terrain was presented and applied to more than two years of OMI observations over the Alpine region and the adjacent planes. The method eliminates topography-related biases caused by the use of a too coarse surface

pressure (or altitude) data in the DOMINO retrieval. Accurate pixel-average surface pressures were calculated by correcting the original values with information from a high resolution topography model. A priori NO₂ profiles used in the retrieval were then scaled to the new surface pressures and tropospheric AMFs and NO₂ VTCs were recomputed using a modified version of the DOMINO retrieval algorithm.

The comparison between original and enhanced retrieval indicates that the coarse surface pressure data set lead to a significant overestimation of NO₂ VTCs over the Alps and an underestimation over the adjacent planes. For clear sky observations with a threshold for the cloud radiance fraction of 50% the original retrieval is about 25% too low in winter and about 5% in summer over the Po Valley and the Swiss Plateau. However, these errors are much smaller when a more stringent threshold for the cloud radiance fraction of 10% is applied, which reduces the data set to essentially cloud-free pixels.

These findings differ from those of our previous study published by Schaub et al. (2007), which estimated the topography-related error to 13–38% for cloud free pixels over the Swiss plateau. The main reason for this discrepancy is the error detected in the interpolation of box AMFs from the lookup table described earlier. The results by Schaub et al. (2007) were based on a few selected cases only with specific p_{TM4} and p_{eff} . Unfortunately, the p_{eff} of the limited pixels (~ 960 hPa) analyzed by Schaub et al. (2007) (as listed in their Table 2) were located near the position with largest errors, while errors at p_{TM4} are much smaller. This causes a very high sensitivity to surface pressure changes. This lower part of the profile is particularly important in determining the AMF_{trop} following Eq. (1) since the a priori NO₂ profile x_a has highest values in the boundary layer close to the ground as shown in Fig. 8. Moving the surface down into a region where the interpolation errors were much larger therefore resulted in much too large changes in AMFs and NO₂ VTCs in their sensitivity study.

Schaub et al. (2007) tried to explain this high sensitivity by assuming that with the surface level shifted to a lower altitude the profile of box air mass factors would be a simple extension of the original profile to the lower altitude (as in their Fig. 13). This would result in a strong reduction in box air mass factors near the surface and hence a strong sensitivity of the AMF_{trop} to surface pressure changes. However, this explanation is an oversimplification since the profiles are not extended but rather rescaled to the new surface altitude as shown in our Figs. 7 and 8, which results in a more moderate sensitivity.

The strong dependence of our results on the chosen cloud radiance threshold suggests that the AMFs calculated for the cloudy part of the pixels are more sensitive to errors in surface pressure than the AMFs of the clear part. This was confirmed by a detailed analysis for a partly cloudy pixel which further revealed that this sensitivity is particularly large when the cloud is located inside the polluted boundary layer.

To examine the reason for the pronounced seasonal differences of our results we performed a systematic sensitivity analysis of the dependence of the topography-related error on those retrieval parameters changing with season. For cloud free pixels, the seasonal differences in the a priori NO₂ profile shape was found to be the dominating factor. Differences in SZA were also found to be important while changes in albedo had no significant effect. Overall, the sensitivity of the retrieval error to the surface pressure error is almost twice as large in winter as in summer.

To analyze the influence of the improved treatment of the topography on the quality of the retrieved NO₂ VTCs we compared the original and enhanced OMI data with NO₂ VTCs deduced from ground-based in situ measurements. Our validation focused on 35 selected stations over the Swiss plateau (station Taenikon) and the Po Valley in Italy where the effects of inaccurate surface pressure are the largest. Only background stations in urban, suburban and rural environments were selected as they are less affected by nearby sources and are therefore expected to be representative for their respective environment. The in-situ NO₂ measurements were corrected for known interferences from higher oxidized nitrogen species such as PAN and HNO₃ using ozone as a proxy for photochemical activity as proposed by Steinbacher et al. (2006). Corrected NO₂ mixing ratios were then scaled to NO₂ VTCs using NO₂ vertical profiles from the TM4 model. With the accurate surface pressure data set, in-situ and OMI NO₂ VTCs exhibit a significant correlation ($r=0.6$ – 0.82) for most stations. A particularly good agreement between OMI and in situ measurements in terms of both correlation and absolute values was found for urban background stations in the Po valley. Considering that the uncertainty in vertical NO₂ columns derived from the in situ measurements is generally larger than the differences between the original and new retrieval, it is difficult to draw firm conclusions from this validation. Conclusions for winter and fall are more robust since the uncertainties in the correction factors applied to the in situ measurements are smallest in these seasons. The most significant improvement seen with the new retrieval is therefore its better agreement for both urban and suburban stations as it partially corrects the underestimation of NO₂ VTCs retrieved with p_{TM4} . However, for rural and suburban stations, the ratios between OMI and in-situ NO₂ VTCs exhibit an obvious seasonal variation with highest values close to 2 in spring months.

This work is only the first step in a process of replacing the external parameters used for the retrieval by more accurate high-resolution data sets. Work on an improved ground reflectance data set is in progress and will be followed by replacing NO₂ a priori profiles by output from a regional scale model. It is expected that these changes will be more important than the topography effects discussed here. However, only when all these parameters will be available at a resolution appropriate for the scale of an individual satellite pixel a consistent retrieval will be possible.

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References

- Acarreta, J. R., De Haan, J. F., and Stammes, P.: Cloud pressure retrieval using the O₂–O₂ absorption band at 477 nm, *J. Geophys. Res.*, 109, D05204, doi:10.1029/2003JD003915, 2004.
- ATBD GDP 4.0: Algorithm Theoretical Basis Document for GOME Total Column Densities of Ozone and Nitrogen Dioxide, UPAS/GDOAS: GDP 4.0, ERSE-DTEX-EOPGTN-04-0007, Iss./Rev. 1/A, 2004.
- Bertram, T. H., Heckel, A., Richter, A., Burrows, J. P., and Cohen, R. C.: Satellite measurements of daily variations in soil NO_x emissions, *Geophys. Res. Lett.*, 32(24), L24812 doi:10.1029/2005GL024640, 2005.
- Blond, N., Boersma, K. F., Eskes, H. J., van der A, R. J., Van Roozendaal, 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.
- 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., Eskes, H. J., Veefkind, J. P., Brinksma, E. J., van der A, R. J., Sneep, M., van den Oord, G. H. J., Levelt, P. F., Stammes, P., Gleason, J. F., and Bucsela, E. J.: Near-real time retrieval of tropospheric NO₂ from OMI, *Atmos. Chem. Phys.*, 7, 2103–2118, 2007, <http://www.atmos-chem-phys.net/7/2103/2007/>.
- Boersma, K. F., Jacob, D. J., Bucsela, E. J., Perring, A. E., Dirksen, R., van der A, R. J., Yantosca, R. M., Park, R. J., Wenig, M., Bertram, T. H., and Cohen, R. C.: Validation of OMI tropospheric NO₂ observations during INTEX-B and application to constrain NO_x emissions over the eastern United States and Mexico, *Atmos. Environ.*, 42, 4480–4497, 2008a.
- Boersma, K. F., Dirksen, R., Veefkind, J. P., Eskes, H. J., and van der A, R. J.: Dutch OMI NO₂ (DOMINO) data product HE5 data file user manual, TEMIS website, <http://www.temis.nl/airpollution/no2.html>, 2008b.
- Boersma, K. F., Jacob, D. J., Trainic, M., Rudich, Y., DeSmedt, 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, 2009, <http://www.atmos-chem-phys.net/9/3867/2009/>.
- Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noël, S., and Rozanov, V. V.: SCIAMACHY: Mission objectives and measurement modes, *J. Atmos. Sci.*, 56(2), 127–150, 1999.
- Bucsela, E. J., Celarier, E. A., Wenig, M. O., Gleason, J. F., Veefkind, J. P., Boersma, K. F., and Brinksma, E. J.: Algorithm for NO₂ vertical column retrieval from the Ozone Monitoring Instrument, *IEEE T. Geosci. Remote*, 44, 1245–1258, 2006.
- Bucsela, E. J., Perring, A. E., Cohen, R. C., et al.: Comparison of tropospheric NO₂ in situ aircraft measurements with near-real-time and standard product data from the Ozone Monitoring Instrument, *J. Geophys. Res.*, 113, D16S31, doi:10.1029/2007JD008838, 2008.
- Burrows, J. P., Weber, M., Buchwitz, M., Rozanov, V., Ladstätter-Weissenmayer, A., Richter, A., DeBeek, R., Hoogen, R., Bramstedt, K., Eichmann, K. U., Eisinger, M., and Perner, D.: The global ozone monitoring experiment (GOME): Mission concept and first scientific results, *J. Atmos. Sci.*, 56, 151–175, 1999.
- Callies, J., Corpaccioli, E., Eisinger, M., Hahne, A., and Lefebvre, A.: GOME-2: Metop's second generation sensor for operational ozone monitoring, *ESA Bull.*, 102, 28–36, 2000.
- De Haan, J. F., Bosma, P. B., and Hovenier, J. W.: The adding method for multiple scattering computations of polarized light, *Astron. Astrophys.*, 183, 371–391, 1987.
- Dentener, F., van Weele, M., Krol, M., Houweling, S., and van Velthoven, P.: Trends and inter-annual variability of methane emissions derived from 1979–1993 global CTM simulations, *Atmos. Chem. Phys.*, 3, 73–88, 2003, <http://www.atmos-chem-phys.net/3/73/2003/>.
- Dobber, M., Kleipool, Q., Dirksen, R., Levelt, P., Jaross, G., Taylor, S., Kelly, T., Flynn, L., Leppelmeier, G., and Rozemeijer, N.: Validation of Ozone Monitoring Instrument level-1b data products, *J. Geophys. Res.*, 113, D15S06, doi:10.1029/2007JD008665, 2008.
- Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the upper and lower Atmosphere – Theory, Experiments and Applications, Academic Press, San Diego, CA, 2000.
- GOME-2 ATBD: Algorithm Theoretical Basis Document for GOME-2 Total Columns of Ozone, Minor Trace Gases, and Cloud Properties, GDP 4.2 for O3M-SAF OTO and NTO, DLR Technical Note DLR/GOME-2/ATBD/01, 34, Issue/Revision 1/B, 2007.
- Grosjean, D. and Harrison, J.: Response of chemiluminescence NO_x analyzers and ultraviolet ozone analyzers to organic air pollutants, *Environ. Sci. Technol.*, 19, 862–865, 1985.
- Jaeglé, L., Steinberger, L., Martin, R. V., and Chance, K.: Global partitioning of NO_x sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions, *Faraday Discuss.*, 130, 407–423, 2005.
- King, M. D., Kaufman, Y. J., Menzel, W. P., and Tanré, D.: Remote sensing of cloud, aerosol and water vapor properties from the Moderate Resolution Imaging Spectrometer (MODIS), *IEEE T. Geosci. Remote*, 30, 2–27, 1992.
- Koelemeijer, R. B. A., Stammes, P., Hovenier, J. W., and de Haan, J. F.: A fast method for retrieval of cloud parameters using oxygen A-band measurements from Global Ozone Monitoring Experiment, *J. Geophys. Res.*, 106, 3475–3490, 2001.
- Koelemeijer, R. B. A., de Haan, J. F., and Stammes, P.: A database of spectral surface reflectivity in the range 335–772 nm derived from 5.5 years of GOME observations, *J. Geophys. Res.*, 108,

- 4070, doi:10.1029/2002JD002429, 2003.
- Lamsal, L. N., Martin, R. V., van Donkelaar, A., et al.: Ground-level nitrogen dioxide concentrations inferred from the satellite-borne Ozone Monitoring Instrument, *J. Geophys. Res.*, 113, D16308, doi:10.1029/2007JD009235, 2008.
- Levelt, P. F., van den Oord, G. H. J., Dobber, M. R., Mälkki, A., Visser, H., de Vries, J., Stammes, P., Lundell, J. O. V., and Saari, H.: The Ozone Monitoring Instrument, *IEEE T. Geosci. Remote*, 44, 1093–1101, 2006a.
- Levelt, P. F., Hilsenrath, E., Leppelmeier, G. W., van den Oord, G. H. J., Bhartia, P. K., Tamminen, J., de Haan, J. F., and Veefkind, J. P.: Science Objectives of the Ozone Monitoring Instrument, *IEEE T. Geosci. Remote*, 44, 1199–1208, doi:10.1109/TGRS.2006.872336, 2006b.
- Martin, R. V., Chance, K., Jacob, D. J., et al.: An improved retrieval of tropospheric nitrogen dioxide from GOME, *J. Geophys. Res.*, 107(D20), 4437, doi:10.1029/2001JD001027, 2002.
- Martin, R. V., Jacob, D. J., Chance, K. V., Kurosu, T. P., Palmer, P. I., and Evans, M. J.: Global inventory of Nitrogen Dioxide Emissions Constrained by Space-based Observations of NO₂ Columns, *J. Geophys. Res.*, 108, 4537, doi:10.1029/2003JD003453, 2003.
- Martin, R. V., Parrish, D. D., Ryerson, T. B., et al.: Evaluation of GOME satellite measurements of tropospheric NO₂ and HCHO using regional data from aircraft campaigns in the southeastern United States, *J. Geophys. Res.*, 109, D24307, doi:10.1029/2004JD004869, 2004.
- Martin, R. V., Sioris, C. E., Chance, K., et al.: Evaluation of space-based constraints on global nitrogen oxide emissions with regional aircraft measurements over and downwind of eastern North America, *J. Geophys. Res.*, 111, D15308, doi:10.1029/2005JD006680, 2006.
- NABEL: Technischer Bericht zum Nationalen Beobachtungsnetz für Luftfremdstoffe, Empa, Dübendorf, Switzerland, 2007.
- Nolin, A., Armstrong, R., and Maslanik, J.: Near-real time SSM/I EASE grid daily global ice concentration and snow extent, Digital Media, National Snow and Ice Data Center, Boulder, CO, USA, 2005.
- Ordóñez, C., Richter, A., Steinbacher, M., Zellweger, C., Nüß, H. J., Burrows, P., and Prévôt, A. S. H.: Comparison of 7 years of satellite-borne and ground-based tropospheric NO₂ measurements around Milan, Italy, *J. Geophys. Res.*, 111, D05310, doi:10.1029/2005JD006305, 2006.
- Palmer, P. I., Jacob, D. J., Chance, K., Martin, R. V., Spurr, R. J. D., Kurosu, T. P., Bey, I., Yantosca, R., Fiore, A., and Li, Q.: Air mass factor formulation for spectroscopic measurements from satellites: Application to formaldehyde retrievals from the Global Ozone Monitoring Experiment, *J. Geophys. Res.*, 106, 14 539–14 550, 2001.
- Platt, U.: Differential Optical Absorption Spectroscopy (DOAS), in: *Air monitoring by Spectroscopic Techniques*, edited by: Sigrist, M. W., Chemical Analysis Series, 127, 27–76, 1994.
- Press, W. H., Flannery, B. P., Teukolsky, S. A., and Vetterling, W. T.: *Numerical recipes: The art of Scientific Computing*, Cambridge Univ. Press, New York, 1992.
- Richter, A. and Burrows, J. P.: Tropospheric NO₂ from GOME measurements, *Adv. Space Res.*, 29, 1673–1683, 2002.
- Schaub, D., Boersma, K. F., Kaiser, J. W., Weiss, A. K., Folini, D., Eskes, H. J., and Buchmann, B.: Comparison of GOME tropospheric NO₂ columns with NO₂ profiles deduced from ground-based in situ measurements, *Atmos. Chem. Phys.*, 6, 3211–3229, 2006, <http://www.atmos-chem-phys.net/6/3211/2006/>.
- Schaub, D., Brunner, D., Boersma, K. F., Keller, J., Folini, D., Buchmann, B., Berresheim, H., and Staehelin, J.: SCIAMACHY tropospheric NO₂ over Switzerland: estimates of NO_x lifetimes and impact of the complex Alpine topography on the retrieval, *Atmos. Chem. Phys.*, 7, 5971–5987, 2007, <http://www.atmos-chem-phys.net/7/5971/2007/>.
- Schoeberl, M. R., Douglass, A. R., Hilsenrath, E., et al.: Overview of the EOS aura mission, *IEEE T. Geosci. Remote*, 44, 1066–1074, 2006.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric chemistry and physics – from air pollution to climate change*, John Wiley & Sons, New York, 1998.
- Sneep, M., De Haan, J. F., Stammes, P., Wang, P., Vanbauce, C., Joiner, J., Vasilkov, A. P., and Levelt, P. F.: Three-way comparison between OMI and PARASOL cloud pressure products, *J. Geophys. Res.*, 113, D15S23, doi:10.1029/2007JD008694, 2008.
- Stammes, P.: Spectral radiance modeling in the UV-Visible range, IRS2000: in: *Current problems in atmospheric radiation*, edited by: Smith, W. L. and Timofeyev, Y. J., A. Deepak, Hampton, Va, USA, 385–388, 2001.
- Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, S., Buchmann, B., Ordóñez, C., Prévôt, A. S. H., and Hueglin, C.: Nitrogen oxides measurements at rural sites in Switzerland: Bias of conventional measurement techniques, *J. Geophys. Res.*, 112, D11307, doi:10.1029/2006JD007971, 2007.
- Vandaele, A. C., Fayt, C., Hendrick, F., et al.: An intercomparison campaign of ground-based UV-visible measurements of NO₂, BrO, and OClO slant columns: Methods of analysis and results for NO₂, *J. Geophys. Res.*, 110, D08305, doi:10.1029/2004JD005423, 2005.
- van der A, R. J., Peters, D. H. M. U., Eskes, H., Boersma, K. F., van Roozendael, M., de Smedt, I., and Kelder, H. M.: Detection of the trend and seasonal variation in tropospheric NO₂ over China, *J. Geophys. Res.*, 111, D12317, doi:10.1029/2005JD006594, 2006.
- 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.
- Wallace, J. M. and Hobbs, P. V.: *Atmosphere science, an introductory survey*, Academic Press, California, USA, 1977.
- Wang, Y. X., McElroy, M. B., Boersma, K. F., Eske, H. J., and Veefkind, J. P.: Traffic Restrictions Associated with the Sino-African Summit: Reductions of NO_x Detected from Space, *Geophys. Res. Lett.*, 34, L08814, doi:10.1029/2007GL029326, 2007.
- Winer, A. M., Peters, J. W., Smith, J. P., and Pitts Jr., J. N.: Response of commercial chemiluminescent NO-NO₂ analyzers to other nitrogen containing compounds, *Environ. Sci. Technol.*, 8, 1118–1121, 1974.